Final Draft

of the original manuscript

Follow-up structural evolution of Ni/Ti reactive nano and microlayers during diffusion bonding of NiTi to Ti6Al4V in a synchrotron beamline

A.J. Cavaleiro[a], A.S. Ramos[a,*], F.M. Braz Fernandes[b], N. Schell[c], M.T. Vieira[a]

[a] CEMMPRE, Department of Mechanical Engineering, University of Coimbra, R. Luís Reis Santos, Coimbra, 3030-788, Portugal

[b] CENIMAT/I3N, Department of Materials Science, Faculty of Sciences and Technology, Universidade Nova de Lisboa, Caparica, 2829-516, Portugal

[c] Helmholtz-Zentrum Geesthacht, Max-Planck-Str. 1, Geesthacht, 21502, Germany

Abstract

Reaction-Assisted Diffusion Bonding (RADB) of NiTi to Ti6Al4V using either magnetron sputtered Ni/Ti nanomultilayers or Ni/Ti commercial microfoils as filler material was studied. The joining process takes advantage of the exothermal reactive character of the Ni-Ti system to provide extra energy during the bonding process. Therefore, sound joints could be achieved at lower thermal conditions. The oven with load capabilities at the High Energy Materials Science beamline (P07) of the Deutsch Synchrotron (DESY) is ideal to follow the structural evolution of the materials involved in the bonding process. Prior to RABD, Ni/Ti multilayers with a 2.5 μm total thickness and with 12 or 25 nm of modulation period were deposited onto the materials being joined. In alternative, up to 20 alternated thin μ-foils were placed in between the base materials. The materials were heated by induction to the selected temperature during 30 min and quenched to room temperature by blowing helium. During the thermal cycle a 10 MPa pressure was applied. Using thin μ-foils, 650 ºC was required to promote joining, while using multilayer coated materials sound joints were obtained at 600 ºC.

Such low temperatures are attractive from the application/economic point of view, and are crucial to reduce the formation of undesired intermetallic phases, such as $NiTi_2$. The nanoindentation experiments of the joints processed using Ni/Ti nanomultilayers confirm that the presence of the $NiTi_2$ phase is more pronounced at 650 ºC than when the joints are processed at 600 ºC.

* Corresponding Author (sofia.ramos@dem.uc.pt)

1. Introduction

Properties such as shape memory effect, superelasticity, excellent resistance to corrosion, and biocompatibility have turned nitinol (NiTi) into a unique alloy for a variety of applications (Otsuka and Ren, 2005). The mechanical properties - pseudoelasticity and shape memory effect – were first studied by Buelher et al. (1963). However, the cost and difficulty in dissimilar joining have restricted widespread applications of NiTi-based alloys. These alloys present hard machinability and formability; therefore, appropriate joining techniques must be developed in order to produce parts with complex geometries. Joining of NiTi to dissimilar material is regarded as extremely difficult. On the other hand, in addition to its high strength to weight ratio and corrosion resistance, Ti6Al4V can be easily machined and forged, so it has potential for many industries from medical engineering to aerospace (Boyer, 1996). In order to exploit the properties of these materials, suitable joining procedures are required. In this context, Oliveira et al. (2017) recently published a review paper dedicated to welding and joining of NiTi shape memory alloys. Casalino et al. (2005) used statistical and Taguchi approaches to study the laser welding of Ti6Al4V. Dissimilar joining between NiTi and Ti6Al4V would enlarge the field of application of both materials. Conventional fusion welding methods lead to the formation of brittle intermetallics in the weld zone. In fact, the main problem in dissimilar welding of NiTi to Ti6Al4V is the formation of the $NiTi_2$ brittle intermetallic phase. Combination of brittleness with thermal stresses originated from dissimilar welding, leads to the formation of transverse cracks and consequently failure of the joints (Miranda et al., 2015). Zoeram and Mousavi (2014) overcome this problem by laser welding of NiTi to Ti6Al4V using a copper interlayer to limit diffusion and hinder the formation of brittle intermetallics. More recently, Oliveira et al. (2016) used a similar strategy by laser joining NiTi to Ti6Al4V with a niobium interlayer. Joining NiTi and Ti6Al4V by

3

infrared brazing using a silver-rich braze alloy was also investigated (Shiue and Wu, 2005). A promising alternative could be the diffusion bonding technique which uses heat and pressure to promote diffusion between two parts producing a joint without disruptions. Diffusion bonding does not involve melting of base or filler materials, eliminating the problems of segregation, solidification cracking and distortion stresses. Additionally, the interfaces are very thin which is desirable for microjoining purposes. Autogenous and reaction assisted diffusion bonding (RADB) of NiTi to Ti6Al4V proved the feasibility of this joining technique. According to the work of Senkevich et al. (2013), successful autogenous NiTi/Ti6Al4V joints were only achieved at 850 ℃ during 30 to 60 min, under a pressure of 5 MPa. In the RABD process, a reactive multilayer is placed between the parts being joined and the energy released is used to enhance the diffusion bonding process. This strategy was recently adopted by Ma et al. (2018) for similar joining of Ti6Al4V using Ti/Ni multilayer thin films with different Ti:Ni molar ratio. The diffusion bonding experiments were carried out at 800 ℃ during 60 min under pressures of 5 – 15 MPa. Reliable joints were obtained, in particular for the highest Ni content and for 15 MPa which gave rise to a shear strength of 160 MPa (Ma et al., 2018). In his review paper, Adams (2015) addressed the use of reactive multilayers for joining applications through different approaches.

Using Ni/Ti multilayer (ML) thin films to assist the joining process, it was possible to reduce the NiTi to Ti6Al4V diffusion bonding temperature down to 750 ℃ (Simões et al., 2013). Although joints free from porosity and cracks were produced, Simões et al. (2013) concluded that the formation of a multiphase interface with different intermetallic phases, namely $NiTi_2$ and $AlNi_2Ti$, could not be avoided. The feasibility of the RABD process already proved to be successful for similar and dissimilar joining of several materials. Sound and reliable joints of TiAl to itself (Cao et al., 2008), TiAl to

Inconel (Ramos et al., 2009) and NiTi to Ti6Al4V (Cavaleiro et al., 2014a) have been produced by diffusion bonding using Ti/Al, Ni/Al or Ni/Ti nanoscale multilayer thin films as fillers, allowing diffusion bonding at less demanding conditions. RABD using multilayer thin films promotes the formation of thin interfacial regions but requires excellent contact between the bonding surfaces. The gap at the mating surfaces can be accommodated by inserting a stack of alternated metallic microfoils. A combination of Ni/Ti μ-foils with Ni/Al multilayers directly deposited onto the TiAl parts being joined was utilized, but once again the presence of brittle intermetallic phases is responsible for the low shear strength of the joints (Simões et al., 2011). In the case of RABD between NiTi and Ti6Al4V, the presence of the brittle $NiTi_2$ phase could be avoided by reducing the temperature. Therefore, the possibility of decreasing the joining temperature is of paramount importance for obtaining diffusion joints with good mechanical properties. In addition, as demonstrated by Chau et al. (2006), the shape memory effect (SME) of NiTi is very sensitive to variations in alloy composition and therefore any joining process that cause even the slightest diffusion can seriously affect the SME.

