Diffusion bonding of TiAl using reactive Ni/Al nanolayers and Ti and Ni foils

Article in Materials Chemistry and Physics - July 2011

DOI: 10.1016/j.matchemphys.2011.02.059

CITATIONS
42

READS
153

6 authors, including:

F. M. C. Viana
University of Porto
72 PUBLICATIONS 847 CITATIONS

See Profile

M. Koçak
Gedik Holding, Gedik University
186 PUBLICATIONS 2,965 CITATIONS

See Profile

Ana Sofia Ramos
University of Coimbra
67 PUBLICATIONS 986 CITATIONS

See Profile

Some of the authors of this publication are also working on these related projects:

- Diffusion Bonding of Titanium Alloys View project
- Metal Additive Manufacturing Joining with Dissimilar Materials View project
Diffusion bonding of TiAl using reactive Ni/Al nanolayers and Ti and Ni foils

Sónia Simões, Filomena Viana, Mustafa Koçak, A. Sofia Ramos, M. Teresa Vieira, Manuel F. Vieira

CEMUC, Department of Metallurgical and Materials Engineering, University of Porto, R. Dr. Roberto Frias, 4200–465 Porto, Portugal
GRSS Research Center, Institute of Materials Research, Max-Planck Str., Geesthacht, Germany
GEDIK HOLDING, Istanbul, Turkey
CEMUC, Department of Mechanical Engineering, University of Porto, R. Luís Reis Santos, 4300-788 Coimbra, Portugal

ABSTRACT

The diffusion bonding of TiAl using reactive Ni/Al multilayer thin films with Ti and Ni foils was investigated. Bonding experiments were performed at 800 and 900 °C, at a pressure of 5 MPa and for bonding times of 30 and 60 min. The bonding surfaces were modified by sputtering, by deposition of Ni and Al nanolayers to increase the diffusivity at the interface, and Ti and Ni foils were used to fill the bond gap. The mechanical properties of the joints were evaluated by nanoindentation and shear strength tests. Using foils in-between the nanocrystalline multilayers, which would be a useful method for correcting the absence of flatness of the parts to be joined, has drawbacks as it induces the formation of hard, brittle intermetallic compounds, responsible for the low shear strength of the joints.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Intermetallic alloys demonstrate a range of fascinating properties, especially when weight reduction of the components is a critical factor for structural applications, such as for aircraft, spacecraft and automobile engines. In the last two decades, several investigations have been conducted into the development of intermetallic alloys. Among these alloys, the two-phase γ-base TiAl is the most promising due to its high specific strength and stiffness at elevated temperature, in combination with good corrosion resistance, when compared to conventional titanium alloys.[1–4]

The successful development of joining technologies is very important for the increasing application of these alloys. Several techniques have been suggested as adequate for bonding TiAl alloys [4–18], brazing [10–14] and diffusion bonding [15–18] appear to be the most promising. With these techniques, it is possible to bond similar or dissimilar metals and nonmetals with good mechanical properties, comparable with the base material, while avoiding the main problem of fusion welding processes, namely the thermal shock that leads to high residual stresses at the interface.

Brazing of TiAl alloys with Ti–Cu–Ni [10,11] or Ti–Ni [14] braze alloys is reported in the literature as capable of producing sound joints, appropriate for high temperature applications. Two benefits of this joining technology are the low pressure required and the overcome of the thermal shock problem observed in the conventional fusion welding. However, the formation of a multiphase interface with different intermetallic compounds and, consequently, varying mechanical behavior along the entire interface cannot be avoided. Additionally, the brazing temperature is still very high.

Diffusion bonding promotes the formation of a fine interfacial region but requires excellent contact at the interface; this is only possible with a combination of high bonding temperatures and pressures for relatively long stages. Since it is a solid state joining process, diffusion bonding eliminates the problems of segregation, solidification cracking, and distortions stresses usually found in fusion welding processes. The literature has demonstrated the possibility of joining titanium aluminides by diffusion bonding, but temperatures above 1000 °C are required [15,16].

