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The Al_2O_3-titanium adhesion in the view of the diffusion bonding process

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One of the key aspects of the diffusion bonding technology is the adhesion at the interface, to whom most of the mechanical properties can be ascribed. Titanium has been largely used in diffusion bonding involving aluminium oxide, as it reacts with the ceramic promoting adhesion. The present work attends to the interface formation between Al_2O_3 and titanium, during diffusion bonding experiments performed under vacuum. It is verified, by SEM microstructure characterisation, EDS microanalysis, X-ray diffraction and microhardness measurements, that the adhesion occurred by the ceramic dissolution, in presence of titanium, in elementary aluminium and oxygen atoms, followed by the oxygen diffusion into the titanium. The aluminium accumulation at the interface is favourable to the Ti_3Al formation observed. © *2002 Kluwer Academic Publishers*

1. Introduction

The diffusion bonding process has been one of the technological tools used in order to increase the use of ceramic materials, despite its poor mechanical behaviour in terms of fracture toughness. The bonding of ceramics to metals enables a number of structural design solutions that can associate the benefits in wear, chemical attack resistance and high temperature service capabilities of the former, with a tough and easy to manufacture metallic structure.

The success of a metal to ceramic joint obtained by diffusion bonding depends on how easy a sound bonding can be achieved between them, how strong is this bonding and how the couple can absorb their differences. Thermal expansion mismatch is critical, as it frequently takes the form of residual stresses that are deleterious to the mechanical strength of the joint [1]. In practical terms, the reactivity between metal and ceramic facilitates the bonding formation at the interface. This reactivity is usually treated by the equilibrium thermodynamics, although the equilibrium condition can lead to the undesirable formation of large and brittle reaction layers. Kinetic aspects have to be taken into account in order to establish the better compromise between the chemical reaction that leads to the bonding and the growth of a reaction layer that can give undesirable characteristics to the interface.

Heikinheimo and de With [2] identified, for the Al_2O_3/Ti system, the presence of Ti_3Al, TiAl and a solid solution of O in α-Ti at an interface formed in high vacuum at temperatures ranging from 950 to 1100°C. According to the authors, the morphology of the interface depends on the amount of titanium available for the reaction. The TiAl intermetallic was observed by the authors being always in contact with the ceramic, with the TiAl/Ti_3Al ratio increasing as the titanium source for reaction increases. TiO can also be find at Al_2O_3/Ti interfaces, mainly at lower temperatures [3, 4]. The titanium oxide is also frequently observed in Al_2O_3 brazed joints, using brazing where the titanium is present in small concentration as active element in alloys like Ag–Ti, [5], Cu–Ti [6] and Ag–Cu–Ti [7]. Diffusivity and the initial concentration of atoms in the system can also result in reaction products not predicted by the equilibrium thermodynamics [8].

The present work deals with the characterisation of the Al_2O_3/Ti interface formed in Al_2O_3/AISI304 steel diffusion bonded joints, using titanium as interlayer material.

2. Experimental

Discs (10 mm diameter, 5 mm height) of Al_2O_3 and AISI 304 stainless steel were diffusion bonded using a 0.5 mm thick commercially pure titanium interlayer (see Table I for chemical composition of the materials), under vacuum of 5×10^{-5} mbar and an external applied pressure of 15 MPa. The bonding temperatures and times ranged from 700 to 1000°C and 15 to 180 minutes, respectively, and the cooling rate was 4°C/min. The bonding surfaces involved were previously polished with 0.25 μm diamond paste, resulting in a surface roughness R_a of 0.27 to 0.35 μm for the ceramic and 0.10 to 0.20 μm for both steel and titanium interlayer. A cleaning procedure using acetone and ultrasonic vibration was employed in order to remove any residue from the bonding surfaces. In addition, the ceramic was also heat treated at 850°C for 30 minutes to remove eventual residues of lubricant or tissue originated from the polishing operation.

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TABLE I Chemical composition of the materials employed in the bonding experiments (weight %)

Aluminium Oxide	Na_2O (0.08)	SiO_2 (0.01)	Fe_2O_3 (0.03)	CaO (0.04)	MgO (0.04)	Al_2O_3 bal.	—
AISI 304 stainless steel	Cr (18–20)	Ni (8–10)	Mn (1.2)	Si (0.6)	Cu (0.2)	C (0.08)	Fe bal.
Titanium	N (0.07)	O (0.15)	Mn (0.20)	H (0.01)	Fe (0.30)	C (0.10)	Ti bal.

