JOURNAL OF MATERIALS SCIENCE **38** (2003) 2409–2414

Joining Ti-47Al-2Cr-2Nb with a Ti/(Cu,Ni)/Ti clad-laminated braze alloy

A. GUEDES, A. M. P. PINTO
Departamento de Engenharia Mecânica, Universidade do Minho, Campus de Azurém, 4800-058 Guimarães, Portugal
E-mail: aguedes@dem.uminho.pt

M. F. VIEIRA, F. VIANA
Departamento de Engenharia Metalúrgica e Materiais, GMM/IMAT, Faculdade de Engenharia, Universidade do Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal

The joining of Ti-47Al-2Cr-2Nb using Ti-15Cu-15Ni (wt%) as braze alloy was investigated. Experiments were conducted at 980 and 1000°C for 10 min. The microstructure and the chemical composition of the interfaces were studied by scanning electron microscopy (SEM) and by energy dispersive X-ray spectroscopy (EDS), respectively. For both processing conditions the reaction between the γ-TiAl alloy and the braze alloy produced layered interfaces, which are essentially composed of α_2-Ti_3Al and of Ti-Ni-Cu-Al and Ti-Ni-Cu intermetallic compounds. Microhardness tests showed that all reaction layers are harder than either the γ or the $(\alpha_2 + \gamma)$ lamellar grains of the intermetallic alloy.
© *2003 Kluwer Academic Publishers*

1. Introduction

Intermetallic alloys are an emerging class of materials that may have a wide variety of applications, especially when weight reduction and enhanced temperature capability are critical inputs for structural designs. Among these alloys, two phase γ-based TiAl alloys are advancing towards implementation on structural components of aircraft, space and automobile engines [1–4]. The density normalized strength and Young's modulus variations with temperature of γ-TiAl alloys open a new regime for metallic materials for service temperatures of 550–750°C [1]. As several intermetallics, γ-TiAl alloys suffer from low ductility and fracture toughness at room temperature, which along with their poor formability still cause a severe hindrance to their full-scale implementation [5].

Since nearly all structural applications of γ-TiAl alloys will require joining, either to themselves or to other materials, the development of adequate joining techniques is fundamental to integrate them into functional structures. Furthermore, joining simple γ-TiAl parts to form components with a more complex shape will allow to overcome some of the fabrication problems that arise from the brittle nature of these alloys. Electron beam welding, brazing, diffusion brazing and diffusion bonding are the most reported joining techniques [5–18]. Diffusion brazing and diffusion bonding seem to be the most straightforward techniques to produce joints with mechanical properties comparable to those of γ-TiAl alloys at high temperature or at least the performance of the joined components is not jeopardised by failure originated at the joint area. The mechanical behaviour of joints is highly dependent on the features of the interface, namely on the chemical and mechanical characteristics of the reaction products and their distribution across the interface. Assessing the influence of the processing variables upon the chemical and microstructural features of the interfaces is fundamental to understand the mechanisms that govern their formation and therefore essential either to develop any reliable joining process or to be able to exert some control upon the mechanical behaviour of the joints.

The present study focuses on the influence of the processing temperature upon the chemical and microstructural features of diffusion brazed γ-TiAl joints. Microhardness tests were used to predict the mechanical characteristics of the interfaces. This work is part of a broader project that aims to develop cost-effective and reliable joining routes for γ-TiAl based alloys.

2. Materials and experimental procedures

The γ-TiAl alloy (Ti-47Al-2Cr-2Nb, at.%) used in this investigation was produced from gas atomised elemental powders by Crucible Research and has a duplex microstructure, which consists of a mixture of γ-TiAl grains and lamellar (α_2-Ti_3Al + γ-TiAl) grains. Samples of the intermetallic alloy with $10 \times 7 \times 3$ mm were cut with a diamond saw and then ground with SiC emery paper down to 1200 grade. A Ticuni foil (Ti-15Cu-15Ni, wt%) with a thickness of 90 μm was used as filler metal. Ticuni is a clad-laminated alloy that consists of a sandwich of a 16 μm Cu-Ni foil between two 37 μm Ti foils. The solidus and the liquidus temperatures of Ticuni are 910 and 960°C, respectively. Prior to joining both alloys were degreased in acetone with ultrasonic agitation and air-dried. A small pressure (50 Pa) was