The main objective of this work is to investigate the feasibility of reducing the NiTi/Ti6Al4V RABD temperature using Ni/Ti multilayer thin films, as well as alternated Ni and Ti μ-foils. Phase evolution during the bonding process was evaluated using in-situ synchrotron radiation in transmission mode. Ex-situ characterization permits to assess the morphology/composition of the joint region.
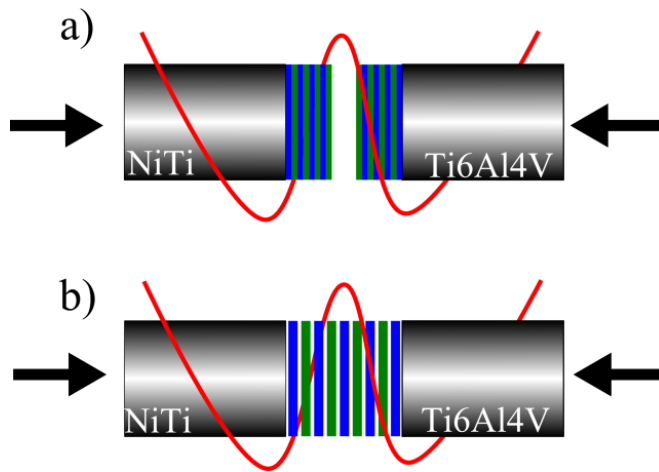
Figure 1: Schematics of the joining process using a) multilayer thin films and b) μ-foils as filler material.

2. Materials and Methods

2.1. Materials

For the in-situ joining process, NiTi and Ti6Al4V round bars (ϕ = 5 mm) were acquired (Nimesis Technologies and Goodfellow, respectively). The shape memory alloy is enriched in Ni (51.5-52.0 Ni at.%). Specimens with approximately 5 mm length were prepared using a circular precision cutting saw. A good contact between the foils/nanolayered system and the base materials is fundamental to ensure that the surface exhibited good quality and consequently standard metallographic procedure was employed until a mirror-like surface finish was obtained.

The Ni/Ti nanomultilayers were directly deposited onto both materials being joined using a semi-industrial dual cathode d.c. magnetron sputtering equipment with high purity targets (titanium - 99.99% and nickel - 99.98%). The sputtering equipment is provided with an ion gun to clean the samples' surface by bombardment with a positive/negative ion flux. Before cleaning the surfaces, the chamber was pumped down to ~3×10^{-4} Pa and afterwards filled with argon until a working pressure of 0.5 Pa was attained. To avoid heating and possible reaction during the deposition process, a bulk

copper substrate holder was utilized to act as a heat sink. In order to achieve the desired 1:1 stoichiometric composition, the Ti and Ni targets operated at 5.1×10^{-2} W mm^{-1} and 2.5×10^{-2} W.mm^{-1}, respectively. For this purpose, a Ti:Ni thickness ratio of 1.6 has to be ensured. An initial Ti layer was chosen to guarantee a good adhesion to the substrates, while Ni was used as the top layer due to the excellent oxidation resistance. After optimizing the deposition conditions, it was straightforward to change the modulation period (bilayer thickness) of the multilayers by varying the rotation speed of the substrate holder. Two different modulation periods (Λ) were selected (12 nm and 25 nm), while the total thickness of the thin films was kept around 2.2 μm. Nickel and titanium μ-foils were acquired to Goodfellow and Advent Research Materials Ltd., respectively; their thickness was chosen ensuring that the overall equiatomic relation was maintained. Therefore, to achieve a 10 μm period arrangement, 4 μm Ni and 6 μm Ti alternate foils were stacked in a plastic mould that was removed before the bonding process. The 94 μm thick arrangement starts and finishes with a Ti μ-foil.

2.2 RADB process and characterization

The joints were produced and characterized in-situ by x-ray diffraction (XRD) using synchrotron radiation at the High Energy Materials Science beamline (HEMS-P07) at Petra III in DESY (German Synchrotron). A high brilliance 80 keV energy beam passes through kapton windows into a modified Bahr DIL 805 A/D dilatometer that applies 10 MPa pressure while heating the sample by induction. The thermal cycle was conducted under vacuum ($4x10^{-3}$ Pa). The synchrotron beam was used in transmission mode and the diffracting photons were detected by a Perkin-Elmer 2D flat panel. The sample-to-detector distance was 1300 mm. A good relation between the quality of the x-ray spectra, sample positioning resolution and the duration of the analysis was reached for a

beam of 1mm height x 50 μm width and a 2s acquisition time. Since the base materials have different heights and due to the thermal expansion during the analysis, in each thermal cycle step, a set of 21 shots scanning along the sample guarantees that the bond zone is characterized. From previous work, it is expected that the Ni/Ti layers react at around 400 ºC (Cavaleiro et al., 2014b), and consequently, the thermal cycle, presented in Figure 2, was defined. The materials were heated by induction up to the maximum temperature, maintained during 30 min and quenched by blowing helium. The joints were processed, either for the μ-foils, as well as for the MLs, at a maximum bonding temperature of 600, 650 and 750 ºC. The sets of shots were carried out at the beginning (RTi), at 350, 400 and 450 ºC, at maximum temperature during the 30 min dwell time (3 sets), and at room temperature after the thermal cycle is complete (RTf).
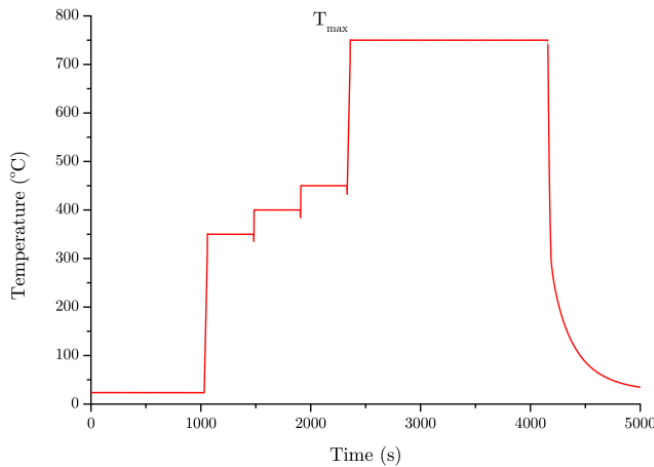

Figure 2: Temperature profile used for in-situ x-ray analysis of the RADB process.