The interface formed between the Al_2O_3 and the titanium interlayer was characterised by Scanning Electron Microscopy/Energy Dispersive Spectroscopy (limit detection for elements with atomic number higher than 11), on samples prepared at their cross sections by conventional metallographyc procedures and by etching with an aqueous solution containing 10% HF and 5% HNO_3 (in volume). Vickers microhardness (50 grams load) measurements were performed in order to evaluate the interdiffusion extension across the interface. Some of the samples obtained at 700 and 800°C had the Al_2O_3/Ti interface mechanically separated, enabling it to SEM observation and to X-ray exposure that resulted in additional reaction products characterisation with adequate accuracy, mainly in the early stages of the bonding process.

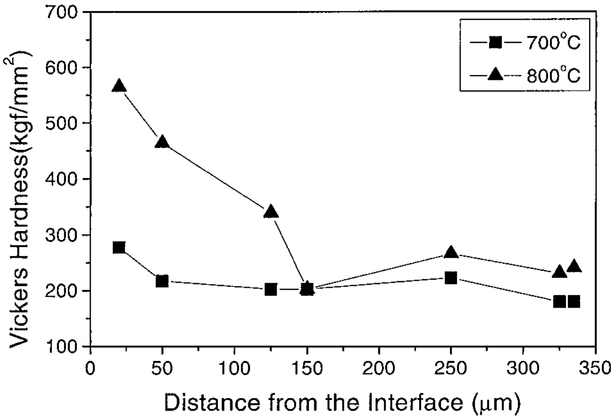

Figure 2 Microhardness profile in titanium as a function of the distance from the Al_2O_3/Ti interface, for samples diffusion bonding at 700 and 800°C for 120 minutes.

3. Results

From the bonding process point of view, adhesion between the ceramic and the titanium interlayer did not occur, at the temperature of 700°C, with bonding times shorter than 120 minutes. At 800°C, bonding was observed at times as short as 15 minutes, but even at times of 120 minutes in this temperature, no reaction layer could be observed on cross sections of the interface observed by SEM, see Fig. 1. At the same figure, the interface seems to be continuous and free of defects. Microhardness measurements, performed on cross sectioned samples diffusion bonded at 700 and 800°C (both at 120 minutes) indicated a hardening effect on the titanium interlayer at distances up to 50 and 125 μm far from the interface, respectively (see Fig. 2). EDS microanalysis did not reveal the presence of aluminium in this hardened region.

Despite the observation of cross-sectioned samples did not reveal the presence of reaction products at lower temperatures, bonding surfaces observed after mechanical separation at the Al_2O_3/Ti interface evidenced their presence in early stages on samples obtained at 700 and 800°C at times of 120 minutes. The Figs 3A and B show these titanium bonding surfaces observed by SEM, where it is evident that the fraction of bonding area increases with the temperature. X-ray diffraction patterns showed in Figs 4A and B reveal the presence of small peaks of the Ti_3Al intermetallic. Quantitative EDS microanalysis performed on these surfaces resulted in an atomic ratio Ti/Al of 3, which confirms

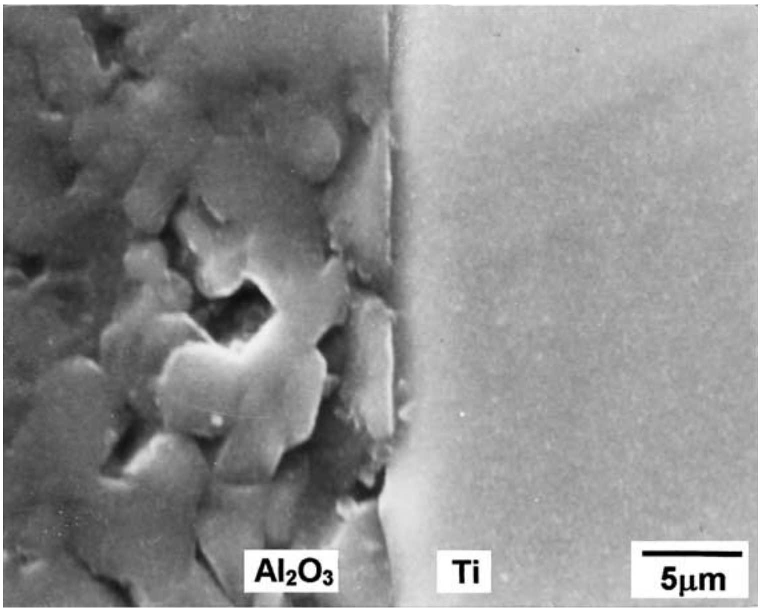

Figure 1 Al_2O_3/Ti interface formed by diffusion bonding at 800°C/120 minutes.