applied to the γ-TiAl alloy/Ticuni/γ-TiAl alloy assemblage during the brazing thermal cycle. Brazing was performed at 980 and 1000°C for 10 min in a vertical furnace, which was evacuated to a vacuum level better than 10^{-4} mbar. The heating and cooling rates were fixed at $3°C \cdot min^{-1}$. In order to perform the microstructural and chemical characterisation of the interfaces, cross-sections of the joints were prepared using standard metallographic techniques. The interfaces were examined by SEM and chemically analysed by EDS at an accelerating voltage of 15 keV. Microhardness tests were performed on the γ-TiAl alloy and throughout the interfaces with a FISHERSCOPE H100 equipped with a Vickers indenter. The nominal load (100 mN) was applied electromagnetically and the load resolution was better than 1 μN.

3. Results

For both processing conditions the reaction between the Ticuni foil and the γ-TiAl alloy produced layered interfaces that could be divided into three characteristic reaction layers. These layers are labelled in Figs 1 and 2,

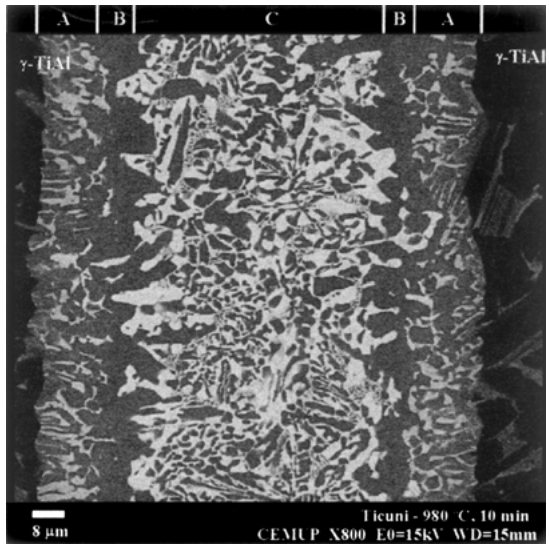

Figure 1 BEI of the obtained by brazing at 980°C.

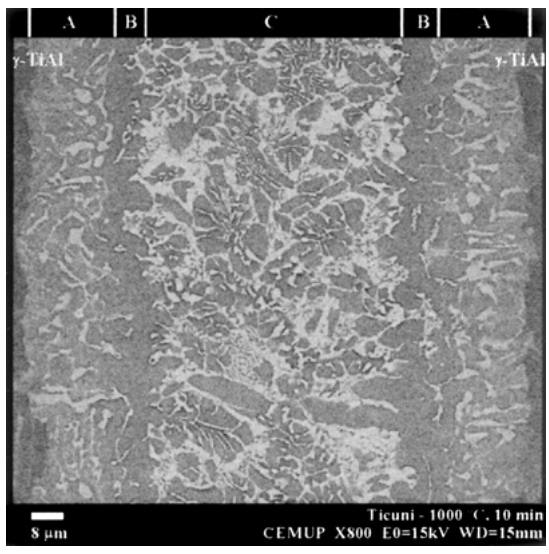

Figure 2 BEI of the interface obtained by brazing at 1000°C.

TABLE I Average chemical composition (at.%) throughout the interface[a]

	980°C				1000°C			
Layer/zone	Ti	Al	Cu	Ni	Ti	Al	Cu	Ni
A	60.9	28.8	3.7	5.0	61.2	30.6	3.1	3.7
A/black zones	68.8	29.1	1.2	0.6	73.3	25.1	0.9	0.3
A/white zones	38.5	33.5	11.3	15.0	38.8	33.4	11.6	14.5
B	74.2	24.8	0.8	0.0	73.6	24.5	1.1	0.4
C	66.1	18.2	7.2	7.6	66.6	19.6	6.6	6.3
C/black zones	74.1	24.5	0.6	0.6	73.9	24.3	1.0	0.5
C/white zones	56.8	14.8	13.3	14.1	58.7	13.1	10.8	15.5

[a]Cr + Nb = balance.

