J Mater Sci (2010) 45:4351–4357
DOI 10.1007/s10853-010-4303-0

EUROMAT 2009

Diffusion bonding of TiAl using Ni/Al multilayers

Sónia Simões · Filomena Viana · Volker Ventzke · Mustafa Koçak · A. Sofia Ramos · M. Teresa Vieira · Manuel F. Vieira

Received: 15 October 2009 / Accepted: 5 February 2010 / Published online: 19 February 2010

Abstract With the stimulus of temperature and pressure Ni and Al can quickly react and produce the intermetallic compound NiAl. This reaction is highly exothermic and high temperatures can be attained in the surroundings. These characteristics make Ni/Al multilayers very attractive to technological applications as localised heat sources. In this study, Ni/Al multilayer thin films are used to promote bonding between TiAl intermetallic alloys. Ni and Al alternated nanolayers were deposited by d.c. magnetron sputtering onto TiAl samples, with periods of 5, 14 and 30 nm. Joining experiments were performed at 900 °C for 60 or 30 min, in a vertical furnace with a vacuum level better than 10^{-2} Pa. Applied pressures of 5 MPa were tested. The microstructure of the cross-sections of the bond interface was analysed by energy dispersive X-ray spectroscopy and characterised by scanning electron microscopy. The observation of the microstructure for 14 and 30 nm period multilayers revealed sound bonding, while for 5 nm period porosity and cracks within the interlayer thin film were observed. The interface is divided into three distinct zones: one with columnar grains, another with very small equiaxed grains and the third with larger equiaxed grains. The joining process appears to depend on the diffusion of Ni and Ti across the interface and is assisted by the nucleation of nanometric grains at the interface. The mechanical strength of the joints was evaluated by shear tests. The bonds produced at 900 °C/5 MPa/60 min/14 nm exhibited the highest shear strength of 314 MPa.

S. Simões (✉) · F. Viana · M. F. Vieira
CEMUC, Department of Metallurgical and Materials Engineering, University of Porto, R. Dr. Roberto Frias, 4200-465 Porto, Portugal
e-mail: sonia.simoes@fe.up.pt

V. Ventzke · M. Koçak
Institute of Materials Research, GKSS Research Center, Max-Planck Str., Geesthacht, Germany

A. Sofia Ramos · M. Teresa Vieira
CEMUC, Department of Mechanical Engineering, University of Coimbra, R. Luís Reis Santos, 3030-788 Coimbra, Portugal

Introduction

TiAl alloys are good candidates for elevated temperature applications in the aerospace and automobile industry due to their high specific strength, low density, good corrosion resistance and excellent high temperature properties [1–3].

The development of joining processes for TiAl alloys is fundamental to integrate them into functional structures and to widen their application field. The bonding of these alloys is very difficult due to their high reactivity and to the tendency to form brittle intermetallic phases [1–3].

Several techniques have been suggested as adequate for bonding TiAl alloys, namely induction brazing [1], friction welding [4], laser welding [5], diffusion bonding [2, 3] and superplastic forming/diffusion bonding [6–8]. Among these, diffusion bonding emerges as one of the most promising techniques [2, 3]. With diffusion bonding it is possible to bond similar or dissimilar metals and nonmetals, very high quality joints are formed, the properties of the parent materials are unchanged and the process lends itself to automation. Defect free joints can be produced by diffusion bonding TiAl at 1000–1200 °C, depending on the bonding time and pressure [2, 3, 9–11]. Nevertheless, the high pressure and temperature associated with a long dwell time can induce structural changes and residual stresses at the interface and this is a problem for industrial applications. Diffusion bonding at 1000 °C with a 5 h stage and at 10 MPa pressure are the best reported conditions for achieving high strength joints for TiAl alloys [2, 3]. Experiments conducted at lower temperatures or for shorter times have produced low strength joints mainly due to a high incidence of defects [2, 3].

An alternative approach to diffusion bonding is the modification of the joining surfaces by multilayer deposition. In fact, using multilayers increases the diffusivity and reactivity of the interface by promoting nanocrystallinity and increasing the number of interfaces. This approach, which brings the advantages of diffusion bonding at "low" processing pressure and temperature, has been tested in previous investigations [12, 13]; TiAl alloys were bonded using a multilayer of alternated Ti and Al nanolayers, which effectively reduced the temperature of the bonding cycle to 900 °C [12, 13].