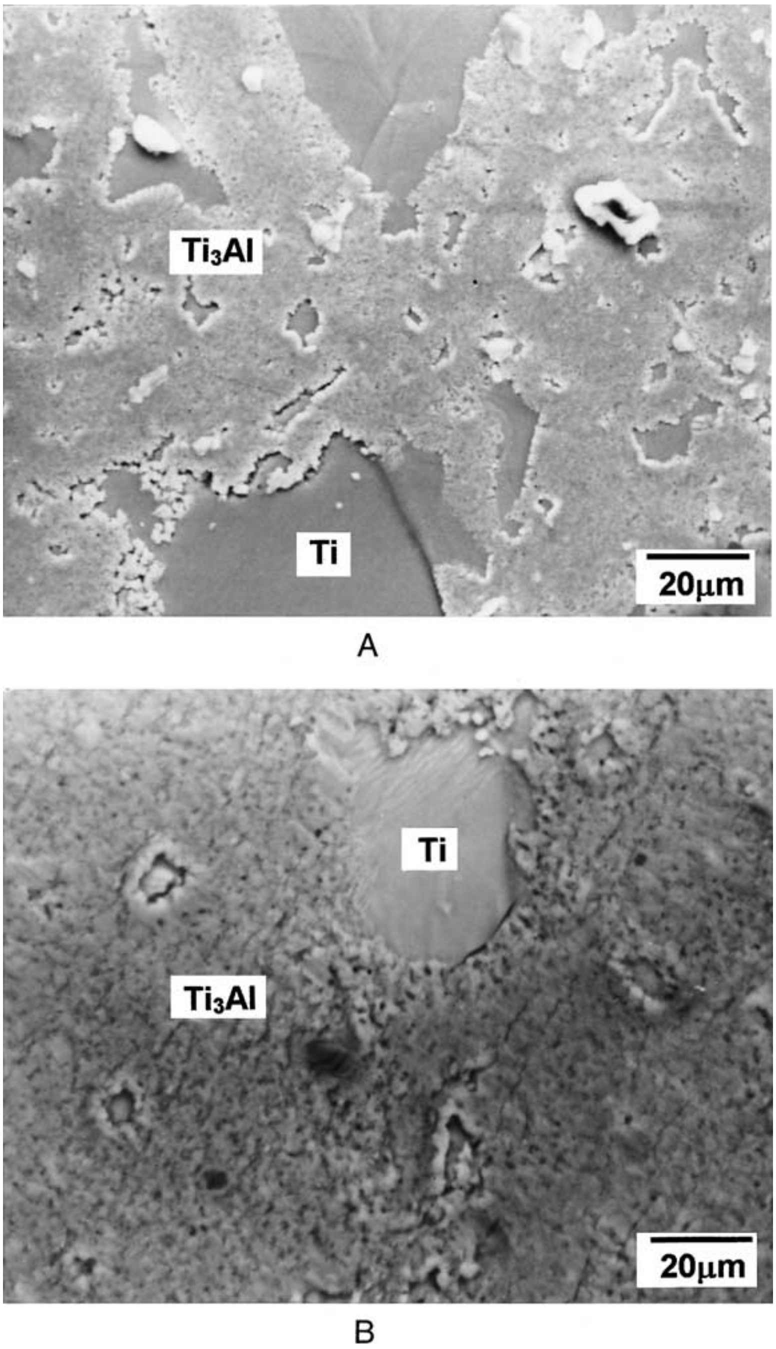

Figure 3 Aspect of the titanium bonding surface after mechanical separation at the Al_2O_3/Ti interface: A- sample diffusion bonded at 700°C/120 minutes; B- sample diffusion bonded at 800°C/120 minutes.

the results of X-ray diffraction. For the sample diffusion bonded at 800°C, small peaks of Al_2O_3 are also present on the titanium surface, indicating that at this temperature the interface formed seems to be stronger than the ceramic itself, and the fracture path turns to the ceramic substrate. On the other hand, a brittle fracture aspect is also observed in the titanium, see Fig. 5.

The formation of a continuous layer (about 6 μm thick) of Ti_3Al is observed on a cross-sectioned sample diffusion bonded at 900°C for 120 minutes, see Fig. 6. In the same figure, it can be observed that a surface pore of the ceramic is completely filled by the titanium. Consequently the incidence of porosity at the interface is expected to be minimum at these bonding conditions.