After the bonding process, ex-situ analyses of the joints were conducted by scanning electron microscopy (SEM) using a FEI QUANTA 400 F field emission gun microscope equipped with energy dispersive spectroscopy (EDS). The analyses were carried out at an accelerating voltage of 15 kV. The samples were cut perpendicularly to the interface and standard metallographic preparation was employed.

8

The mechanical behaviour of the RABD joints processed using 12 nm period nanomultilayers was evaluated by nanoindentation in a Micro Materials – Nano hardness equipment (Berkovich diamond indenter). Hardness and reduced Young's modulus were determined by the Oliver and Pharr analysis method (Oliver and Pharr, 1992). The nanoindentation experiments were run up to a maximum load of 1.5 mN. To obtain hardness and reduced Young's modulus maps across the joints interface and base materials, indentation matrixes with 8 rows and 12 columns were defined (96 measurements). The distance between rows and columns was 5 and 3 μm, respectively.

3. Results and Discussion

3.1. RADB using μ-foils

Using Reactive Assisted Diffusion Bonding process with Ni/Ti μ-foils at 650 ºC for 30 min sound joining between NiTi and Ti6Al4V is attained. The presence of Ni/Ti μ-foils assists the joining process and comparing it to direct diffusion bonding without μ-foils, it is possible to decrease the temperature and the dwell period necessary to attain sound joints. Decreasing further the joining temperature (600 ºC), the base materials detached in the bond zone and the different foils were intact and separated revealing that the temperature was too low.

In-situ XRD analysis of the joints processed at 650 and 750 ºC using Ni/Ti μ-foils are presented in Figure 3.
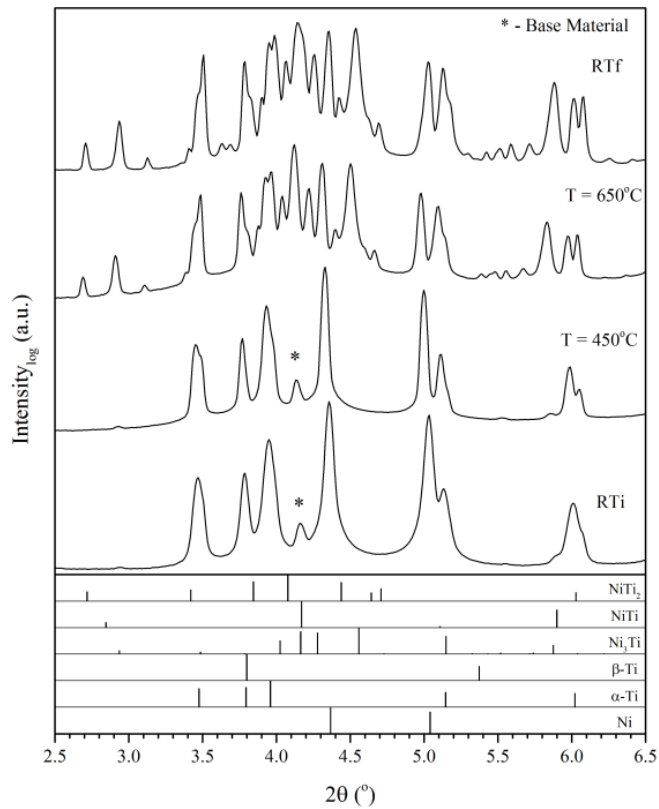
Figure 3: Phase evolution of the joints processed using Ni/Ti μ-foils at different temperatures (a) 650 ℃ and (b) 750 ℃.

Starting the analysis with the XRD diffractogram at room temperature (RTi), it is possible, as expected, to identify the presence of the phases from both constituents of the μ-foils, nickel and titanium as well as traces from the NiTi base material. Even though the thickness of the joint zone (thickness of around 100 μm) is wider than the beam width, the NiTi is still present in both diffractograms and consequently, some Ti6Al4V should also be expected. Since the Ti alloy phase is similar to the Ti from the μ-foil, it is impossible to differentiate between the base and filler materials. The presented room temperature diffractogram was chosen among a set of 21 "shots" that scanned the bond zone. Therefore, in this scan the influence of the base materials should be minimal and consequently the peak can be identified as mostly α-Ti from the μ-foil.
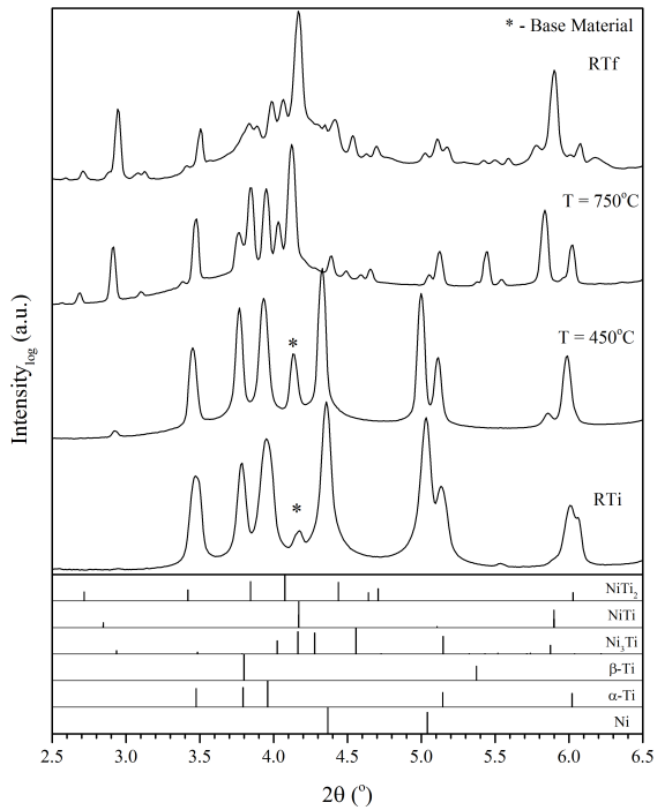
(b)

Figure 3: Phase evolution of the joints processed using Ni/Ti μ-foils at different temperatures (a) 650 ℃ and (b) 750 ℃.