TABLE II Average thickness (μm) of the reaction layers and of the interface for both processing conditions. Layers *A* and *B* are on both sides of layer *C*, see Figs 1 and 2

Layer	980°C	1000°C
A	16	21
B	8	8
C	63	64
Interface	111	122

which are back-scattered electron images (BEI) of the interfaces, as *A*, *B* and *C*. The results of the EDS analysis performed throughout the interface and the average thickness of each layer are listed in Tables I and II, respectively. All compositions are expressed in atomic percentage.

First, it should be noted that for both processing conditions used in this investigation the chemical composition of the γ-TiAl alloy remains unaltered after joining.

All black zones throughout the interface are essentially composed of Ti and Al (Ti + Al > 97.8%) with Ti:Al atomic ratios within the range of 2.4 and 3.1. All white zones are Ni- and Cu-rich (26.1% < Ni + Cu < 27.4%), with Ni contents being 1 to 5% higher than Cu contents. The Ti:Al atomic ratio of the white zones is close to 1 in layer *A* and approximately 4 in layer *C*.

Layer *A* consists of a mixture of coarse black zones and thinner white ones. Some zones of this layer present a structure that consists of alternated black and white columns, which seem to have grown almost perpendicularly to the surface of the intermetallic alloy. These zones are more frequently observed for joining at 980°C than for joining at 1000°C. Layer *A* grows from about 16 to 21 μm when the processing temperature is raised from 980 to 1000°C. The increase of the extension of the interface, from 111 to 122 μm, when the processing temperature is raised, is mainly due to the growth of layer *A*.

Layer *B* is composed of a quasi-continuous and rather irregular black zone, which is about 8 μm thick for both processing conditions.

Layer *C*, as layer *A*, consists of a mixture of black zones and white ones that display different shapes and sizes. The microstructure of layer *C* is greatly affected by the processing temperature contrarily to its thickness that remains close to 65 μm. For instance, when joining is performed at 1000°C most of the black

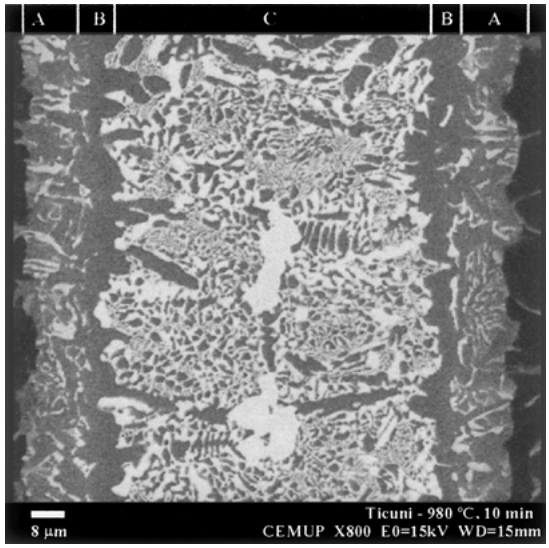

Figure 3 BEI of a peculiar zone of the interface obtained by brazing at 980°C.