The Al_2O_3/Ti interface formed at 1000°C for 120 minutes is showed in Fig. 7. The reaction layer formed is about 14 μm thick, consisting to the Ti_3Al according to EDS microanalysis. Adjacent to the Ti_3Al, the metallographyc etching reveals the microstructure of the Ti interlayer formed by equiaxial grains, where no Al was detected by the EDS microanalysis. Microhardness measurements resulted in values as high as 900 HV (compare to Fig. 2). Further into the titanium, a needle region is formed, and the presence of iron originating from the steel substrate is observed. The iron content, according to EDS microanalysis, is about 0.5% in the needles and 7.5% in the matrix (atoms %).

4. Discussion

The presence of the Ti_3Al at the Al_2O_3/Ti interface indicates that the bonding mechanism, within the

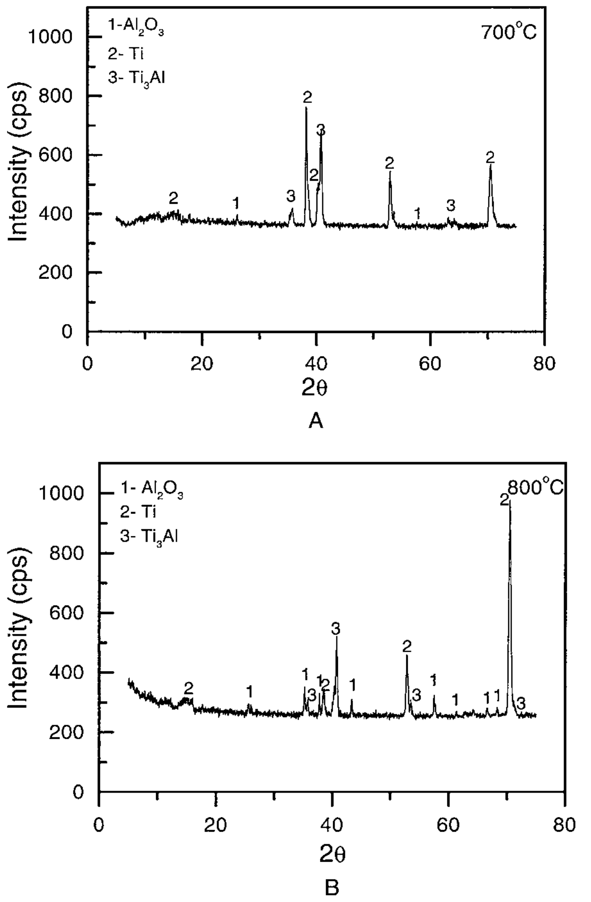

Figure 4 X-ray diffraction performed on the titanium bonding surface after mechanical separation at the Al_2O_3/Ti interface: A- sample diffusion bonded at 700°C/120 minutes; B- sample diffusion bonded at 800°C/120 minutes.

experimental condition employed, is the dissolution of the ceramic (in presence of Ti) followed by the formation of the intermetallic, according to the reaction: $6Ti + Al_2O_3 \rightarrow 3O_{[Ti]} + 2Ti_3Al$. According to Loehman [9], the free energy for this reaction is between 490 to 507 kcal/mol for temperatures ranging from 700 to 1000°C. This energy counterbalances the free energy for ceramic dissolution that is about 327 to 304 kcal/mol at the same temperature range [10]. The solid solution of oxygen into titanium ($O_{[Ti]}$) is evidenced by the hardening effect observed and by the absence of aluminium in this region. The oxygen diffusivity into α-Ti is relatively high [11], as so as the solubility of the oxygen into the metal. Furthermore, the O—Ti phase diagram shows that oxygen stabilises the α-Ti phase. Consequently, the formation of Ti_3Al instead of TiO can be ascribed to the aluminium excess at the interface, which does not diffuses into the titanium like oxygen does. According to David and coworkers [11], the presence of oxygen in solution causes a remarkable hardening effect into titanium. As Fig. 8 shows, the oxygen content into titanium is expected to be 15 at% for the sample diffusion bonded at 1000°C for 120 minutes (900 HV), which is far below the solubility limit. The formation of TiAl reported by some authors, mainly at higher temperatures (when the dissolution rate of the ceramic is expected to be higher) [5, 12], was not verified.