After increasing the temperature to 450 ℃, the nickel and titanium peaks are still identified revealing that the reaction did not occur yet, resulting in a reaction temperature higher than the temperature observed for Ni/Ti ML films (Cavaleiro et al., 2014b). It should be noted that the individual layer thicknesses, and thus the diffusion distances, are completely different. As the temperature is raised to the maximum (650 or 750 ℃), interdiffusion occurs and different phases appear in the bond zone for both joints:

1. Ni/Ti μ-foils @ 750 ℃: $Ni + Ti \rightarrow NiTi + NiTi_2 + Ni_3Ti + Ni$ (traces)

2. Ni/Ti μ-foils @ 650 ℃: $Ni + Ti \rightarrow NiTi + NiTi_2 + Ni_3Ti + Ti + Ni$ (traces)

Besides de formation of the desired equiatomic phase NiTi, during the joining process the intermetallics Ni_3Ti and $NiTi_2$ were also identified, for both processing temperatures. In both joints traces of nickel are still present at maximum temperature as well as after the joining process revealing that diffusion is not yet complete and not all reactants were transformed onto the desired final products. Titanium is also present throughout the process. Once again, it is not possible to distinguish between the Ti from the μ-foils and from the Ti6Al4V base material, due to the reasons stated before. In both cases, for the first set of scans processed at maximum temperature the intermetallic phases are all already formed and identified. Maintaining the maximum temperature, some changes in peak intensities are observed: the peak intensity of Ni_3Ti, NiTi and $NiTi_2$ increase, while the intensity of the Ni peak decreases (Figure 4). These results are in agreement with the occurrence of diffusion between Ni and Ti, followed by reaction to form intermetallic phases. Differences between the joints processed at different temperatures are clear for the maximum temperature scans, namely in the relative intensity of the NiTi phase. For the joint processed at 750 ºC it is almost only NiTi that is present, although traces of $NiTi_2$ and Ni_3Ti are still detected. This means that 100 ºC difference is enough to almost complete the diffusion process and homogenize the bond region.
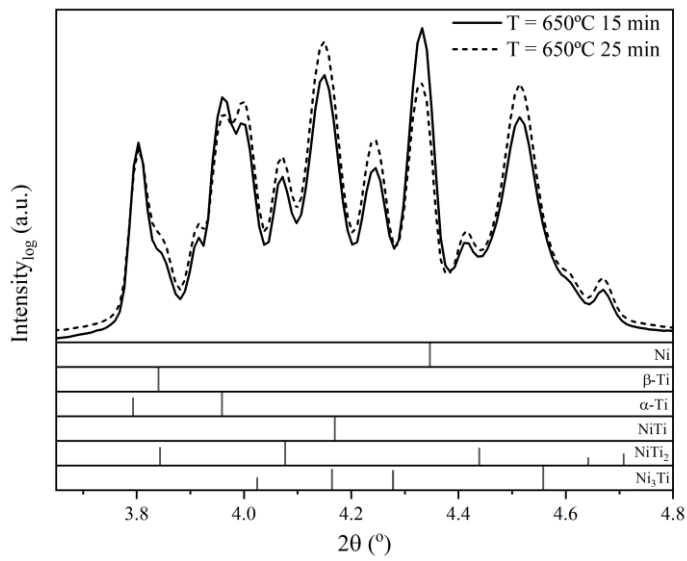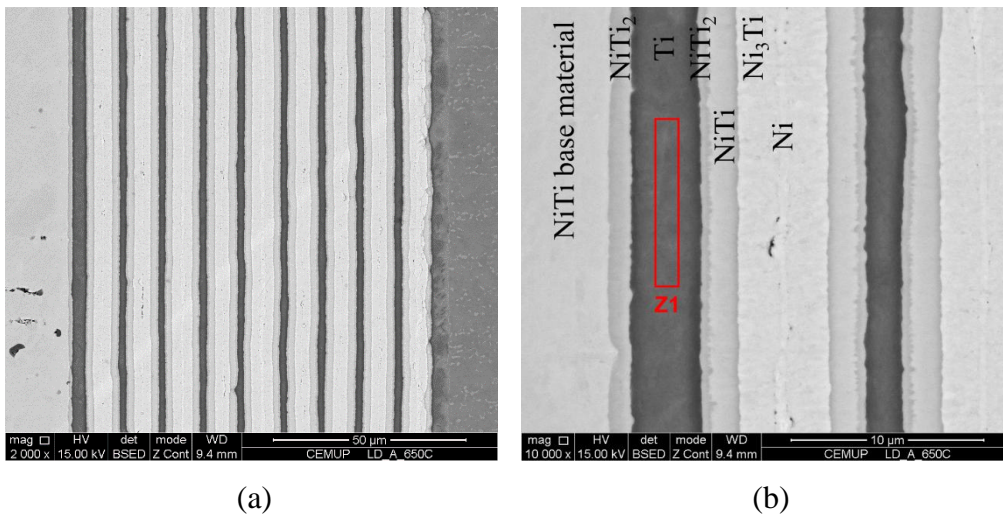
Figure 4: X-ray diffractograms of the joints processed using Ni/Ti μ-foils at 650 ºC, after 15 and 25 min.

