

Interface compounds formed during the diffusion bonding of Al₂O₃ to Ti

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The interfacial reaction products of Ti/Al₂O₃ joints obtained in the context of real diffusion bonding technology were investigated by means of X-ray diffraction analysis, X-ray photoelectron spectroscopy, and transmission electron microscopy. Some Ti reacted with Al₂O₃ giving titanium oxides, but the main mass transport occurred into the bulk Ti due to Al₂O₃ dissolution. The formation of a Ti[Al, O] solid solution followed by an order/disorder reaction yielded Ti₃Al. Further Al enrichment at the interface could lead to the formation of TiAl, which was not observed in the present work due to either the short residence time at the bonding temperatures or to its lower oxygen solubility. For joints obtained at 800°C and observation of shear test fracture surfaces it was ascertained that the crack always propagated within the Ti₃Al layer. © 2000 Kluwer Academic Publishers

1. Introduction

Reactions taking place between Ti and Al₂O₃ are of particular interest for the production of solid-state joining processes, in which the metal is not only used because of its favourable reactivity but also as a thermal stress relief interlayer to minimise the effects of residual stresses. The reliability of the joint depends on the metal-oxide reactivity and, consequently, on the interfacial microstructure.

Ti/Al₂O₃ interface reactions have been extensively treated in the literature [1–8]. However there is still some disagreement about mechanism and formation sequence of the interface reaction products since different experimental constructions may affect both thermodynamic and kinetic conditions and thus the diffusion path in the Ti-Al-O system. For instance, long term diffusion bonding experiments reported by Li *et al.* [1] suggest two possible diffusion paths at 1100°C: Al₂O₃/TiAl/Ti₃Al/α-Ti/β-Ti, for infinite Ti supply, that is thick Ti foils or Al₂O₃/Ti₃Al/α-Ti/β-Ti, for finite Ti supply, that is thin Ti foils. However, between 650 and 860°C Lu *et al.* [3] observed another sequence: Al₂O₃/Ti₃Al/α-Ti in conditions of infinite Ti supply. Moreover, vapour deposition of thin film at room temperature [4–7] showed that Ti reacts with Al₂O₃ forming titanium oxides as well.

The purpose of the present work is to investigate the interfacial reaction products of Ti/Al₂O₃ joints obtained in the context of real diffusion bonding technology, namely residence times of up to 3 h at high temperature followed by slow cooling rates.

2. Materials and experimental methods

Ti sheets of commercial purity ~500 μm thick were used as stress relief interlayer between diffusion bonded

Al₂O₃ and AISI304 stainless steel blocks. The joints were obtained at 800°C/3 hours, 900°C/2 hours and 1000°C/2 hours by solid state diffusion bonding under a mechanical pressure of 15 MPa and vacuum better than 2 × 10⁻³ Pa. Heating and cooling rates were close to 5°C/minute. Samples were shear tested along the ceramic/Ti interface [9] and some were selected for microstructural analysis.

X-ray diffraction using Cu K_α radiation was used for phase identification at the fracture surfaces. For the sample bonded at 900°C a phase profile was obtained by successively grinding planes parallel to the bonding surface, from the ceramic into the metal, and acquiring their x-ray diffraction patterns.

X-ray photoelectron spectroscopy has been employed in order to determine the elemental composition, chemical nature and oxidation state of the elements comprising the fracture surface of the 800°C sample. Both the ceramic and the metal sides of the fracture were analysed. XPS spectra were obtained for Ti (2p), Al (2p), O (1s) and C (1s). To compensate for the energy shift due to sample charging, the observed binding energies were adjusted by assigning the value for the C (1s) line from the adventitious carbon, to be 285.0 eV. The evolution of the chemical binding state with depth was obtained by successively sputtering with argon ions in the analysis chamber. Finally, small buttons of TiAl and Ti₃Al were prepared in an arc furnace under inert Ar atmosphere to be subsequently used as standards for the identification of the intermetallics formed at the Ti/Al₂O₃ interface.

Cross-sectional transmission electron microscopy (TEM) thin foils were prepared following the technique described by Strecker *et al.* [10] and observation was performed in a CM120 (Philips) equipment operating at 120 kV. Compositional information was acquired

by means of an energy dispersive X-ray spectroscopy (EDX) device fitted to the TEM microscope.

3. Results

3.1. TiAl and Ti₃Al intermetallic standards

Fig. 1 shows X-ray diffraction patterns indicating that the alloys are constituted only by TiAl and Ti₃Al respectively. Their polished surface had been naturally oxidised and the XPS measurements showed (Fig. 2) that Al and Ti were present mainly in their oxide form. A shift of the Al (2p) and Ti (2p) spectra occurred with increasing sputtering time and, as such it was not possible to determine the real energy shift that should be characteristic of these type of intermetallics, as it has been observed by Mecener *et al.* [11]. Therefore only the compositional ratio of Ti and Al listed in Table I was used to calibrate the intermetallics. An enrichment of Al was detected at their oxidised surface. Similar results were published by the above authors in thin oxide layers and this tendency was confirmed by Dettenwanger *et al.* [12], that have studied thick oxide layers on TiAl. The present experiments have shown that Al is more oxidised than Ti and that some migration of Al to the surface occurs.