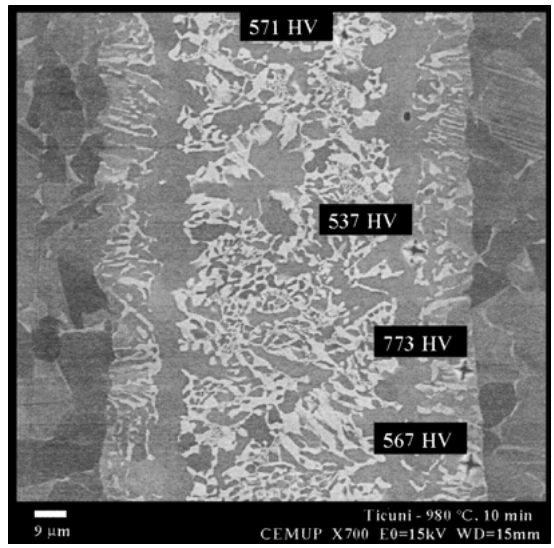

Figure 5 SEI of the interface obtained by brazing at 980°C, showing Vickers indentations and the corresponding hardness values.

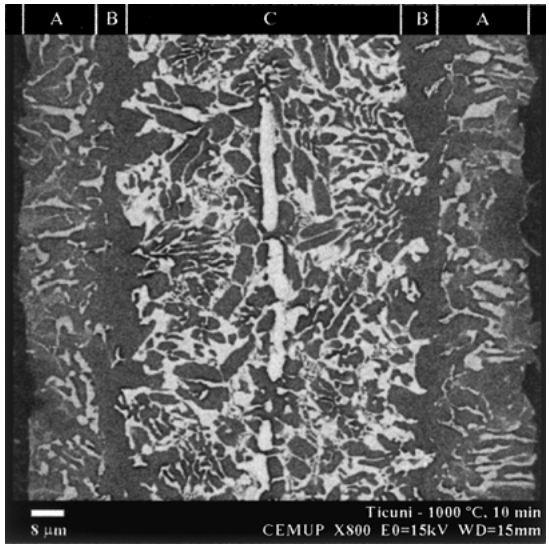

Figure 4 BEI of a peculiar zone of the interface obtained by brazing at 1000°C.

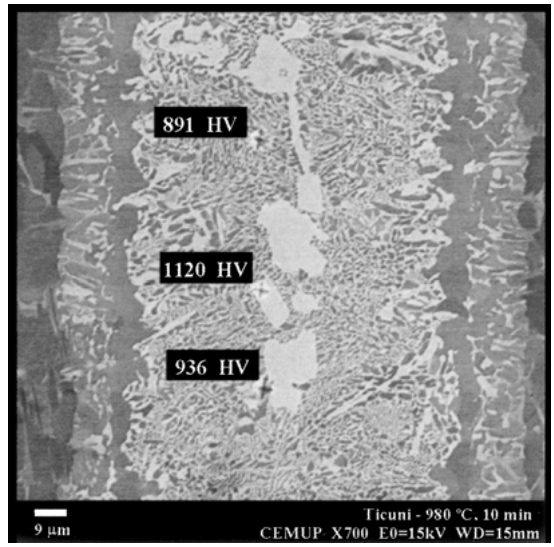

Figure 6 SEI of a peculiar zone of the interface obtained by brazing at 980°C, showing Vickers indentations and the corresponding hardness values.

particles have grown thicker; some of them seem to have formed agglomerates that exhibit a feather-like shape.

It is also worth to mention that, some regions of layer *C* (Figs 3 and 4) present a different microstructure from the representative ones shown in Figs 1 and 2. For instance, when joining is performed at 980°C, layer *C* is wider than usual and presents, in broader terms, a finer microstructure. In addition, for both processing temperatures, at the centre of these peculiar regions, which are randomly dispersed at the centre of the joint, coarse white particles are observed. However, the composition of these particles is markedly different if joining is performed at 980°C (68.5Ti-1.7Al-5.7Cu-24Ni) or at 1000°C (28.7Ti-24Al-20.5Cu-26.6Ni).