Recently, nanoscale multilayer foils and thin films have attracted much attention for use in joining techniques [19–24]. A common feature of these multilayers is the large amount of heat released during the reaction between the layers to form a new phase. Of those discussed in the literature, Ni/Al multilayers have been extensively characterized [25–29]. The authors have
previously determined that deposition by sputtering of a multilayer thin film is known to improve diffusivity of the bonding TiAl interfaces, simultaneously reducing diffusion bond temperature, time and pressure [30–32]; the interfacial region remains in the order of a few micrometers, and can be tailored to match the composition of the base material. However, a smooth, flat bonding surface is still required due to the inability of the multilayer to fill any gap at the matching surfaces. Using Ni/Al multilayer thin films [32], sound joints were obtained by diffusion bonding at 900 °C, at a pressure of 5 MPa for 60 min; the 14 nm period multilayer produced the joint with the highest shear strength (314 MPa).

In this article, a modified bonding technique is investigated in an attempt to combine the diffusivity of interfaces (substrate/multilayer and multilayer/bonding foils) with a decrease in the importance of the contact between the parts to be joined, by inserting Ni and Ti foils in the interface. The increased diffusivity of the multilayer is used to promote bonding at reduced temperature and time and Ti and Ni foils are used to fill the bond gap.

2. Experimental procedure

The γ-TiAl alloy used in this investigation has a duplex microstructure with a chemical composition of Ti–45Al–5Nb at.%. Specimens of 10 mm × 10 mm × 10 mm were polished down to 1 µm diamond suspension. Ni and Al alternated nanolayers were deposited onto γ-TiAl by d.c. magnetron sputtering using pure nickel and aluminium targets. The deposition parameters were selected in order to obtain an equiatomic average chemical composition. Films with a modulation period (Λ – bilayer thickness) of 5, 14 and 30 nm and total thickness ranging from 3.0 to 3.5 µm were deposited. Ti and Ni foils (two Ti foils 5 µm thick and a central Ni foil 1 µm thick) were placed between the coated parts. Diffusion bonding joints were produced with temperatures of 800 and 900 °C, a pressure of 5 MPa and bonding time of 30 and 60 min, in a vertical furnace with a vacuum level better than 10⁻² Pa. Fig. 1 shows the schematic illustration of the diffusion bonding process.

In order to perform the microstructural and chemical characterizations of the interface, cross-sections of the joints were prepared using standard metallographic techniques. The bond interface was characterized by scanning electron microscopy (SEM) at an accelerating voltage of 15 keV and analysed by energy dispersive X-ray spectroscopy (EDS). A high resolution FEI QUANTA 400 FEG SEM with EDAX Genesis X4M was used for this purpose. The EDS measurements were made at an accelerating voltage of 15 keV by the standardless quantification. The results obtained by this method provide a rapid quantification with automatic background subtraction, matrix correction and normalization 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 show that for the substrate the lateral spread and depth of the interaction volume are 1.8 and 1.4 µm, respectively, while for the interface region the estimated values are 1.5 and 1.0 µm, respectively.

2. Experimental procedure

The γ-TiAl alloy used in this investigation has a duplex microstructure with a chemical composition of Ti–45Al–5Nb at.%. Specimens of 10 mm × 10 mm × 10 mm were polished down to 1 µm diamond suspension. Ni and Al alternated nanolayers were deposited onto γ-TiAl by d.c. magnetron sputtering using pure nickel and aluminium targets. The deposition parameters were selected in order to obtain an equiatomic average chemical composition. Films with a modulation period (Λ – bilayer thickness) of 5, 14 and 30 nm and total thickness ranging from 3.0 to 3.5 µm were deposited. Ti and Ni foils (two Ti foils 5 µm thick and a central Ni foil 1 µm thick) were placed between the coated parts. Diffusion bonding joints were produced with temperatures of 800 and 900 °C, a pressure of 5 MPa and bonding time of 30 and 60 min, in a vertical furnace with a vacuum level better than 10⁻² Pa. Fig. 1 shows the schematic illustration of the diffusion bonding process.

In order to perform the microstructural and chemical characterizations of the interface, cross-sections of the joints were prepared using standard metallographic techniques. The bond interface was characterized by scanning electron microscopy (SEM) at an accelerating voltage of 15 keV and analysed by energy dispersive X-ray spectroscopy (EDS). A high resolution FEI QUANTA 400 FEG SEM with EDAX Genesis X4M was used for this purpose. The EDS measurements were made at an accelerating voltage of 15 keV by the standardless quantification. The results obtained by this method provide a rapid quantification with automatic background subtraction, matrix correction and normalization 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 show that for the substrate the lateral spread and depth of the interaction volume are 1.8 and 1.4 µm, respectively, while for the interface region the estimated values are 1.5 and 1.0 µm, respectively.