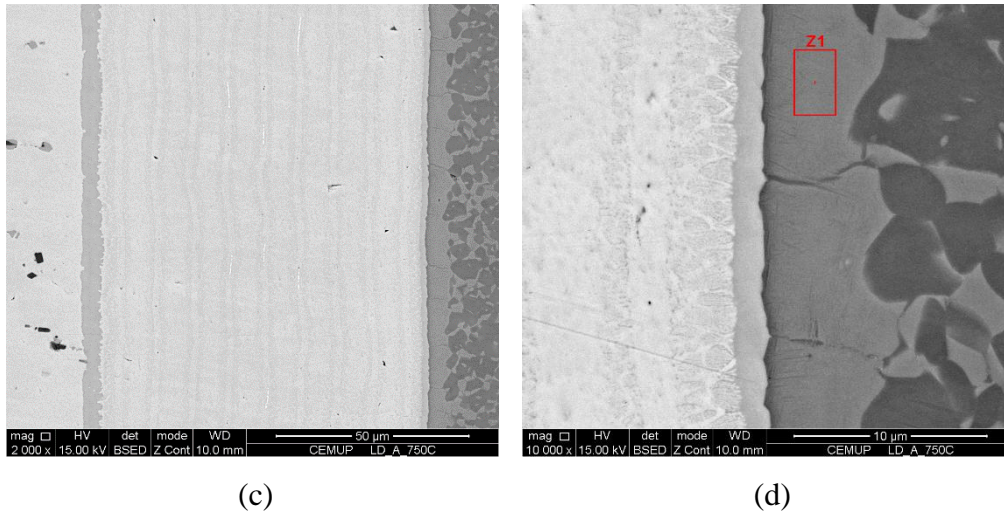Successful joints produced using Ni/Ti μ-foils as filler material are shown in Figure 5.

(a)   (b)

mag □	HV	det	mode	WD	⎯⎯ 50 µm ⎯⎯
2 000 x	15.00 kV	BSED	Z Cont	10.0 mm	CEMUP LD_A_750C

mag □	HV	det	mode	WD	⎯ 10 µm ⎯
10 000 x	15.00 kV	BSED	Z Cont	10.0 mm	CEMUP LD_A_750C

(c)   (d)

Figure 5: SEM micrographs of RADB samples processed using Ni/Ti µ-foils at (a), (b) 650 ℃ and (c), (d) 750 ℃.

In accordance with the results of x-ray diffraction, different bands can be observed on the bond zone corresponding to the different phases that were formed during the joining process. Due to the joint geometry and diffusion direction, the joining process will be a 1D process (the length of the faying surfaces is much wider than the bond zone) where the composition gradient formed results in different bands through the interface. The different bands present are more evident in the lower temperature joint, since in this case the process is far from finish. EDS analysis, similarly to the XRD analysis, reveals the presence of unreacted µ-foils, in particular Ti, which means that the diffusion/joining process is not complete (Z1 Figure 5b – 98 at.% Ti). EDS analyses were also carried out in the different bands observed in Figure 5b. Combining the SEM/EDS results with the phases already identified by synchrotron XRD, the different bands can be recognized and ordered from the Ti to the Ni µ-foils as follows: Ti – $NiTi_2$ – NiTi – Ni_3Ti – Ni (Figure 5b). This composition gradient can be understood having in mind the interdiffusion between the Ni and Ti µ-foils. The residual nickel band is thinner than the titanium residual band which means that up to 650 ℃, diffusion is preferential on the nickel side, because Ni diffuses faster than Ti. In the case of the joint

processed at 750 ºC, the different bands are difficult to distinguish due to high diffusion kinetics, making the EDS analysis challenging. Nevertheless, based on the XRD results, a tentative identification of the bands with different grey tones can be done. In a previous work, when joining multilayer coated TiAl using Ti and Ni µ-foils, $NiTi_2$ was the only nickel titanide formed, but in this case the Ti foils were five times thicker than the Ni ones (Simões et al., 2011).

It is also possible to observe that at high temperature (750 ºC), the grain boundaries of the Ti6Al4V alloy close to the bond zone are brighter than the ones further away from the interface (Figure 5c). Ti6Al4V is a dual phase alloy constituted by α-Ti grains surrounded by β-Ti phase. During the joining process nickel from the filler material diffuses and reaches the Ti6Al4V base material. EDS analysis reveal a Ni content close to 7 at.% (Z1 Figure 5d). Due to Ni diffusion, close to the interface the grain boundaries of the Ti6Al4V alloy are highlighted (Figure 5d).

3.2 RADB using Ni/Ti Multilayers

Using Ni/Ti ML thin films as filler materials, NiTi/Ti6Al4V joints were firstly processed at 750, 800 and 900 ºC (Simões et al., 2013). This is already below the temperature used by Kundu et al. (2011) to diffusion bond Ti6Al4V to stainless steel without filler material. NiTi/Ti6Al4V joints can found industrial application in medical devices, actuators and aerospace gas turbine engines. In the present work NiTi/Ti6Al4V joints were processed at low temperatures. Using Ni/Ti multilayers, either with 12 nm as well as with 25 nm period, sound joints were produced at a bonding temperature of 600 ºC. This low temperature has never been reported for diffusion bonding of NiTi to Ti6Al4V, which is particularly relevant for industrial applications.

In-situ x-ray phase evolution using the two Ni/Ti nanolayered systems are shown in Figure 6. At room temperature, and since in the case of the reactive MLs the bond interface is much thinner than the beam size (50 μm), the analysed volume of the filler is small and therefore the nickel peak is difficult to distinguish. For the shortest period (12 nm), and due to the high disorder of the sputtered Ni layers, it is not possible to distinguish the Ni (111) diffraction peak. For the 25 nm period, the Ni main peak is visible. Due to intermixing, the x-ray peaks for short periods are consistent with a quasi-amorphous structure, which was already addressed in a previous paper by Cavaleiro et al. (2015).
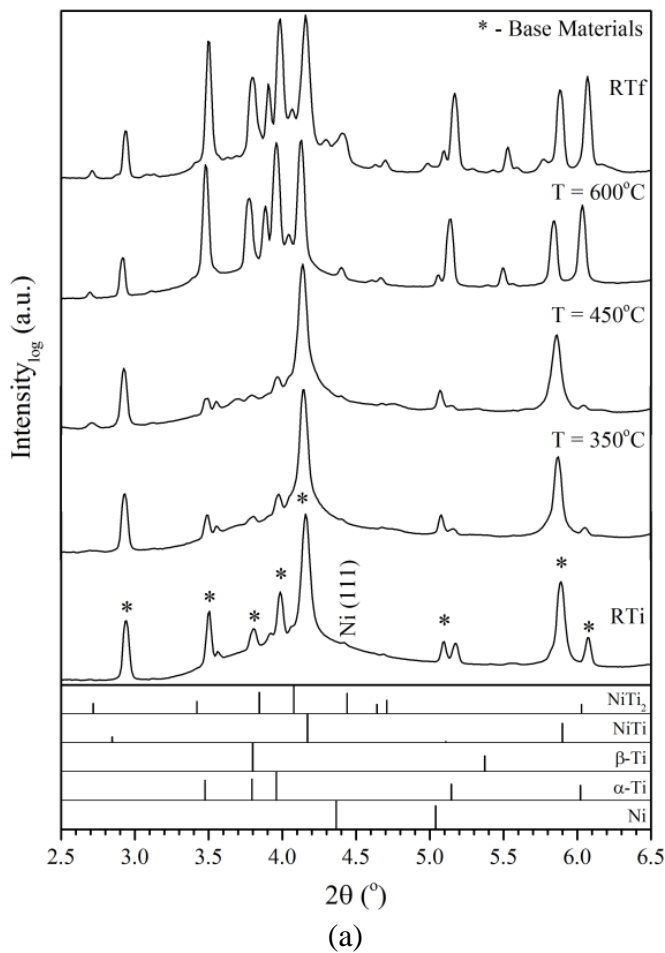