In this study a more reactive multilayer is tested: Ni/Al multilayers are known to transform into NiAl in a highly exothermic reaction. These multilayers can further improve the diffusion bonding process by acting as a localised heat source, in addition to the improved diffusivity [12–14]. Ni/Al multilayer thin films were deposited by sputtering onto TiAl substrates and the coated parts were joined by diffusion bonding. Structural characterisation of the interface was performed by SEM and mechanical properties were evaluated by shear tests.

Experimental procedure

The base material used in this investigation was γ-TiAl alloy with a duplex microstructure. Diffusion bonding specimens were cut to 10 × 10 × 10 mm for microstructural investigation and 25 × 7×5 mm for mechanical tests. The surfaces of the samples were polished down to 1 μm diamond suspension followed by ultrasonic cleaning with acetone and alcohol prior to joining.

Alternated Ni and Al nanolayers were deposited by d.c. magnetron sputtering onto the polished surface of the TiAl substrates using pure nickel and aluminium targets. Films with a modulation period (Λ—thickness of one Ni layer and one Al layer) of 5, 14 and 30 nm and a total film thickness ranging from 3 to 3.5 μm were produced. The schematic illustration of the coated samples and the transmission electron microscopy (TEM) image showing the morphology of an as-deposited Ni/Al multilayer thin film with a 14 nm period are presented in Fig. 1. The chemical composition of the as-deposited films was determined by electron probe microanalysis in order to confirm the desired equiatomic chemical composition.

Joining experiments were performed at 900 °C with a bonding time of 60 and 30 min and a pressure of 5 MPa, in a vertical furnace with a vacuum level better than 10^{-2} Pa. In order to perform the microstructural and chemical characterisations of the interface, cross-sections of the joints were prepared using standard metallographic techniques. The microstructure of the bond interface was characterised by scanning electron microscopy (SEM) at an accelerating voltage of 15 keV and analysed by energy dispersive X-ray spectroscopy (EDS). The EDS measurements were made at an accelerating voltage of 15 keV by the standardless quantification. The results obtained by this method provide a fast quantification with an automatic background subtraction, matrix correction and normalisation to 100% for all of the elements in the peak identification list. The volume of interaction has been estimated by Monte Carlo simulations of electron trajectories using CASINO software. The results shows that for the substrate the lateral spread and thickness of the interaction volume are 1.8 and 1.4 μm, respectively, while for the interface region the estimated values are 1.4 and 1.0 μm, respectively.

Specimens for shear tests were extracted from each joint by electro-discharge machining (EDM), as schematically shown in Fig. 2. For each joint only the three central specimens were tested. The shear testing was performed at room temperature at a loading rate of 0.2 mm/min. Figure 3 shows a schematic illustration of shear test apparatus used in this investigation.

Fractography was conducted on the fractured surfaces of the shear specimens using a scanning electron microscope.

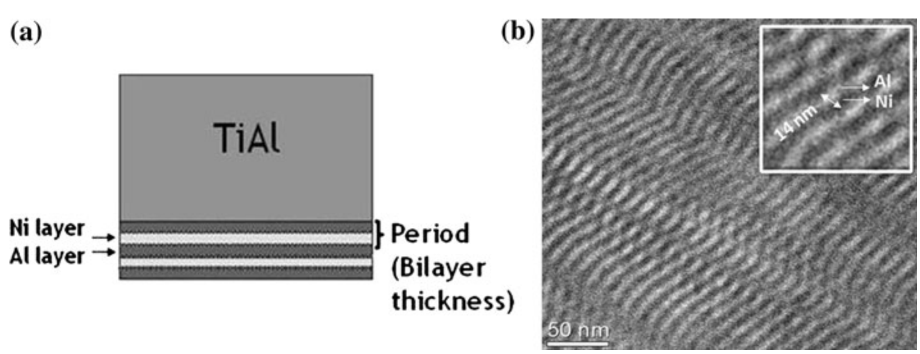


Fig. 1 **a** Schematic illustration of the coated samples and **b** TEM image showing the morphology of an as-deposited Ni/Al multilayer with Λ = 14 nm

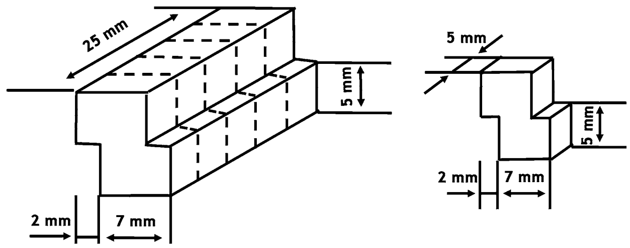


Fig. 2 Geometry of joint and of shear test specimens extracted from each joint by electro-discharge machining (EDM)