TABLE I Compositional ratio of the Ti and Al metallic components obtained by XPS measurements

Sample	Sputtering Time (min)	Ti _{met} /(Ti + Al) _{met}
Ti ₃ Al	0	0.49
	30	0.60
	150	0.69
TiAl	0	0.48
	30	0.50
	150	0.55

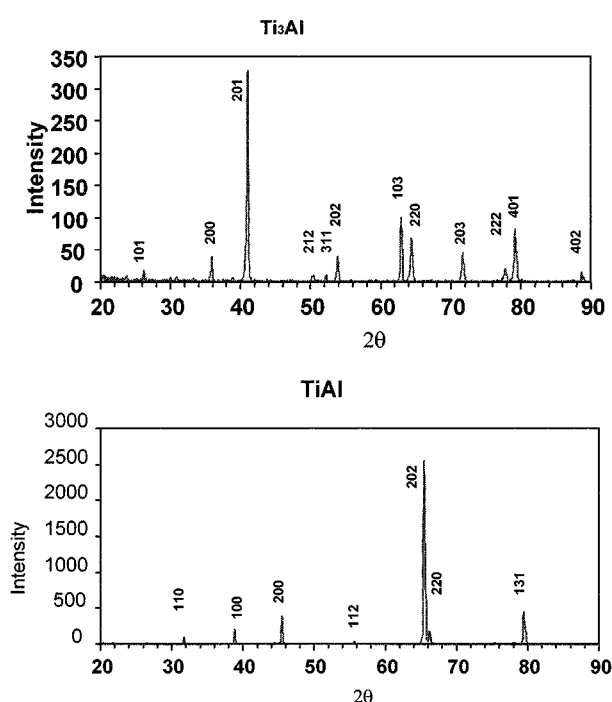


Figure 1 X-ray diffraction patterns of the TiAl and Ti₃Al standards.

3.2. 800°C bond

The Ti (2p) and Al (2p) XPS spectra taken successively at the metal (Al₂O₃ → Ti) and at the ceramic (Ti → Al₂O₃) sides of the 800°C sample fracture surfaces are shown in Fig. 3. It can be seen that Ti was oxidised in a sequential manner and the spectra shows a mixture of Ti²⁺, Ti³⁺ and Ti⁴⁺. The amount of Ti⁴⁺ decreased with sputtering time while metallic Ti was present at both sides of the fracture. Al was present in its oxide form at both fracture surfaces and with increasing sputtering time some metallic Al was detected. From this observation it may be stated that at the bonding interface the aluminum has been reduced to Al⁰ and titanium has been successively oxidised to Ti²⁺, Ti³⁺ and Ti⁴⁺.

Again a shift of the Al (2p) and Ti (2p) spectra was observed with increasing sputtering time and therefore the observed energies of the metallic components could not be associated to the presence of a given intermetallic phase. Since the analysed surfaces were in an oxidised state, the fracture composition was determined by the intersection of Ti/(Ti + Al) ratio plots for the metallic components of the spectra, against sputtering time, see Fig. 4. The intersection is located in a region with approximately 65 at.% Ti and 45 at.% Al, thus compatible with an oxidised Ti₃Al. Moreover, the composition of the metallic component at the Ti side of the fracture tends to the Ti₃Al composition while the composition at the ceramic side of the fracture appears to agree with the TiAl composition.

The TEM observations (Fig. 5) show that a finely dispersed Ti₃Al is the intermetallic phase at the Ti/Al₂O₃ interface, having approximately the composition 25–30 at.% Al and 75–70 at.% Ti but TiAl could not be detected. Some Ti was observed in the Al₂O₃ (up to 2 at.%) whilst the Ti-α adjacent to the Ti₃Al had Al contents of about 10 at.-%.

3.3. 900°C bond

Fig. 6 shows that X-ray diffraction patterns taken on the fracture surface of the 900°C detected some Ti₃Al. Calculations based on x-rays peak displacement showed that, when close to the Al₂O₃, the Ti-α cell parameters are larger than the published values and Fig. 7 is a graph of the Ti *c/a* ratio versus distance from the Al₂O₃/Ti interface. From this data it can be seen that within a ~50 μm wide region the *c/a* ratio decreases from 1.622 to 1.587 nm. Since EDX measurements at SEM resolution cannot detect Al, it can be provisionally concluded that the penetration depth of that element is not very accentuated. Therefore the measured displacement was associated only to the presence of oxygen in solid solution.