(a)

Figure 6: Phase evolution of the joints processed at 600 ℃ using Ni/Ti MLs thin films with (a) Λ =12 nm (b) Λ =25 nm.
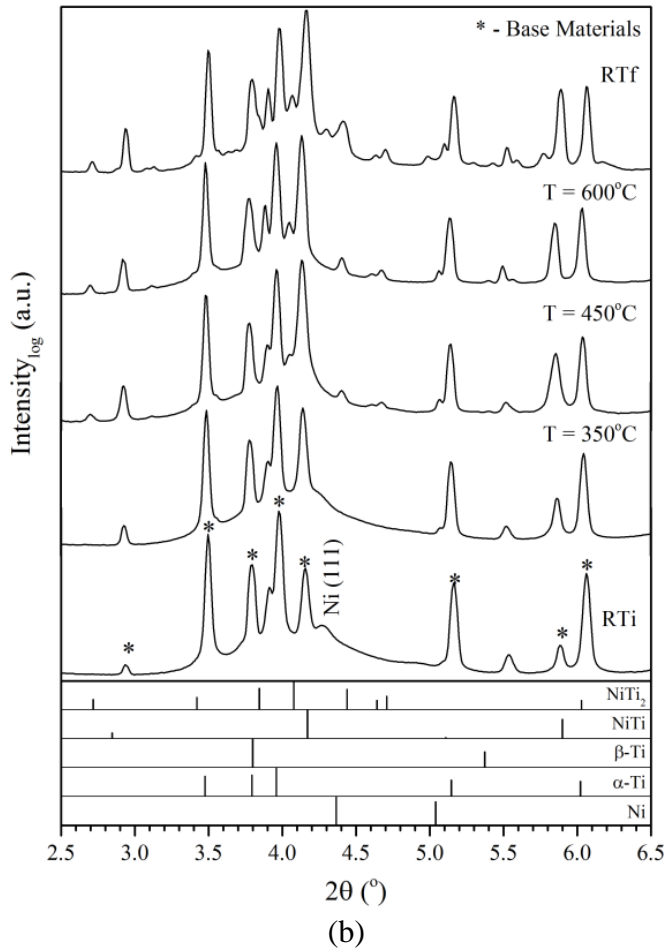
Figure 6: Phase evolution of the joints processed at 600 ºC using Ni/Ti MLs thin films with (a) Λ =12 nm (b) Λ =25 nm.

At 350 ºC and 400 ºC no significant changes were observed on the x-ray scans. For both periods, at 450 ºC the Ni peak disappears due to the Ni and Ti reaction and the formation of NiTi occurs. The presence of the $NiTi_2$ phase is also already observed. For the Ni/Ti μ-foils the reaction is not discernible at the intermediate temperature steps, meaning that, as expected, the reaction occurred later than for the Ni/Ti ML thin films. The lower reaction temperature comparing with the μ-foils can be explained considering the high number of interfaces in the MLs, the short diffusion distances (a few nanometer against a few micron) and the high reactivity of the ML thin films due to their nanometric grain size. In fact, the nanometric thickness of the individual layers limits the grain growth in ML thin films. This can also explain the absence of unreacted Ni,

17

even at 600ºC. Using MLs with 12 and 25 nm period, no differences were observed in

the x-ray diffractograms.

The phase evolution is similar for both periods and can be summarized as follows:

- $Ni + Ti \rightarrow \textbf{NiTi} + NiTi_2$
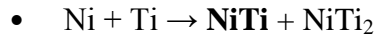
NiTi/Ti6Al4V joints were also processed at 650 ºC. The increase of the bonding

temperature results in relative intensity of the $NiTi_2$ XRD peaks higher than for 600ºC.

Ni diffusion towards the base material could contribute to the formation of $NiTi_2$ as it

gives rise to a Ni-depleted interface.

SEM analysis of the bond interface was also conducted for the joints processed using

ML thin films at bonding temperature of 600 and 650 ºC, and for $\Lambda = 12$ and 25 nm
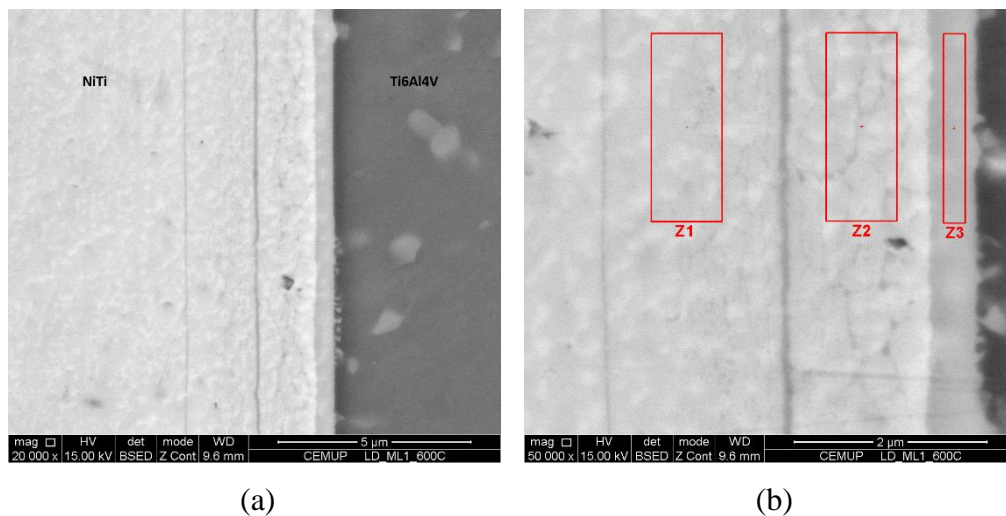
(Figure 7 and 8).