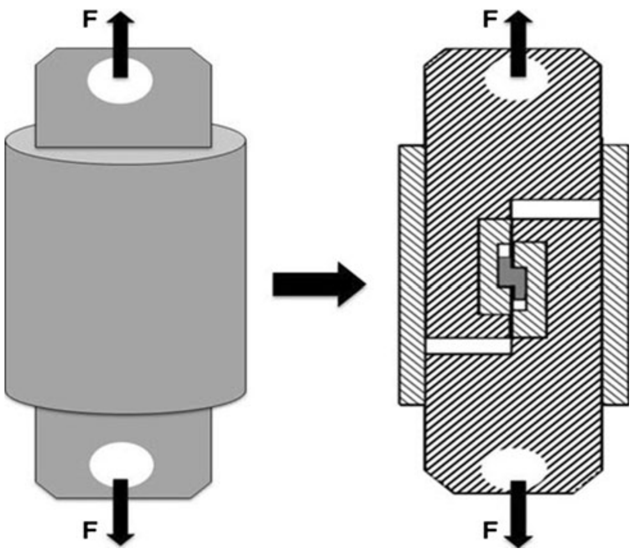


Fig. 3 Schematic illustration of shear test apparatus

Results and discussion

Microstructural aspects

The microstructures of the bond interfaces obtained at a temperature of 900 °C for 60 min with 5 MPa are illustrated in Fig. 4. The interface can be divided into three distinct zones: zone 1 (close to base material) exhibits columnar grains, very small equiaxed grains are observed at zone 2 while zone 3 (close to bond line) has larger equiaxed grains. The microstructure of the TiAl base alloy is unchanged by the joining procedure. Abnormal grain growth is observed in some regions of zone 3. Apparently sound joints, without pores or cracks, are observed for all the bonding conditions. However, if we examine the images of the 5 nm period sample more carefully (Fig. 4c), we can observe very small porosity and very fine cracks, indicated by arrows in this figure, at the central line of zone 3 and at the interface of zones 1 and 2.

EDS chemical compositions of the different zones are listed in Table 1. It should be noted that the chemical composition of the the γ-TiAl alloy remains unaltered after joining, as observed for the microstructure. Zone 1 is essentially composed of 30 at% Ti, 52 at% Al and 15 at% Ni. Zones 2 and 3 present 53 at% Ni and 45 at% Al, the Ti content is very low. There is a diffusion flux of Ti atoms from the TiAl alloy side towards the centre of the interface and of Ni atoms in the opposite direction (towards the substrate). Furthermore, we also observed the presence of some Nb and Cr from the TiAl alloy, but this was restricted to zone 1.

The ternary Ti–Ni–Al [15] phase diagram was used in conjunction with the EDS analysis to predict the nature of the reaction products detected at the interfaces. The Ti–Ni–Al isothermal section at 900 °C was chosen for this purpose as it is the isotherm closest to the bonding temperature.

According to the Ti–Ni–Al phase diagram in Fig. 5, zone 1 corresponds to the τ_2 phase (Al_2NiTi) and both zones 2 and 3 to β_1 phase (NiAl). Based on these results, the joining mechanism appears to depend on the diffusion of Ni and Ti across the interface, the results of EDS analysis confirm the net flux of Ni towards the TiAl alloy and of Ti towards the multilayer, the columnar growth of the intermetallic phase of zone 1 in a direction perpendicular to the interface also confirms this assumption. In the central region of the interface, the composition is almost constant and grains grow with equiaxed morphology, this structure is similar to the structure of the multilayer when heated to high temperature [16]. The intermetallic phase is the same in zones 2 and 3, the only difference being the slightly higher Ti content of zone 2 associated with a smaller grain size. The association of a higher Ti content with smaller grain size suggests the hypothesis that the higher Ti content retards the formation of NiAl. It should be noted that Ti content reaches 12 at% in some samples.

For the 14 nm period multilayers, decreasing the bonding time to 30 min still leads to a good joint without pores or cracks (Fig. 6). Ti EDS profiles for bonded samples with 14 nm period Ni/Al multilayers and bonding times of 30 and 60 min are presented in Fig. 7. The EDS analysis shows that, with a shorter bonding time, zone 2 is thicker and has higher Ti content, confirming the hypothesis presented above. For joints with 60 min dwell time, the Ti profile across the interface is steeper and the Ti content in zone 3 is slightly higher, just as if the intermetallic phase in zone 1 acts as barrier to further diffusion across the interface. This difference in diffusion of titanium across the interface observed for different bonding times can explain the fact that the regions with very small grains are more evident in the sample subject to 30 min bonding time.