Finally, a 600 nm thick Ti₃Al layer was observed at the ceramic/titanium interface see Fig. 8. The presence of TiAl could not be detected and the adjacent Ti-α matrix was enriched with ~14 at.% Al.

3.4. 1000°C bond

A ~3 μm thick Ti₃Al layer formed at the alumina/Ti interface, and at the presently employed TEM resolution

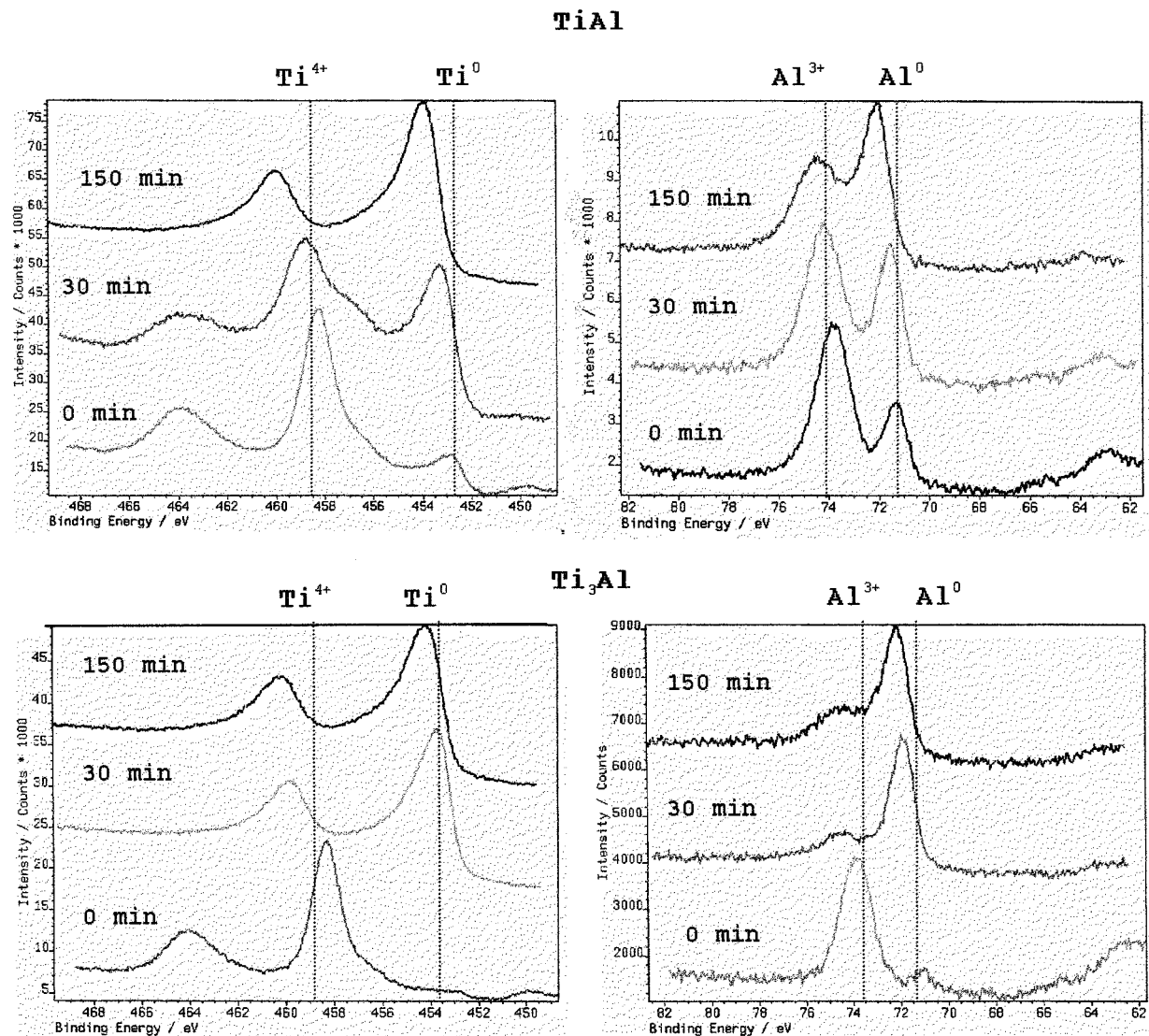


Figure 2 TiAl and Ti₃Al XPS spectra as a function of sputtering time.

no second layer was observed. The Ti- α adjacent to the intermetallic had an Al content of about 10–16 at.% and comprised Ti₃Al precipitates closer to the intermetallic layer and Al rich domains, which although exhibiting a smaller Al content already had the Ti₃Al structure. The dark field image of the Al-rich domains, obtained from the [116] α -Ti zone axis diffraction pattern, is shown in Fig. 9.