The strength of the different zones of the interface was evaluated by microhardness tests. Figs 5 and 6 are secondary electron images (SEI) of the interface, for joining at 980°C, showing series of indentations performed throughout the joint. For both processing conditions all the reaction layers are harder than either the γ grains (324 ± 59 HV) or the ($\alpha_2 + \gamma$) lamellar grains (404 ± 74 HV) of the intermetallic alloy. The hardness of layer *A* is 649 ± 87 HV and 557 ± 86 HV for joining at 980 and 1000°C, respectively. The hardness of layer *B* (590 ± 54 HV) remains the same for both processing conditions. The hardness of layer *C* is 596 ± 18 HV and 551 ± 68 HV for joining at 980 and 1000°C, respectively. However, the peculiar zones of layer *C* for joining at 980°C are significantly harder: the hardness of the mixture of thin black particles and white particles is 800 ± 58 HV and the coarse white particles that are located at the centre of the interface is approximately 1120 HV (see Fig. 6). It should be noted that only one indentation was performed on these particles and therefore the hardness mentioned above has to be taken as a qualitative information; it indicates that the Ti- and Ni-rich particles are extremely hard.

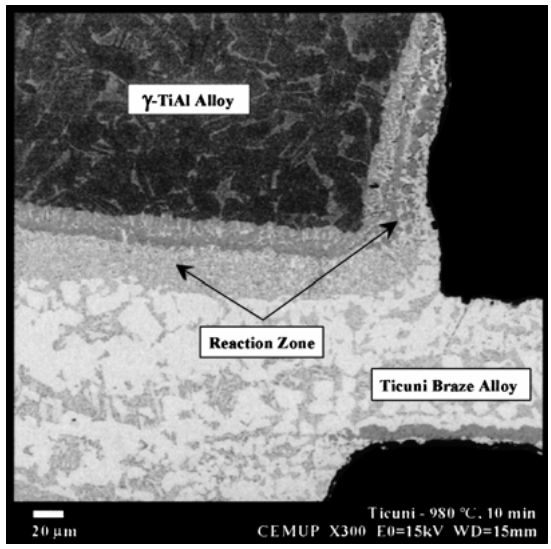

Figure 7 BEI of the end side of an overlap joint, showing the wetting and the reaction between the Ticuni foil and the γ-TiAl alloy.

4. Discussion

For both processing temperatures used in this investigation none of the foils (Ti and Cu-Ni) that constitute the Ticuni braze alloy should have reached the liquid state. However, due to the interdiffusion of Ti, Cu and Ni atoms within the Ticuni foil, a liquid phase, which wetted and reacted with the γ-TiAl alloy, was formed. In fact, the reaction zone located at the lateral surface of the intermetallic alloy, shown in the upper right corner of Fig. 7, could only result from the flowing of the braze alloy. The reaction between the melt and the γ-TiAl alloy led to the formation of several compounds that promote the bridging between the parts to be joined. The nature of these interfacial reaction products will be discussed hereafter.

EDS does not allow the identification of the phases that constitute the interface. However, equilibrium phase diagrams could be used in conjunction with SEM and EDS as predictive tools of the nature of the phases that constitute the interface. Since the interfaces are essentially composed of Ti, Al, Ni and Cu the equilibrium quaternary phase diagram would provide valuable information. Unfortunately, this phase diagram has not yet been established but one could assume, as Lee *et al.* [5, 10] did, that Ni and Cu atoms behave in a similar way since both have similar atomic sizes and electronegativities, the same crystalline structure and unlimited solid solubility. In addition, Cu and Ni present practically the same distribution throughout the interface. Therefore, the Ti-Ni-Al and the Ti-Cu-Al ternary phase diagrams can be used to bypass the lack of the quaternary phase diagram, as long as one adds Cu and Ni contents together.

The Ti-Ni-Al and Ti-Cu-Al isothermal sections at 750°C and 500°C (Fig. 8), respectively, were chosen for this purpose. These specific sections were selected for two reasons: (1) they are, for both systems, the lowest temperature isotherms available within the range of the compositions detected at the interfaces and (2) there are no invariant reactions below the temperature of the isotherm, which means that all phases indicated in both isotherms are stable at room temperature and that only minor changes in their composition should be expected upon cooling.