Mechanical characterisation

The strength of the joints was evaluated by shear tests and for the tested bonding conditions, the results are presented in Fig. 8. In this figure it is possible to observe the shear

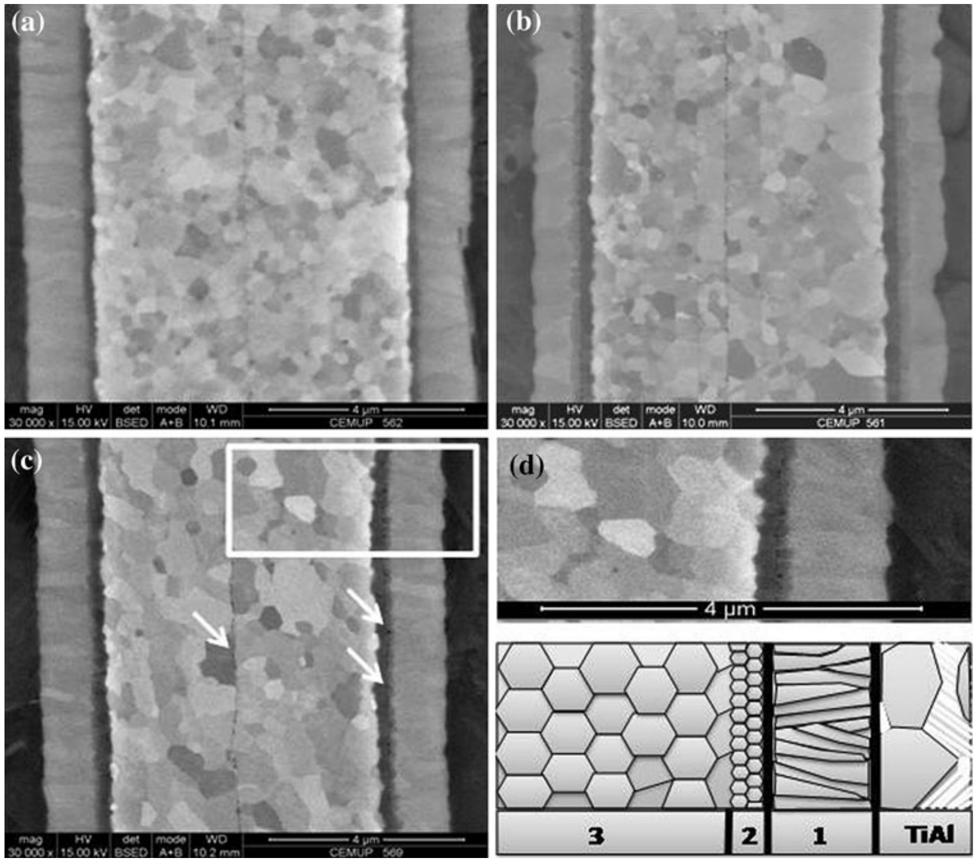


Fig. 4 SEM image of the bond interface obtained at 900 °C for 60 min at 5 MPa for: **a** 30 nm, **b** 14 nm and **c** 5 nm modulation period. A detail of the interface and scheme of the three different zones observed are illustrated in **d**

Table 1 EDS chemical composition of different zones of the bond interface obtained at 900 °C for 60 min at 5 MPa for the 14 nm period multilayer

	Al	Ti	Ni	Cr	Nb
Substrate	49.27	45.33	0.00	2.15	3.25
Zone 1	51.73	29.07	15.00	1.18	2.61
Zone 2	53.40	2.00	44.60	0.00	0.00
Zone 3	53.17	1.67	45.16	0.00	0.00

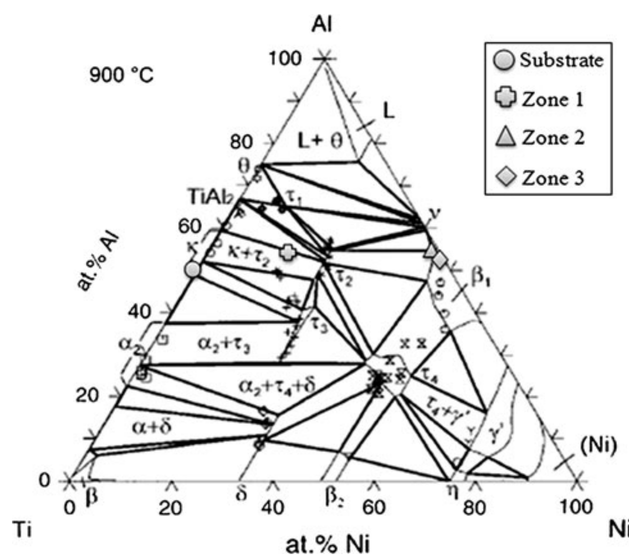


Fig. 5 Isothermal section at 900 °C of the Ti–Ni–Al phase diagram [15]. The chemical compositions marked on the diagram are the compositions of the three reaction zones from the bond interface obtained at 900 °C for 60 min at 5 MPa and a 14 nm period multilayer

strength values obtained for the bonds produced at 900 °C/5 MPa/60 min with 14 and 30 nm period and at 900 °C/5 MPa/30 min with 14 nm period Ni/Al multilayers.