4. Discussion

A number of works interested in the interface reactions between Ti and Al₂O₃ and making use of XPS and/or AES techniques, deal with thin layer depositions of Ti on Al₂O₃ at room temperature [4–6]. These studies reveal that at 25°C Ti reacts with the alumina and formation of metallic Al takes place. However, there is some disagreement about the formation of Ti oxides. Rühle and co-workers [5], and Lefakis *et al.* [7] attribute the presence of different oxidation states of Ti to the formation of Ti₂O₃ at the metal/ceramic interface, whereas Lu *et al.* [3] consider Ti solid solution in the alumina, that is, the formation of (Ti,Al)₂O₃. Lee *et al.* [13] have shown by means of Ti ion implantation in an Al₂O₃

substrate both at room temperature and at 750°C, that the Ti⁺ reduces some Al³⁺ to Al⁰ or Al^{x+}, while Ti⁺ ions themselves are oxidised to Ti^{2+,3+,4+} or reduced to Ti⁰. These authors consider the possibility of formation of TiO, Ti₂O₃, Al₂TiO₅ and the presence of Ti in octahedral sites replacing Al in the Al₂O₃ structure, thus justifying the presence of an intermediate oxidation state for the Al. It is worth mentioning however, that the presence of Al^{x+} was associated to higher implantation energies, which means a higher density of structural defects and thermal effects caused by that technique.

The present XPS measurements have shown that Ti oxidised to Ti^{4+,3+,2+}, the amount of Ti⁴⁺ decreasing with sputtering time on both fracture surfaces, thus indicating that the presence of TiO₂ was certainly due to oxidation caused by air exposure. However, the compositional profile at the ceramic side of the fracture showed that close to the Al₂O₃ the Ti was mainly present in an oxide form and that it has reacted with Al₂O₃ forming metallic Al, which confirms the literature data. Meanwhile TEM observations did not reveal the formation of other oxides at the ceramic/metal interface but some Ti (up to 2 at.%) was detected at the ceramic side of