Fig. 1. Schematic illustration of the diffusion bonding process.

Fig. 2. SEM images of diffusion bonding interfaces with 14 nm period multilayer thin films: (a) produced at 800 °C, (b) magnification of the selected region marked in (a), (c) produced at 900 °C and (d) magnification of the selected region marked in (c).
The crystallographic information from the joint interfaces was obtained by electron backscatter diffraction (EBSD). EBSD is a surface technique since only the topmost 50 nm of the sample contributes to the diffraction pattern. The indexation of the Kikuchi patterns obtained by EBSD allows phase identification in localized zones of the samples; for Ti and Al the minimum lateral spread of the interaction volume ranges from 50 to 100 nm [33], with an accelerating voltage of 15 keV. For the indexation, it was used ICDD PDF2 (2006) database. The careful preparation of the surface of the samples for EBSD is the key factor critical in achieving good quality EBSD patterns. Therefore, the samples for EBSD were submitted to additional polishing stage using colloidal silica. This final chemo-mechanical polishing reduced the surface damage. The Kikuchi patterns were obtained with the sample tilted at 70° from the horizontal.

The mechanical characterization was performed by hardness and shear strength tests. Nanoindentation tests were carried out along the entire interface using a Nanostress (Micro Materials) equipped with a Berkovich diamond indenter. A maximum load of 1.5 mN was attained in all the tests. In order to determine the hardness of the different zones at the interface, two indentation matrices of 3 columns by 15 rows formed Ti region, zone 5. Zone 6 is formed at the center of the shear specimen. The identification of the interface reaction zones corresponding to each nanoindentation test was performed by SEM.

The shear strength testing apparatus and the geometry of the shear specimens, developed at GKSS, are described elsewhere [32]. For each joint, three specimens from the central region were tested. The shear testing was performed at room temperature at a shear rate of 0.2 mm min⁻¹. Fractography analysis was conducted by SEM on the fractured surfaces of the shear specimens.

3. Results and discussion

3.1. Phase evolution

The microstructural and chemical analysis shows that interfaces with apparent soundness were produced by bonding experiments using the three multilayer periods at 900°C. For the 14 and 30 nm period multilayers, decreasing the bonding time to 30 min still leads to a good joint without pores or cracks. At 800°C only the Ni/Al thin films with 14 and 5 nm periods promote joining.

The solid state diffusion across the interface promotes the formation of six different zones identified in Fig. 2. The different grey tones in these backscattered images show the variation in composition across the interface. It should be noted that the microstructure of the TiAl base alloy is unchanged by the joining procedure. The influence of period and temperature on the microstructure of the bond interfaces can be observed in Fig. 2. Raising the bonding temperature from 800°C to 900°C promotes an increase in the total thickness of the interface; for the 14 nm period, the total thickness increases from 18.1 to 21.7 μm. The thickness of the reaction zones depends on temperature and period, raising the temperature increased mainly the thickness of zones 3 and 4. The reaction products formed at the interfaces were characterized using a combination of EDS and EBSD pattern analysis. EBSD patterns are particularly important for the thinner layers where the layer thickness is smaller than the volume of interaction of EDS measurements. Fig. 3 shows two examples of EBSD pattern indexation for zones 1 and 2 of a joint processed at 800°C using a 14 nm period multilayer thin film. For the 14 nm period multilayer, the phases identified by EBSD at each interfacial zone are listed in Table 1. Based on these results, a phase evolution at the interface can be drawn with high probability for each joining temperature. At 800°C, interdiffusion between γ-TiAl (base material) and NiAl (multilayer) lead to the formation of reaction zone 1, which corresponds to AlNITi phase; the NiAl multilayer thin film (zone 2) transforms to NiAl during the heating cycle. Following zone 2, the diffusion between the multilayers and Ti foil leads to the formation of Ti enriched phases, zones 3 and 4, namely AlNi2Ti, and Ti3Al.

At 900°C the diffusion is more intense and the Al content at the interface is higher than the one measured after bonding at 800°C. The intense diffusion of Al leads to the formation of a new Al-rich phase (Al2NiTi) in zone 1; this zone contains grains of two different phases, AlNITi and Al2NiTi. The interdiffusion of the multilayer and the Ti foil leads to a phase evolution similar to the one observed at 800°C; zone 2 (NiAl multilayer region) and zone 3 are composed of NiAl and AlNi2Ti phases, as observed for 800°C. A continuous AlNITi layer (zone 4), not detected at 800°C, develops between the

Table 1 Phases identified by EBSD analysis at different zones of the diffusion bond at 800 and 900°C.