All black zones are essentially composed of Ti and Al with Ti:Al atomic ratios within the range of 2.4 and 3.1. According to the Ti-Al phase diagram [20], the α_2-Ti_3Al compound is stable at 500°C for Ti:Al atomic ratios comprised between 1.8 and 4 approximately. Therefore, layer *B* and all black zones in layers *A* and *C* must correspond to the α_2 phase.

The global composition of layer *A* lays on or near the two phase field Ti(Ni,Cu)Al + Ti_3Al, closer to Ti_3Al. The white zones in this layer are plotted near the single phase field Ti(Ni,Cu)Al. Therefore, layer *A*

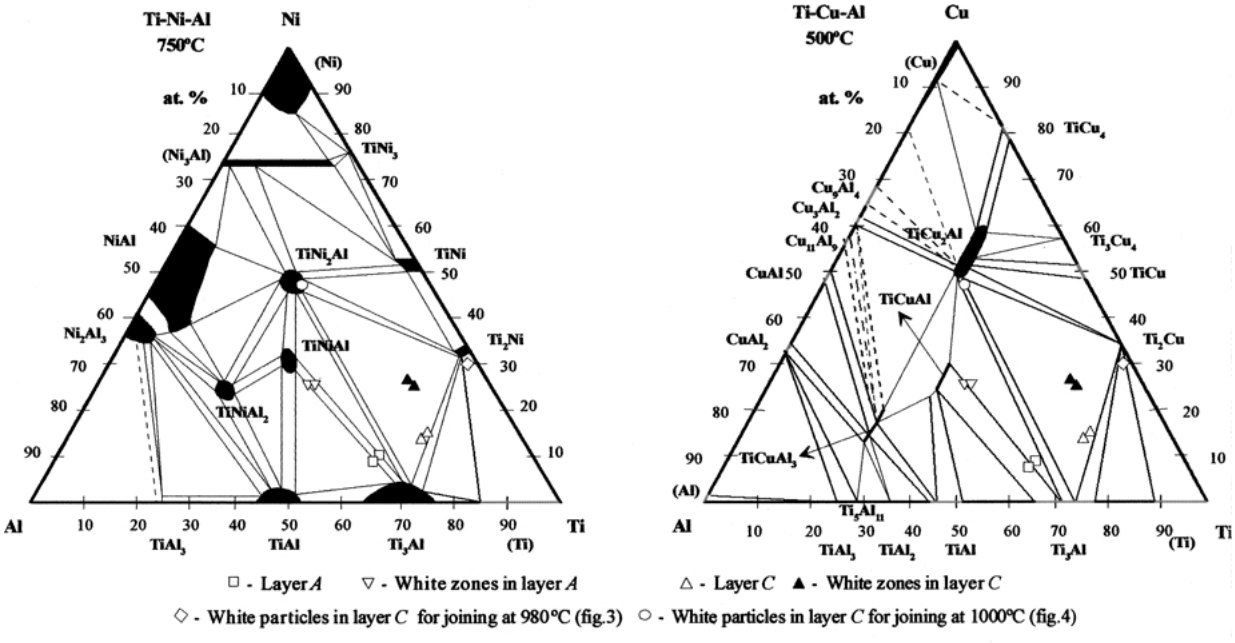

Figure 8 Ti-Ni-Al and Ti-Cu-Al isotherms [19] in which the compositions of some of the reaction layers and particles detected at the interfaces are plotted. For all plots, Ni and Cu contents are added together.

should be composed of α_2-Ti_3Al (black zones) and of Ti(Ni,Cu)Al (white zones).