The strength of the joint produced with the 30 nm period multilayer is very low, 46 MPa, while for the smaller multilayer period, 14 nm, the strength reaches 342 MPa. When the bonding time is reduced from 60 to 30 min, for the 14 nm period multilayer, the strength of the joints is drastically reduced to values ranging from 109 to 247 MPa. In addition to the reduction in strength, the increased dispersion of results is an indication of the poor quality of the joint and of the unreliability of the joint procedure.

The highest shear strength was obtained for the bonds produced at 900 °C/5 MPa/60 min/14 nm, with an average value of 314 MPa. This value is similar to other values reported in the literature. Çam et al. [2] observed a shear strength value of 388 MPa for diffusion bonding of TiAl

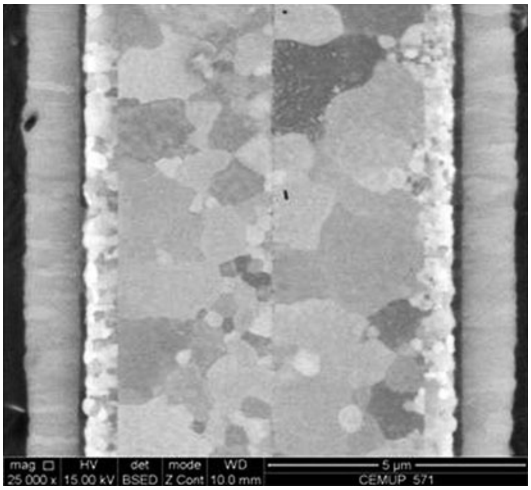


Fig. 6 SEM image of the cross-sections of the bond interface obtained at 900 °C for 30 min at 5 MPa for $\Lambda = 14$ nm

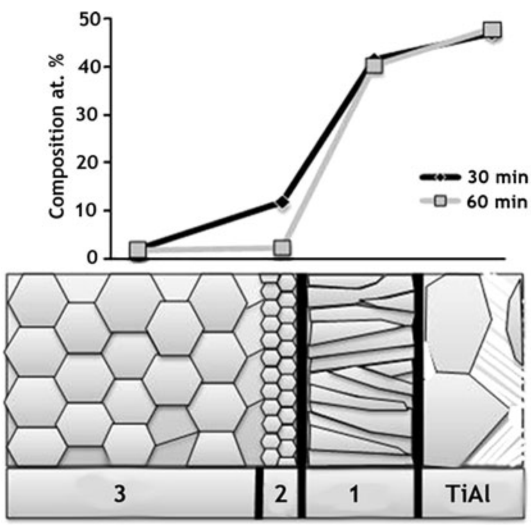


Fig. 7 Titanium EDS profiles across the bond interface formed at 900 °C for 30 and 60 min at 5 MPa for $\Lambda = 14$ nm, scheme of the interface is used to identify the analysed zones

alloy at 1000 °C/10 MPa/5 h and for the lower bonding conditions (950 °C/10 MPa/3 h) this value decreased to 266 MPa. These results show that it is possible to reduce the temperature, pressure and time of the TiAl diffusion bonding experiments and still obtain reliable high strength joints, by using Ni/Al nanolayers.

The period of the Ni/Al nanolayers is an important parameter in the bonding process. The shear strength value decreased abruptly when the period was increased from 14 to 30 nm.