<table>
<thead>
<tr>
<th>Zone</th>
<th>800°C</th>
<th>900°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>AlNITi</td>
<td>Al2NiTi + AlNITi</td>
</tr>
<tr>
<td>2</td>
<td>NiAl</td>
<td>NiAl</td>
</tr>
<tr>
<td>3</td>
<td>AlNi2Ti</td>
<td>AlNi2Ti</td>
</tr>
<tr>
<td>4</td>
<td>Ti3Al</td>
<td>AlNITi</td>
</tr>
<tr>
<td>5</td>
<td>Ti</td>
<td>Ti3Al</td>
</tr>
<tr>
<td>6</td>
<td>Ti2Ni</td>
<td>Ti2Ni</td>
</tr>
</tbody>
</table>

![Fig. 3. EBSD Kikuchi pattern indexation of a joint processed at 800°C using a 14 nm period multilayer thin film: (a) phase AlNITi (zone 1) and (b) phase NiAl (zone 2).](image-url)
Table 2
Mean hardness values of the phases present in the interfaces formed at 800 and 900 °C.

<table>
<thead>
<tr>
<th>Zone 800 °C</th>
<th>Phase(s)</th>
<th>Hardness (GPA)</th>
<th>Mean</th>
<th>STD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zone 900 °C</td>
<td>Phase(s)</td>
<td>Hardness (GPA)</td>
<td>Mean</td>
<td>STD</td>
</tr>
<tr>
<td>TiAl</td>
<td></td>
<td>10.4</td>
<td>0.9</td>
<td></td>
</tr>
<tr>
<td>AlNiTi</td>
<td></td>
<td>14.8</td>
<td>1.2</td>
<td></td>
</tr>
<tr>
<td>NiAl</td>
<td></td>
<td>12.9</td>
<td>1.4</td>
<td></td>
</tr>
<tr>
<td>AlNi2Ti</td>
<td>1</td>
<td>14.1</td>
<td>1.2</td>
<td></td>
</tr>
<tr>
<td>Ti3Al</td>
<td>2</td>
<td>12.4</td>
<td>1.4</td>
<td></td>
</tr>
<tr>
<td>Ti2Ni</td>
<td></td>
<td>8.9</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>Ti</td>
<td></td>
<td>8.9</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>Ti3Al</td>
<td></td>
<td>8.9</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>Ti2Ni</td>
<td></td>
<td>12.4</td>
<td>1.4</td>
<td></td>
</tr>
</tbody>
</table>

* Not measured due to small layer thickness.

AlNi2Ti (zone 3) and Ti3Al (zone 5) phases. The Ti3Al layer formed at 900 °C is thicker than the one formed at 800 °C and the Ti phase is not present. At the center of the interface, zone 6 is composed of Ti2Ni that contains dissolved 9.3 at.% Al.

3.2. Mechanical behavior

The hardness and shear strength were measured to evaluate the mechanical properties of the diffusion bonds. Table 2 presents the mean hardness values of the interface layers formed at 800 and 900 °C.

The reaction layers are harder than the TiAl substrate (10 GPa), except zone 5 (α-Ti at 800 °C or α2-Ti3Al at 900 °C). For both temperatures the highest hardness values are attained between the substrate and the reacted multilayer, zone 1. The hardest intermetallic phases are the AlxNi2Ti intermetallics (x = 1 or 2); AlNiTi + Al3NiTi is the hardest zone, followed by the AlNiTi and AlNi2Ti phases. Actually, the hardest zones are observed at 900 °C, 19 and 17 GPa for zones 1 and 4, respectively. Zone 4 is consists entirely of AlNiTi and zone 1 by AlNiTi and Al3NiTi; so the difference in hardness between these two zones must be associated with a second phase hardening mechanism due to the presence of Al3NiTi. Some phases (AlNiTi, Ti2Ni and Ti3Al) present different hardness values depending on bonding temperature, possibly as the result of composition and grain size differences. The increase in diffusivity with temperature which leads to a general enrichment in Al through the interface is responsible for a solid solution hardening effect in addition to the formation of hard intermetallic phases.