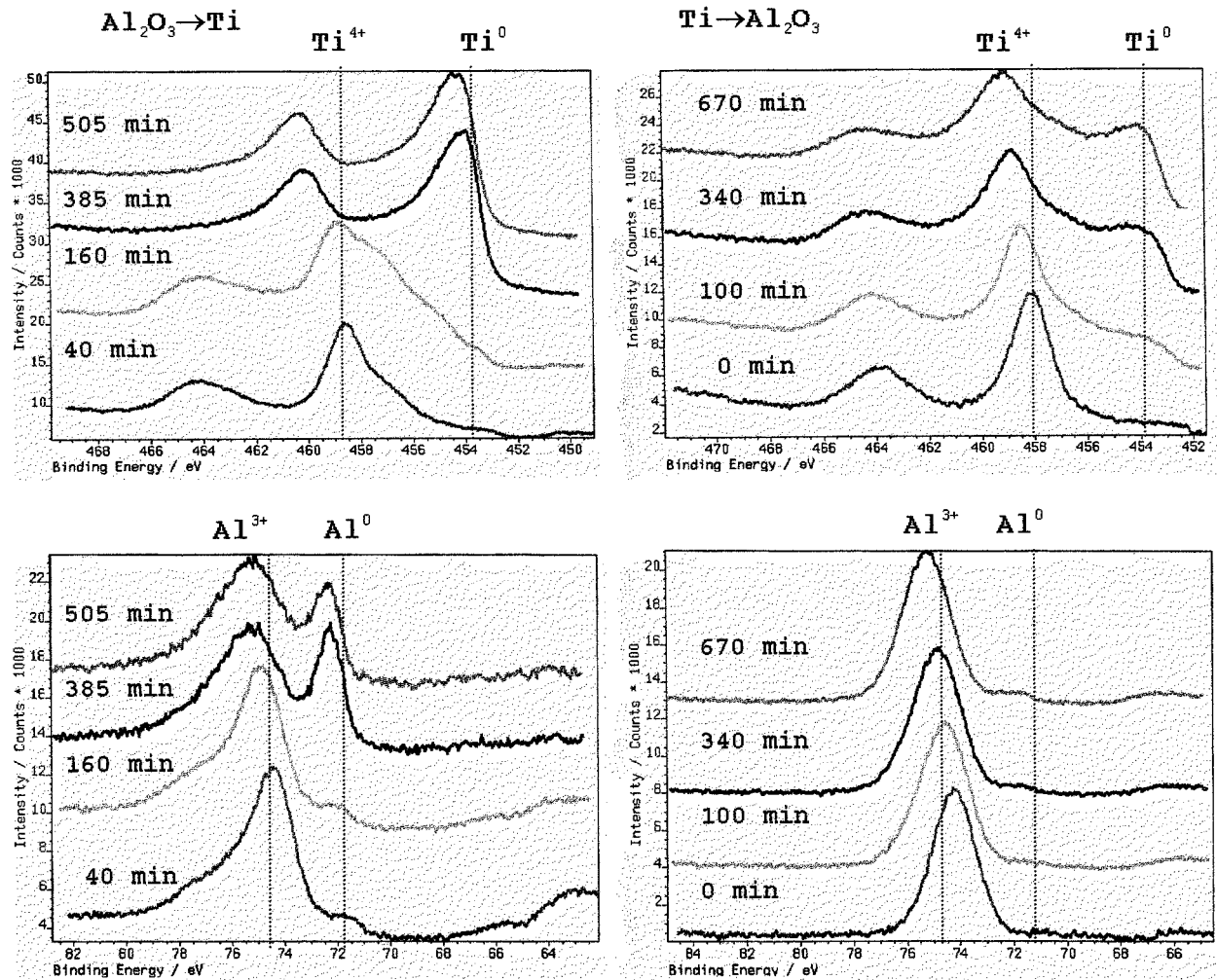


Figure 3 Ti (2p) and Al (2p) XPS spectra taken successively at the metal ($\text{Al}_2\text{O}_3 \rightarrow \text{Ti}$) and at the ceramic ($\text{Ti} \rightarrow \text{Al}_2\text{O}_3$) sides of the 800°C sample fracture surfaces.

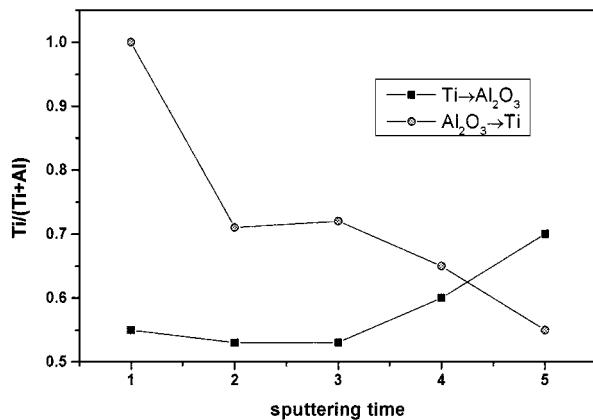


Figure 4 Ti/(Ti+Al) ratio taken on the fractured surfaces of the sample joined at 800°C : XPS spectra plotted against sputtering time.

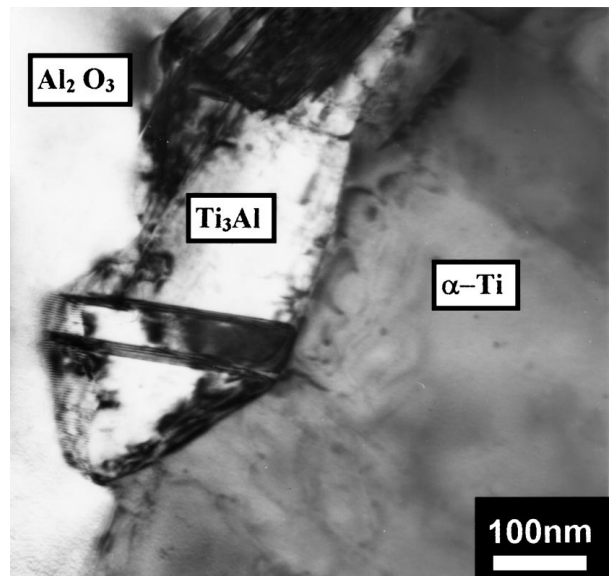


Figure 5 Cross-sectional TEM image of the 800°C joint showing the presence of Ti_3Al at the bonding interface.

the interface, suggesting that the oxidised state of that metal can be associated to its dissolution in the oxide. Both chemical composition and x-ray data indicated that the cracks run always within the Ti_3Al layer.

The formation of reaction products at the $\text{Al}_2\text{O}_3 / \text{Ti}$ interface depends on the local oxygen activity and temperature, see Fig. 10. When α - or β -Ti is in contact with Al_2O_3 under very low external oxygen pressure, as in the case of vacuum diffusion bonding, the oxide is re-

duced and the dissolution of both oxygen and Al takes place. The thermodynamic barrier to Al_2O_3 reduction is large; however, the decrease in free energy associated with the formation of either an intermetallic compound