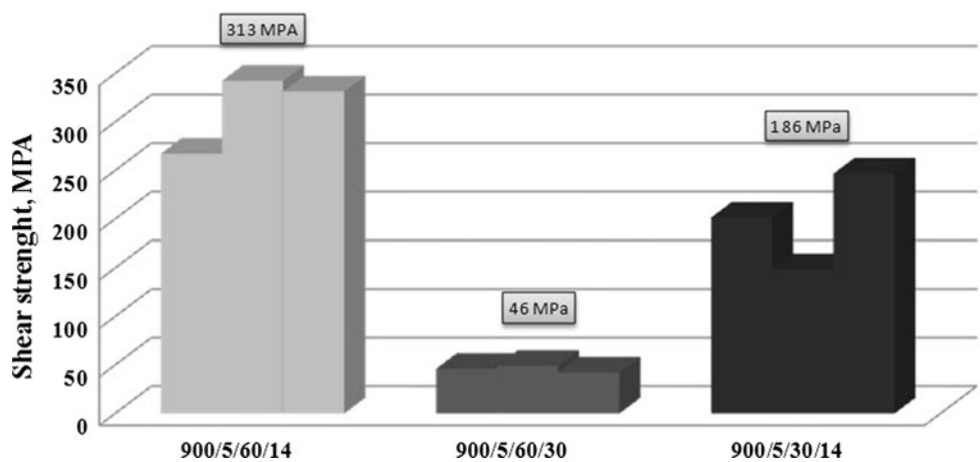
Fractography

Cross-sections of fractured samples with the lowest (900 °C/5 MPa/60 min/30 nm) and highest (900 °C/5 MPa/60 min/14 nm) shear strength were examined by SEM for failure analysis. Figure 9 shows SEM cross-section images of fractured samples with 14 and 30 nm periods and a schematic illustration of the fracture path. From these images it is clear that for the 14 nm period multilayer, the fracture occurs along the reaction layer, mainly through the interface of zone 1 and 2, as indicated, while for the 30 nm period the crack propagates mainly through the NiAl grains of zone 3, but also propagates through the entire interface and also the base TiAl alloy.

The 3D fracture surface analysis of these samples, presented in Fig. 10, shows that for the 14 nm period the surface is very smooth while for 30 nm a much rougher fracture surface is observed. These observations confirm the analysis of the cross-section images; the rough surface of the 30 nm period sample is the result of crack propagation across the entire interface.

Figure 11 shows SEM images of the fracture surfaces along different zones. The fracture surface of the base TiAl (Fig. 11a) exhibits river patterns typical of cleavage fracture. When a fracture propagates through the interface of TiAl and reaction zone, the Al_2NiTi phase, the fracture surface is smooth with no distinctive features to allow

Fig. 8 Shear strength values obtained from the bonds produced at 900 °C for 60 or 30 min at 5 MPa and for 14 and 30 nm of period (bond conditions: °C/MPa/min/nm)



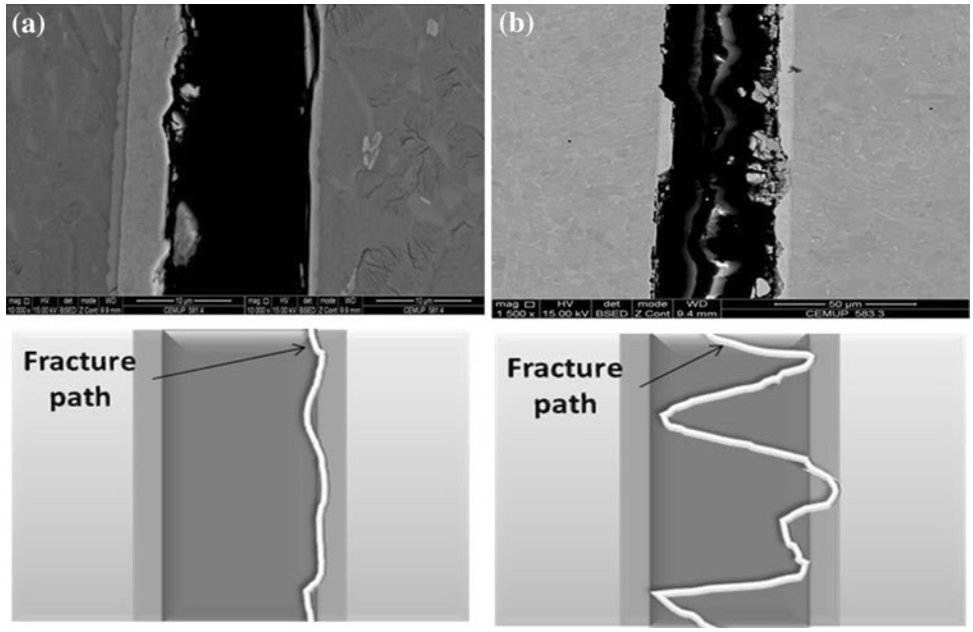


Fig. 9 SEM cross-section images of fractured samples of **a** the lower (900 °C/5 MPa/60 min/14 nm) and **b** the higher (900 °C/5 MPa/60 min/30 nm) strength joints, and the respective schematic drawing of the fracture paths