The Fig. 9 shows the probable diffusion path for the couple Al_2O_3/Ti at the experimental conditions employed. It is drawn on an isothermal section at 1100°C of the Al—1/2O_2—Ti phase diagram [8] and starts at the titanium corner with an enrichment on oxygen, as its diffusivity in titanium is higher. Close to the interface, the aluminium accumulation causes an inclination of the path to the aluminium corner. From the mass balance point of view, it has to cross a straight line between the titanium and the Al_2O_3, penetrating at the Ti_3Al field that is in equilibrium with the ceramic. According to the phase diagram of the Fig. 9, TiAl could be present in equilibrium with Ti_3Al and Al_2O_3, however it should be in contact with the ceramic. Therefore if TiAl was present, it would be verified by the X-ray diffraction performed on bonding surfaces. On the other hand TiO, if present, would be in contact with the α-Ti phase.

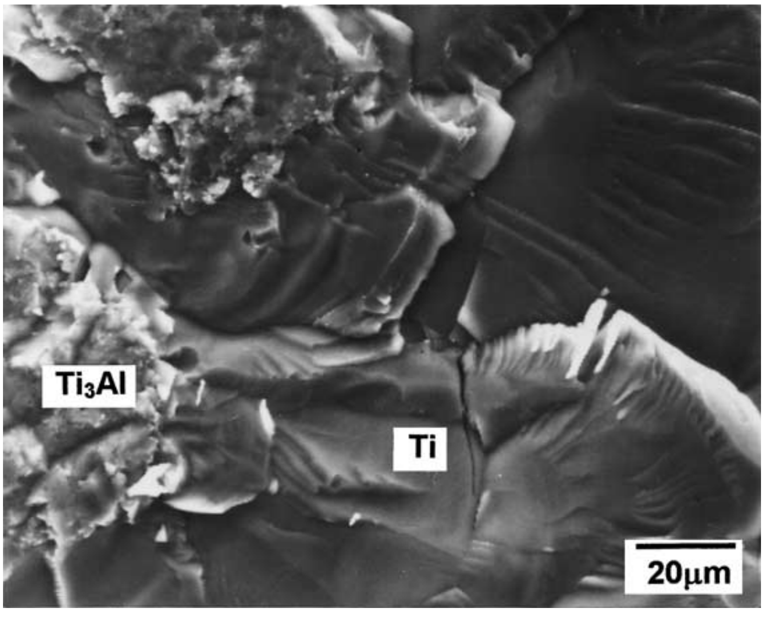

Figure 5 Brittle fracture aspect observed in the titanium fracture surface after mechanical separation at the Al_2O_3/Ti interface. Sample diffusion bonded at 800°C/120 minutes.

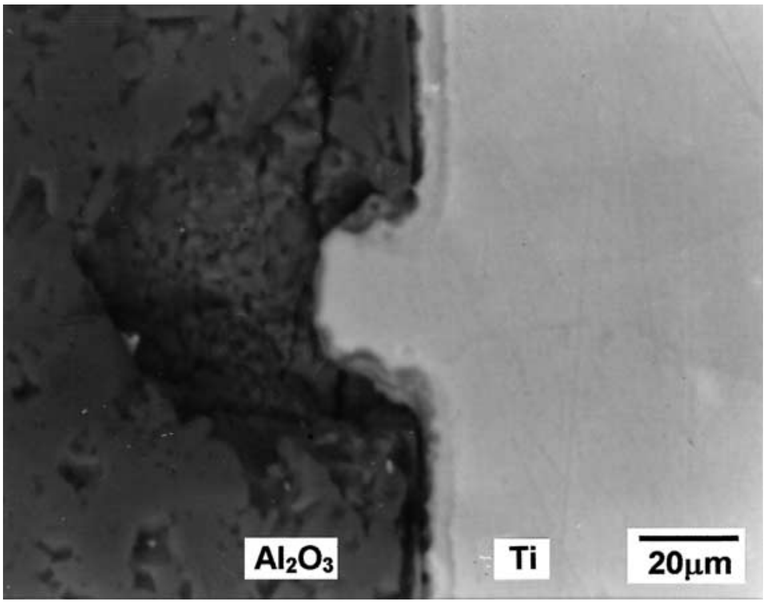

Figure 6 Al_2O_3/Ti interface formed after diffusion bonding at 900°C/120 minutes showing a continuous reaction.