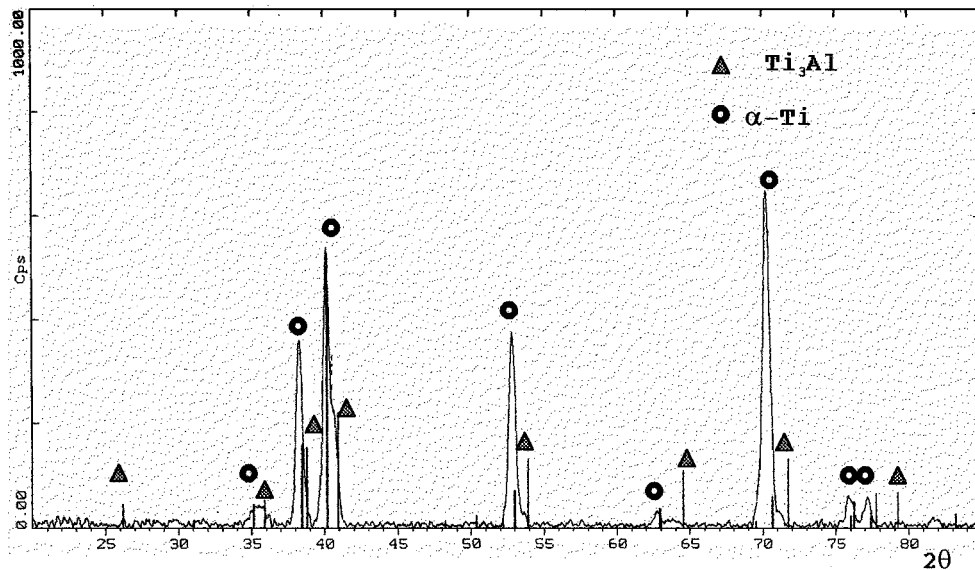


Figure 6 X-ray diffraction pattern of the 900°C joint fracture surface.

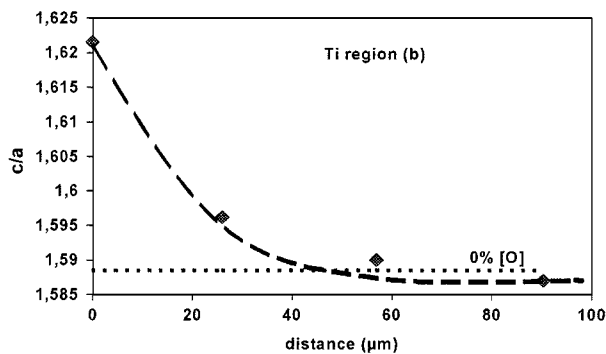


Figure 7 Ti- α cell parameter change as a function of distance from the Ti/Al₂O₃ interface.

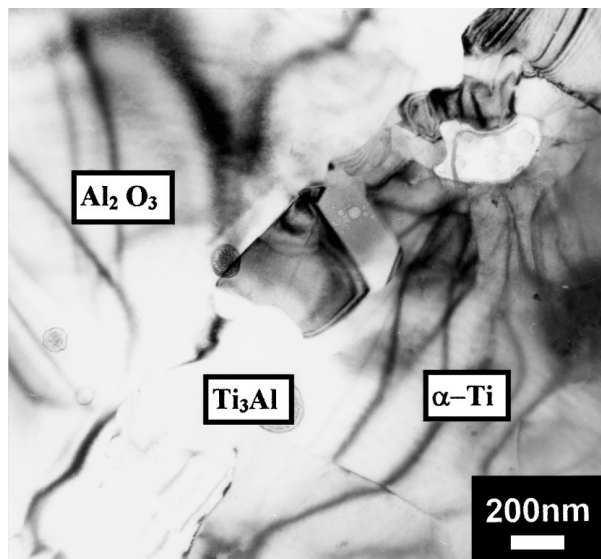


Figure 8 Cross-sectional TEM image of the 900°C joint showing Ti₃Al at the bonded interface.

or a solid solution may allow reduction to proceed. On this context, Li *et al.* [1] showed that the Ti-Al intermetallics free energy is reduced by more than 50% by considering their oxygen solubility. These considerations are in agreement with recent works by Paulastro

and Kivilathi [2] and Zalar *et al.* [8], where the reduction of alumina by Ti is described as initiating by the formation of the same Ti(O,Al) solid solution adjacent to the ceramic that was observed in the present work. Consequently, the Al₂O₃ dissolution and therefore the diffusion of oxygen and aluminum into titanium is a requirement for the formation of the intermetallics reaction layer.

In order to comply with mass balance requirement Ti has to dissociate alumina in the [O]/[Al] ratio of 3 : 2. As the interstitial oxygen diffuses much faster than the substitutional Al, the formation of intermetallics containing Al will be affected by the presence of oxygen. It has been reported, for example, that oxygen shifts the α -Ti/ α -Ti + Ti₃Al phase boundary to higher Ti content [14].