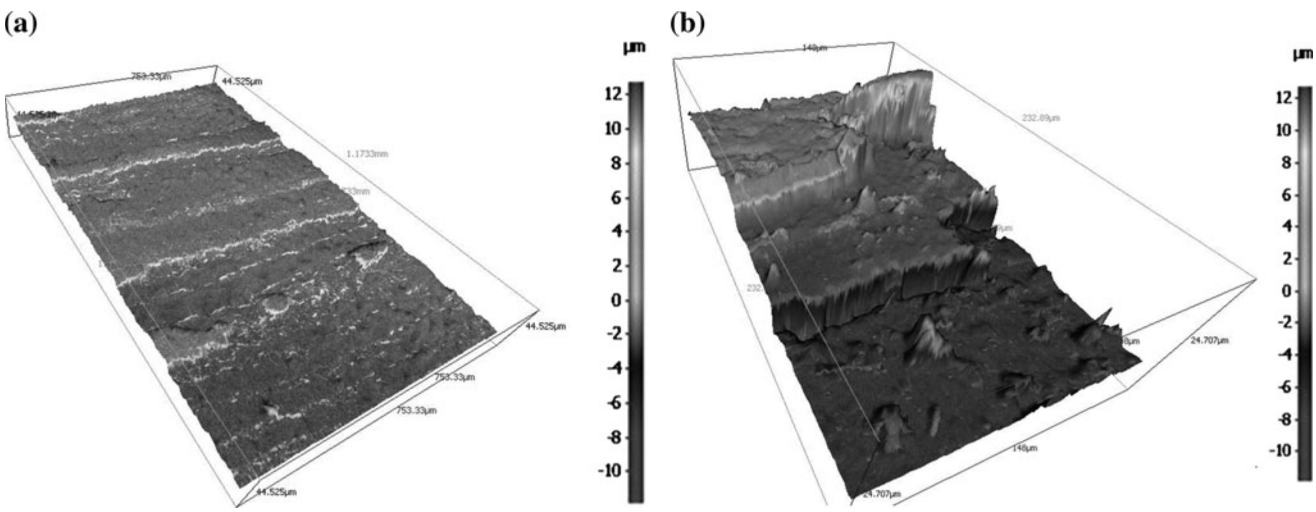


Fig. 10 3D fracture surface analyses for samples joined with: **a** 14 nm and **b** 30 nm period Ni/Al multilayer thin films

identification of the fracture mode. When the fracture occurs across the central zone of the interface, the NiAl phase, the fracture is partially intergranular and partially transgranular, this latter mode is typical of cleavage fractures as can be seen in Fig. 11d). The occurrence of intergranular fracturing across some areas of the NiAl zone suggests the presence of a fragile phase or oxidation at grain boundaries. However, this was not confirmed by the observations and analyses performed in this study.

Conclusions

The diffusion bonding process was enhanced by the presence of Ni and Al alternating nanolayers as interlayer material. Using these multilayer thin films it is possible to reduce the temperature, pressure and time necessary to join TiAl alloys by diffusion bonding and obtain sound and reliable joints. The joining mechanism appears to depend on the diffusion of Ni and Ti across the interface. The period of the multilayer influences bond quality and strength. The use of 5 nm period multilayers results in porosity and cracks inside the interlayer thin film while the use of multilayers with 30 and 14 nm period results in sound joining along the entire bond line.

The bonds produced at 900 °C/5 MPa/60 min/14 nm exhibited the highest shear strength of 313 MPa. The shear strength value decreases abruptly when the period increases from 14 to 30 nm. For the highest strength joint, produced with the 14 nm period Ni/Al multilayer, the fracture