(a)   (b)

Figure 7: SEM micrographs of the RADB samples processed at 600 ºC using a Ni/Ti ML with Λ =12 nm. a) 20 000 and b) 50 000 X magnification.
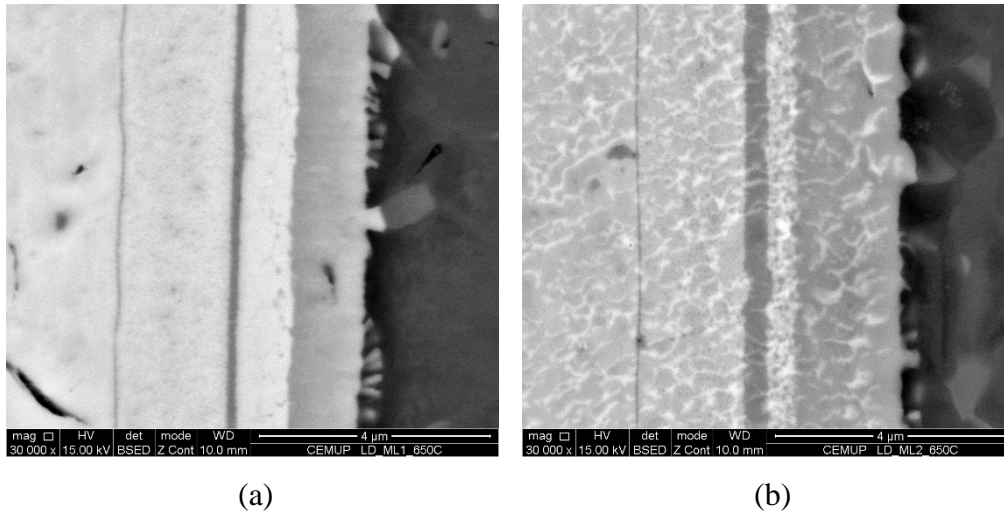
<div align="center">(a)   (b)</div>

Figure 8: SEM micrographs of the RADB samples processed at 650 ℃ using Ni/Ti MLs with (a) Λ =12 nm and (b) Λ =25 nm.

For 600 ℃ and Λ = 12 nm the left side of the interface is undistinguishable from the NiTi base material, while on the Ti6Al4V side the interface is composed of two bands: a NiTi band similar to the left side of the interface, and a ≈500 nm band darker than the rest of the interface (Figure 7). The EDS results of table 1 confirm the presence of NiTi on the majority of the interface, while the chemical composition of the thin and dark band close to the Ti6Al4V side is compatible with the $NiTi_2$ phase. For the highest period, the joint processed at 600 ℃ is similar, namely the thickness of the $NiTi_2$ band.

As the bonding temperature increases, the $NiTi_2$ band becomes thicker; around 1.2 and 1.8 μm at 650 ℃ for 12 and 25 nm periods, respectively (Figure 8). This thickness increase is in accordance with the XRD diffractograms. The ratio between the thickness of the $NiTi_2$ band and the thickness of the joint interface (NiTi + $NiTi_2$) corresponds to the volume fraction of the $NiTi_2$ phase. Therefore, the estimated values for the volume fraction of $NiTi_2$ for the joints processed using nanomultilayers with 12 nm period at 600 and 650 ℃ are ~14 and ~30 %, respectively. For 650 ℃ and with a 25 nm period multilayer, this volume fraction is almost 50 %. The thick $NiTi_2$ band for the highest period was already observed when increasing the bonding temperature up to 750 ℃

Cavaleiro et al. (2014a). In fact, for $\Lambda = 25$ nm at 750 ºC the interface was constituted only by $NiTi_2$, while for $\Lambda = 12$ nm a NiTi band was observed on the NiTi side Cavaleiro et al. (2014a). This could be related with the possibility of Ti diffusion towards the NiTi base materials at high temperatures, which could balance the Ni diffusion on the opposite direction, resulting in less $NiTi_2$. Due to the lower diffusion distances, the Ti diffusion should occur mainly for the short period MLs.

$NiTi_2$ is a fragile phase that should be avoided. Reducing the bonding temperature, by using nanometric period ML thin films as filler materials, is crucial as it reduces the formation of this phase during the joining process.

The hardness and reduced Young modulus results obtained by nanoindentation are presented in figure 9.
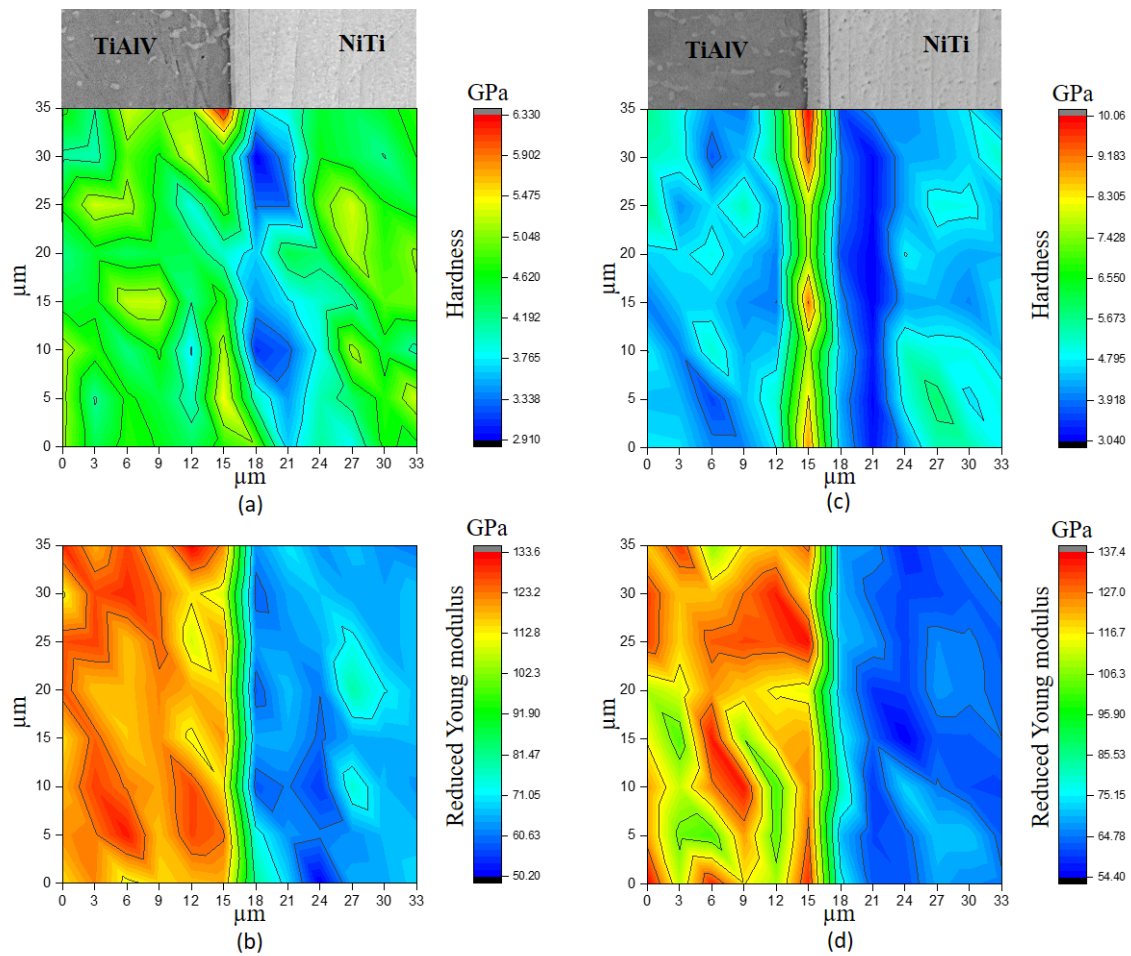
Figure 9: (a), (c) Hardness and (b), (d) Reduced Young modulus of RADB samples processed using a Ni/Ti ML with Λ = 12 nm at (a), (b) 600 ºC and (c), (d) 650 ºC.