The hardness variation observed across the interface, associated with the formation of continuous layers of very hard intermetallics, can be a problem for the joint performance. In fact, the shear strength of these joints is very low; for instance, the joints produced with a 14 nm period multilayer at 900 °C, at a pressure of 5 MPa for 30 min have shear strength of 38 ± 1 MPa. This combination of multilayer thin films with Ni and Ti foils drastically reduces the strength of the joints when compared with joints bonded only with multilayers; shear strength of 314 ± 40 MPa was obtained for the bonds produced with 14 nm period Ni/Al multilayers at 900 °C, under a pressure of 5 MPa during 60 min [32].

The combination of foils with multilayer thin films to diffusion bond TiAl alloys achieves the purpose of filling the bond gap, but bond strength is too low to be interesting for technological applications. The thickness of the bond is increased from 4–5 μm to 20 μm, for joints processed only with Ni/Al multilayers or with multilayers and foils, respectively, which may contribute to the shear test results.

The fracture surfaces of shear test specimens bonded at 900 °C were examined by SEM. Fig. 4 shows SEM images of a fracture surface of the diffusion bond sample using a 14 nm period Ni/Al

Fig. 4. SEM images of the fracture surfaces: (a) low magnification of the entire surface, (b) detail A showing the zones analyzed by EDS and (c) detail B showing intergranular fracture through Ti2Ni phase and cleavage fracture across Ti3Al grains.
multilayer combined with Ti and Ni foils. The fracture surface is very smooth with small plateau areas that seem to cross different zones of the interface. EDS analysis of the zones identified in the images and the corresponding phases, identified by EBSD in accordance with the Al–Ni–Ti phase diagram [34], are presented in Table 3. From these results, it is clear that the fracture occurs mainly through the Ti2Ni, AlNiTi and AlNi2Ti. However, it is also possible to identify Ti3Al and Al2NiTi in small areas. The fracture surface of the AlNiTi, AlNi2Ti and Al2NiTi phases exhibits a very smooth fracture surface with no distinctive features to allow identification of the fracture mode. When the fracture occurred across the Ti2Ni phase, the fracture is intergranular while river patterns, typical of cleavage fracture, were observed when the fracture propagates through the Ti3Al phase. The two halves of the fracture samples were joined in a resin mount, with the fracture surfaces matching each other, and polished to examine the cross section and fracture path. SEM cross-section images of fractured diffusion bonds are presented in Fig. 5. These images confirm the observations of the fracture surface and EDS analysis results. The fracture occurs mainly along the central Ti2Ni layer (zone 6), but also propagates through other zones. These observations may explain the low strength of the joints. The fracture occurred mainly between layers 5 and 6, probably due to the abrupt variation in the hardness values, that change from 9 GPa (zone 5) to 15 GPa (zone 6). However, comparable, or larger, variations in hardness are supported by interfaces of other contiguous zones at the joint, and those interfaces are not the preferable fracture path. A unique feature of this central area of the interface is the large grain size (close to 5 μm) as can be observed in Fig. 3, while other zones present smaller grain size, inferior to 1 μm.

### 4. Conclusions

In this investigation, a modified bonding technique was used to join TiAl reactive multilayer thin films with Ti and Ni thin foils were investigated. At 900 °C, sound joints were obtained using different multilayer periods. At 800 °C joining was observed only when using 14 and 5 nm multilayer periods. Bonding promotes the formation of a layered interface and the formation of several AlNiTi intermetallic compounds. Increasing bonding temperature enhances diffusion across the interface leading to the formation of thicker joints and new intermetallic phases richer in Al.

The shear strength of the joint with the combination of multilayer thin films and thin foils is low; the best value was 38 MPa for joints processed at 900 °C/30 min/5 MPa/14 nm. The fracture occurs mainly through the central regions of the interface, composed of Ti2Ni, AlNi2Ti and AlNiTi phases. When the fracture occurs across the Ti2Ni phase, the fracture is intergranular. The fracture surface exhibits river patterns typical of cleavage fracture when it propagates through the Ti3Al phase.

The hardness profiles along the entire interface show a high variation in hardness values, explaining the fracture behavior observed in fracture surface and cross section SEM images. The fracture occurred particularly at the interfaces of the layers with high hardness differences.

Using foils in-between the nanocrystalline multilayers, which would be a useful method for correcting the absence of flatness of the parts be joined, has drawbacks as it induces the formation of hard, brittle intermetallic compounds, responsible for the low shear strength of the joints.

### Acknowledgments

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