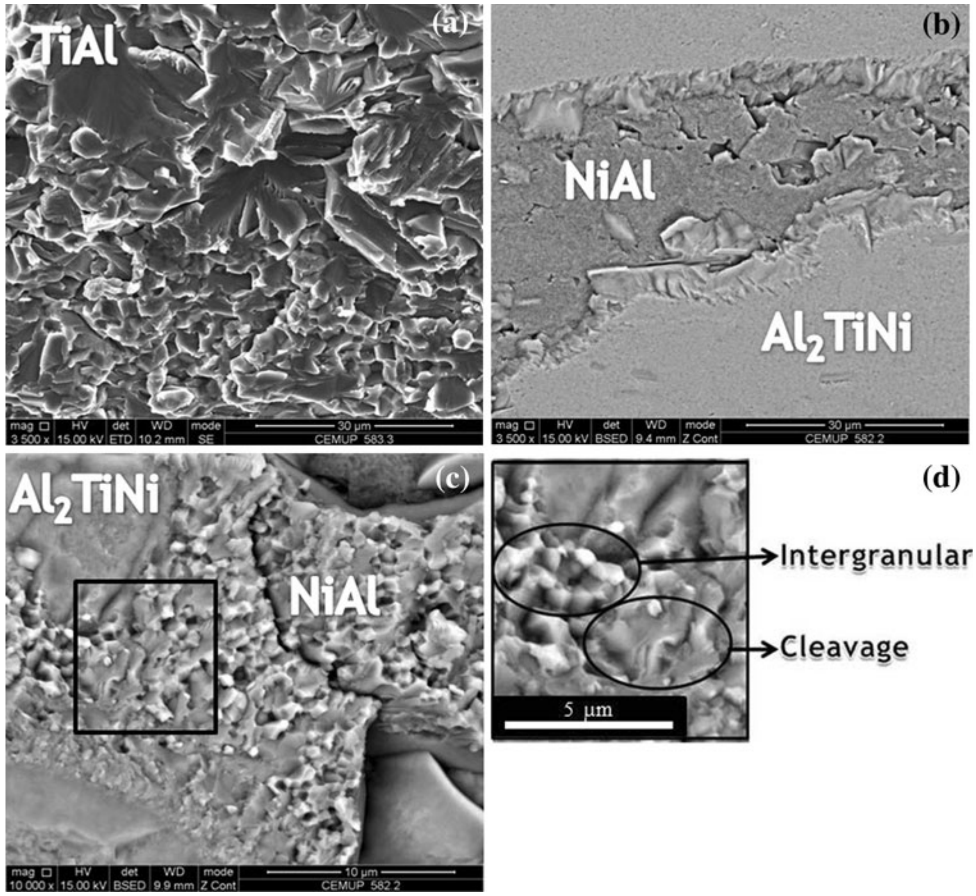


Fig. 11 SEM images of the fracture surfaces: **a** through the base TiAl; **b**, **c** across NiAl and reaction layer between TiAl and the multilayer, the Al_2NiTi phase, and **d** a detail showing intergranular and cleavage fracture across NiAl grains

occurs along the reaction layer and presents a very smooth surface. For the lowest strength joint, produced with the 30 nm period multilayer, the crack propagates through NiAl, the central zone of the interface, exhibiting a much rougher fracture surface. The TiAl alloy exhibits a cleavage fracture mode. NiAl fractures in an intergranular and transgranular/cleavage mode.

Acknowledgements This study was supported by Fundação para a Ciência e a Tecnologia through the project POCI/CTM/55970/2004 co-financed by European Union fund FEDER and the Grant SFRH/BD/30371/2006 financed by POS_C.

References

1. Shiue RK, Wu SK, Chem SY (2003) Intermetallics 11:661–671
2. Çam G, Ipekoglu G, Bohm KH, Koçak M (2006) J Mater Sci 4:5273–5282. doi:10.1007/s10853-006-0292-4
3. Çam G, Koçak M (1999) J Mater Sci 34:3345–3354. doi:10.1023/A:1004624930352s
4. Threadgill PL (1995) Mater Sci Eng A 192–193:640
5. Deevi S (1991) Adv Mater Process 9:44
6. Wu GQ, Huang Z (2001) Scripta Metal 45:895
7. Wu GQ, Huang Z, Lin JG (2002) Mater Lett 56:606
8. Wu GQ, Huang Z, Chen CQ, Ruan ZJ, Zhang Y (2004) Mater Sci Eng A 380:402
9. Nakao Y, Shinozaki K, Hamada M (1991) ISIJ Int 31:1260–1266
10. Yan P, Wallach ER (1993) Intermetallics 1:83–98
11. Glatz W, Clemed H (1997) Intermetallics 5:415423
12. Ramos AS, Vieira MT, Duarte LI, Vieira MF, Viana F, Calinas R (2006) Intermetallics 14:1157–1162
13. Duarte LI, Ramos AS, Vieira MF, Viana F, Vieira MT, Koçak M (2006) Intermetallics 14:1151–1156
14. Duckham A, Spey SJ, Wang J, Reiss ME, Weihs TP, Besnoin E, Knio OM (2004) J Appl Phys 96:4
15. Huneau B, Rogl P, Zeng K, Schmid-Fetzer R, Bohn M, Bauer J (1999) Intermetallics 7:1337–1345
16. Ramos AS, Vieira MT, Morgiel J, Grzonka J, Simões S, Vieira MF (2009) J Alloys Compd 484:335–340