The global composition of layer *C* practically lays on the two phase field $Ti_2(Ni,Cu) + Ti_3Al$. Since the black zones are the α_2 phase then the white zones should correspond to $Ti_2(Ni,Cu)$. However, the plots of the white zones on the isothermal sections lay on the three phase field, $Ti_2(Ni,Cu) + Ti(Ni,Cu)_2Al + Ti_3Al$. This discrepancy may result from the volume interaction on the EDS analysis of the zones that are bellow and around the analysed area, namely the interaction due to the black zones. So the white zones should be in fact richer in Cu and Ni and poorer in Ti than it is indicated by the EDS analysis. Therefore, in comparison to the plots on Fig. 8, their composition should be shifted towards the $Ti_2(Ni,Cu) + Ti(Ni,Cu)_2Al$ field. A magnification of the white zones in layer *C* reveals that some of them are slightly brighter when they are observed on the back-scattering electron mode. This indicates that they may have a different chemical composition and that they may correspond to a different phase. Unfortunately, due to their small size, it was impossible to assess their chemical composition by EDS. Nevertheless, we presume that the white zones in layer *C* are in fact composed of a mixture of two phases: essentially $Ti_2(Ni,Cu)$ and small amounts of $Ti(Ni,Cu)_2Al$. The formation of these two compounds is confirmed by the coarse white particles detected in some peculiar zones of the interface (Figs 3 and 4) at the centre of layer *C*. The plots on the isothermal sections indicate that these particles should correspond to $Ti_2(Ni,Cu)$ for joining at 980°C and to $Ti(Ni,Cu)_2Al$ for joining at 1000°C.

In other studies [5, 10–12] the α_2-Ti_3Al compound has been identified as one of the reaction products when Ticuni is used to join γ-TiAl alloys. Lee *et al*. [5, 11] besides α_2-Ti_3Al, identified $TiCu_2$ and Ti(Cu,Ni) as the major phases near the fracture surface of infrared brazed γ-TiAl joints that failed mainly along the centre of the interface.

In our investigation no evidence of these two last compounds was found, but our interfaces are richer in Al in comparison to those reported by Lee *et al*. [5, 11]. We think that the different composition of the reaction products must be the result of distinct processing thermal cycles. In fact, infrared brazing employs extremely fast heating and cooling rates and a shorter holding stage at the brazing temperature: heating to 1150°C, holding for 1 min and then cooling to 600°C only takes 2 min [11]. Therefore, when a short processing thermal cycle is employed, only a small amount of Al is able to reach the centre of the interface and the formation of Al-free compounds is more likely.

This hypothesis is supported by the results of an experiment made at 900°C [21] with no holding stage. In this experiment, even though joining was unsuccessful, the microstructure and the phases that composed the Ticuni braze alloy were radically changed after the thermal cycle. The Al contents detected throughout the Ticuni foil was always lower than 0.35% and one of the phases that we have detected was composed of 35.6Ti-30.6Cu-33.4Ni. According to the plot on the isothermal section at 870°C of the Ti-Cu-Ni phase diagram [19], it may correspond to the TiCuNi compound. This indicates that either Ti(Cu,Ni) [5, 11] or TiCuNi [21] may be one of the phases that is formed at the interface when there is no Al available.

The difference between the hardness of layer *A* for joining at 980 and at 1000°C, 649 ± 87 HV and 557 ± 86 HV, respectively, may result partially from the zones that present a structure consisting of alternated black and white columns, which are more frequent when brazing is conducted at 980°C. The hardness of these zones is 746±38 HV and why they are substantially harder than the remaining zones of layer *A* is not clear; the columnar morphology in conjunction with a different proportion between the phases which they are composed of, when compared to the other zones of layer *A*, may contribute to this difference of hardness. The peculiar zones of layer *C* for joining at 980°C are harder (800 ± 58 HV) than layer *C* (596 ± 18 HV). The finer morphology of these zones (see Figs 5 and 6 for comparison) and a higher amount of white particles that are essentially composed of $Ti_2(Ni,Cu)$, which is extremely hard (1120 HV), may both be responsible for increase in hardness.

5. Concluding remarks

(1) Joining a Ti-47Al-2Cr-2Nb alloy at 980 and 1000°C for 10 min with a Ticuni braze alloy produces multilayered interfaces that should be essentially composed of α_2-Ti_3Al, Ti-Cu-Ni-Al and Ti-Ni-Cu intermetallic compounds.