Above 882°C the stable phase in the Ti interlayer is β -Ti. As Al and O dissolve into it, this phase begins to transform to α -Ti. From the Al-Ti and O-Ti phase diagrams [15, 16] it can be concluded that at 900°C, either 3 at% Al or 1 at% O are sufficient to stabilise α -Ti with respect to β -Ti. In the present work this is supported by the observation that at 900°C the 50 μ m wide oxygen and Al diffusion layer is composed by α -Ti grains much larger than the α -Ti grains in the centre of the Ti foil, where this phase resulted from the decomposition of β -Ti during cooling. The oxygen penetration can be measured indirectly from Fig. 7 where it can be seen that the c/a change extends up to ~ 50 μ m from the interface. The lattice parameter change is an indication of oxygen diffusion into the Ti. Additionally, by considering the well known $x = (Dt)^{1/2}$ relation, where x is the diffusion distance, D the diffusion coefficient and t the diffusion time, the calculated penetration depth of the oxygen, that is, 50 μ m, is consistent with a diffusion coefficient calculated from the following equation [17]:

$$D_{[O]}^{\text{Ti}\alpha} = 4 \exp\left(\frac{-48,000}{RT}\right)$$

which for $T = 1173$ K gives $D = 4,6 \times 10^{-9}$ cm² s⁻¹, meaning that for $x = 50 \times 10^{-4}$ cm and a time of 3600 s

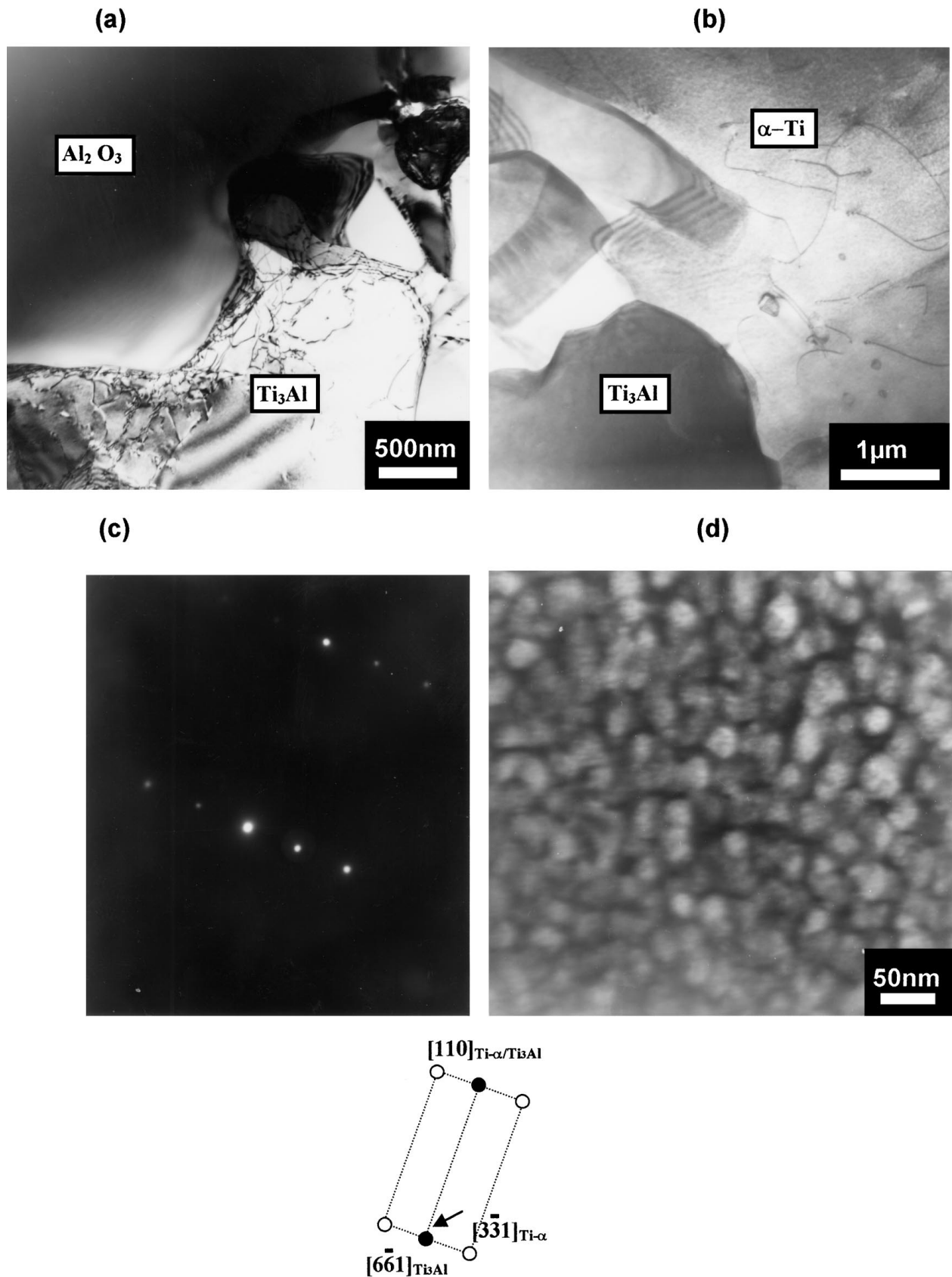


Figure 9 TEM image of the joint produced at 1000°C showing details of (a) the $\text{Al}_2\text{O}_3/\text{Ti}_3\text{Al}$ interface, (b) the $\text{Ti}_3\text{Al}/\alpha\text{-Ti}$ interface, (c) $\alpha\text{-Ti}$ matrix diffraction pattern, and (d) the dark field image of Al rich domains in the $\alpha\text{-Ti}$ matrix adjacent to the intermetallic layer.

the diffusion distance equation yields $D = 6.9 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$, which is reasonably close to the calculated value.