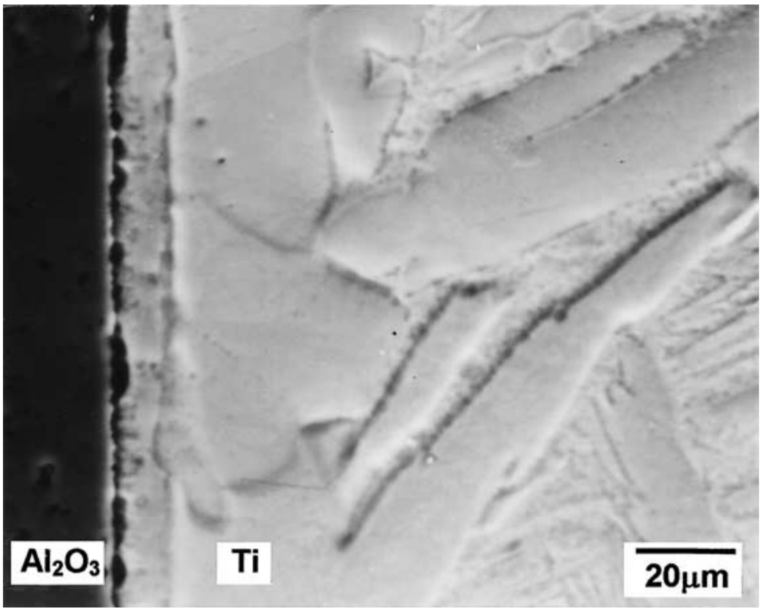

Figure 7 Al_2O_3/Ti interface formed after diffusion bonding at 1000°C/120 minutes.

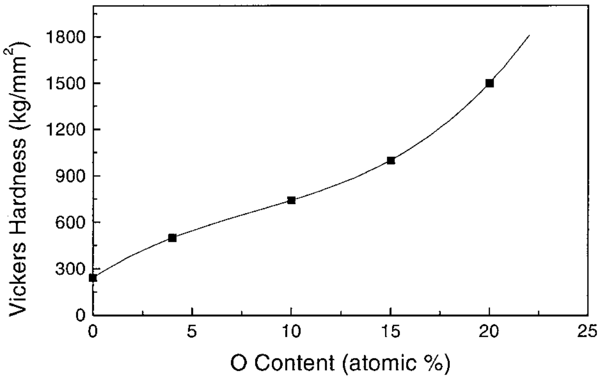

Figure 8 Hardening effect of titanium as a function of the oxygen content in solid solution [11].

The needle aspect of the titanium beyond the α stabilised region, can be ascribed to the high diffusivity/low solubility of the iron (from the steel/Ti interface), with stabilises the β-Ti phase that is preferable

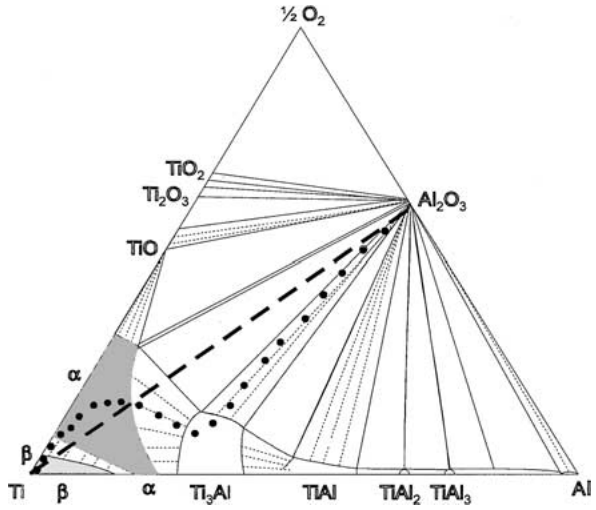

Figure 9 Probable diffusion path of the couple Al_2O_3/Ti obtained according to the experimental conditions employed.

etched and revealed by the metallographyc chemical reagent employed.

5. Conclusions

- Adhesion between Al_2O_3 and titanium at 700°C was only obtained with bonding times of 120 minutes while at 800°C with times as short as fifteen minutes, good adhesion is obtained. For both temperatures, the voids closure process at interface was observed to be not completed.
- At 900 and 1000°C, a wide reaction layer is formed. This reaction layer was identified as the Ti_3Al intermetallic and was also present at the interfaces formed at 700 and 800°C, but in a very thin layer.
- The bonding mechanism observed is the dissolution of the ceramic, the diffusion of oxygen into the titanium and the formation of Ti_3Al at the interface. This mechanism is according to equilibrium thermodynamics for the system.

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