(2) For both processing conditions the interface could be divided into three distinct reaction layers that are essentially composed of α_2-Ti_3Al + Ti(Ni,Cu)Al (layer *A*)/α_2-Ti_3Al (layer *B*)/α_2-$Ti_3Al + Ti_2(Ni,Cu) + Ti(Ni,Cu)_2Al$ (layer *C*), starting from the γ-TiAl surface towards the centre of the interface.

(3) The hardness of any of the reaction layers, ranging from 551 ± 68 HV to 649 ± 87 HV, is higher than either the γ grains or the $(\alpha_2 + \gamma)$ lamellar grains of the intermetallic alloy. Some peculiar zones and the $Ti_2(Ni,Cu)$ particles, both located at the centre of the interface when joining is performed at 980°C, are even harder, reaching 800 HV and 1120 HV, respectively.

Acknowledgements

The authors wish to thank to Dr. Maria Teresa Vieira and to Dr. Valdemar Fernandes (Department of Mechanical Engineering—University of Coimbra) for the assistance provided on performing the microhardness tests.

References

1. D. M. DIMIDUK, *Mater. Sci. and Eng.* A **263** (1999) 281.
2. N. S. STOLOFF, C. T. LIU and S. C. DEEVI, *Intermetallics* **8** (2000) 1313.
3. E. A. LORIA, *ibid.* **8** (2000) 1339.
4. *Idem., ibid.* **9** (2001) 997.
5. S. J. LEE, S. K. WU and R. Y. LIN, *Acta Mater.* **46** (1998) 1283.

6. W. A. BAESLACK, III, H. ZHENG, P. L. THREADGILL and B. G. I. DANCE, *Mater. Charac.* **39** (1997) 43.
7. M. C. CHATURVEDI, N. L. RICHARDS and Q. XU, *Mater. Sci. and Eng.* A **239** (1997) 605.
8. T. NODA, T. SHIMIZU, M. OKABE and T. IIKUBO, *ibid.* **239** (1997) 613.
9. S. ANNAJI and R. Y. LIN, in "Structural Intermetallics 1997," edited by M. V. Nathal, R. Darolia, C. T. Liu, P. L. Martin, D. B. Miracle, R. Wagner and M. Yamaguchi (Metals & Materials Society, The Minerals, 1997) p. 395.
10. S. J. LEE, S. K. WU and R. Y. LIN, *Acta Mater.* **46** (1998) 1297.
11. S. J. LEE and S. K. WU, *Intermetallics* **7** (1999) 11.
12. Q. XU, M. C. CHATURVEDI, N. L. RICHARDS and N. GOEL, in "Structural Intermetallics 1997," edited by M. V. Nathal, R. Darolia, C. T. Liu, P. L. Martin, D. B. Miracle, R. Wagner and M. Yamaguchi (Metals & Materials Society, The Minerals, 1997) p. 323.
13. H. HOLMQUIST, V. RECINA and B. PETTERSSON, *Acta Mater.* **47** (1999) 1791.
14. G. ÇAM, H. CLEMENS, R. GERLING and M. KOÇAK, *Intermetallics* **7** (1999) 1025.
15. G. ÇAM and M. KOÇAK, *J. Mater. Sci.* **34** (1999) 3345.
16. M. HOLMQUIST, V. RECINA, J. OCKBORN, B. PETTERSSON and E. ZUMALDE, *Scripta Mater.* **39** (1998) 1101.
17. H. J. LIU, J. C. FENG and Y. Y. QIAN, *ibid.* **43** (2000) 49.
18. W. GLATZ and H. CLEMENS, *Intermetallics* **5** (1997) 415.
19. P. VILLARS, "Handbook of Ternary Alloy Phase Diagrams," edited by A. Price and H. Okamoto (ASM International, 1994).
20. "Binary, Alloy Phase Diagrams CD-ROM," 2nd ed. plus updates (ASM International, 1996).
21. A. GUEDES, A. M. P. PINTO, M. F. VIEIRA and F. VIANA, unpublished data.

Received 18 June 2002
and accepted 8 January 2003