In the Al and O diffusion zone, the $\alpha\text{-Ti}$ matrix transforms to Ti_3Al , which has an ordered hexagonal struc-

ture based on $\alpha\text{-Ti}$ [16]. This transition can be observed in the diffusion zone of the sample obtained at 1000°C, where Ti_3Al was identified by dark field imaging, see Fig. 9. Further Al diffusion would saturate that compound leading to the formation of $\text{TiAl}[\text{O}]$ solid

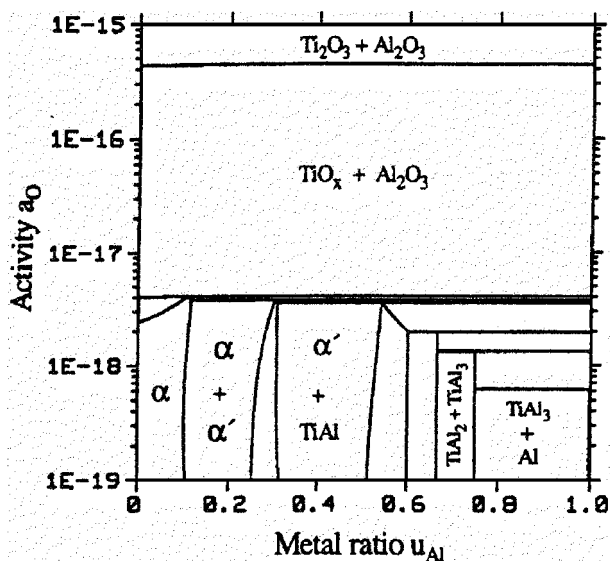


Figure 10 Activity of oxygen as a function of metal ratio μ_{Al} [$=x_{Al}/(x_{Al} + x_{Ti})$] according to reference [2].

solution. This is essentially the mechanism described by Paulastro and Kivilathi [2] and Li *et al.* [1] in the context of finite supply of Ti. Both the experimental determination of the Ti-Al-O phase diagram by Li *et al.* [1] and Paulastro [2] and their $Al_2O_3/TiAl/Ti_3Al/\alpha-Ti/\beta-Ti$ involved very long reaction times up to the establishment of chemical equilibrium. The same is valid for the experimental procedure used by Lu *et al.* [3]. In the present work TiAl could not be detected, but since the samples were obtained in the context of real diffusion bonding technology, namely up to 3 h reaction followed by slow cooling rates, a possible explanation for the absence of TiAl would be that the bonding time did not allow the equilibrium to be reached. Furthermore TiAl was not observed in diffusion bonding obtained below $850^\circ C$ [3]. As already mentioned, the formation of a continuous intermetallic layer depends on the dissolution of Al_2O_3 and thus on the oxygen plus aluminum solubility and diffusion in the aforementioned layer. From the published Ti-Al-O diagrams [1, 2, 14, 18] it can be seen that Ti_3Al is the equilibrium phase at temperatures below $800^\circ C$ and that it has a higher solubility for O than TiAl does. Zalar *et al.* [8] obtained a limited reaction between Al_2O_3 and the intermetallics Ti_3Al and no reaction with the TiAl, respectively, at temperature as high as $750^\circ C$. In other words, the formation of intermetallics reduces the diffusion of oxygen and aluminum into the bulk Ti and lowers the reaction rate that takes place at the diffusion front. Therefore dissolution of the TiAl in favour of the more permeable Ti_3Al during cooling can also be possible.

5. Conclusions

The growth of interface reaction layers during Ti to Al_2O_3 diffusion bonding at temperatures from 800 to

$1000^\circ C$ was investigated and a layer formation sequence can be proposed.

Although a slight interaction between Ti and Al_2O_3 and the occurrence of oxidised Ti, the main cause for the formation of intermetallics at the bonding interface is the dissolution of Al_2O_3 giving a Ti[Al₂O₃] solid solution.

At the diffusion front oxygen eventually transforms β -Ti into α -Ti and Ti_3Al starts to form following an order/disorder reaction in the aluminium rich regions.

Further Al enrichment at the interface could lead to the formation of TiAl, which was not observed in the present work due to either the short residence time at the bonding temperatures or to its lower oxygen solubility.

Under shear forces the Ti- Al_2O_3 joint produced at temperatures higher than $800^\circ C$ will fracture at the metal-ceramic interface, the crack running within the Ti_3Al layer.

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