The hardness of the base materials is similar, but the low Young modulus of NiTi allow it to be unequivocally identified, and consequently the joint interface. The nanoindentation matrixes crossed the joint interfaces as revealed by the hardness and reduced Young modulus maps (Figure 9). For the joint processed at 650 ºC the hardness values are higher for one of the central columns of the indentation matrix, which should correspond to the $NiTi_2$ band adjacent to the Ti6Al4V base material (Figure 8(a)), while for the joint processed at 600 ºC no hardness increase is detected at the joint interface because the amount of $NiTi_2$ phase is not significant (note the difference in the

maximum hardness values in the scale bars of figure 9(a) and (c)). In addition, close to the interface a slight decrease of the NiTi hardness can be observed in both cases. The nanoindentation results corroborate the SEM/EDS analysis and confirm the more pronounced effect of the $NiTi_2$ fragile phase as the joint temperature increases, resulting in a hardness increase that can be deleterious for the mechanical performance of the joints. For the 600 ºC processing temperature the hardness map obtained by nanoindentation has no disruptions, being almost "blind" with respect to the joint interface.

4. Conclusions

Joining NiTi to Ti6Al4V by Reaction Assisted Diffusion Bonding using Ni/Ti multilayer thin films or µ-foils was successfully carried out. The heat due to the layered filler materials reaction assists the diffusion bonding process, being possible to promote joining at relatively low temperatures and short dwell times. Using nanomultilayers sound joints can be processed at 600 ºC, while for the µ-foils it is only possible to attain sound joining at 650 ºC. For both methodologies, the undesired formation of $NiTi_2$ phase is more pronounced if the joining process is conducted at higher temperatures. The presence of $NiTi_2$ results in a hardness increase at the joint interface processed at 650 ºC using a 12 nm period nanomultilayer. At 600 ºC the effect of the $NiTi_2$ phase is not detected in the hardness map obtained by nanoindentation. For the µ-foils a minimum temperature of 750 ºC is required to ensure complete diffusion/reaction and attain homogenization of the interface. In this case, besides the formation of $NiTi_2$, the formation of the Ni_3Ti phase is also observed. By taking advantage of the nanometric character of the ML thin films, and consequent high diffusivity and reactivity, sound

joints are achieved at less demanding conditions than through the use of alternate μ-foils. For industrial applications, the decrease of the bonding parameters constitutes an economic advantage. In addition, the total thickness of the ML filler materials is adequate for microjoining applications, while the μ-foils are too thick.

Declarations of interest: none.

References

Adams, D.P., 2015. Reactive multilayers fabricated by vapor deposition: A critical review", Thin Solid Films 576, 98-128.

Boyer, R.R., 1996. An overview on the use of titanium in the aerospace industry. Mater. Sci. Eng. A 213(1-2), 103–114.

Buehler, W.J, Gilfrich, J.V., Wiley, R.C., 1963. Effect of low-temperature phase

 changes on the mechanical properties of alloys near composition TiNi. J. Appl. Phys.

 34, 1475-1477.

Cao, J., Feng, J.C., Li, Z.R., 2008. Microstructure and fracture properties of reaction-

 assisted diffusion bonding of TiAl intermetallic with Al/Ni multilayer foils. J. Alloys

 Compd. 466, 363-367.

Casalino, G., Curcio, F., Memola, F., Minutolo, C., 2005. Investigation on Ti6Al4V

 laser Welding using statistical and Taguchi approaches. J. Mater. Process. Tech. 167,

 422-428.

Cavaleiro, A.J, Ramos, A.S., Braz Fernandes, F.M., Schell, N., Vieira, M.T., 2014a. In

 Situ Characterization of NiTi/Ti6Al4V Joints During Reaction-Assisted Diffusion

 Bonding Using Ni/Ti Multilayers. J. Mater. Eng. Performance 23, 1625-1629.

Cavaleiro, A.J., Santos, R.J., Ramos, A.S., Vieira, M.T., 2014b. In-situ thermal

 evolution of Ni/Ti multilayer thin films. Intermetallics 51, 11–17.

Cavaleiro, A.J., Ramos, A.S., Vieira, M.T., Martins, R.M.S., Braz Fernandes, F.M.,

 Morgiel, J., Baehtz, C., 2015. Phase transformations in Ni/Ti multilayers investigated

 by synchrotron radiation-based x-ray diffraction. J. Alloys Compd. 646, 1165-1171.

Chau, E.T.F., Friend, C.M., Allen, D.M., Hora, J., Webster, J.R., 2006. A technical and

 economic appraisal of shape memory alloys for aerospace applications. Mater. Sci.

 Eng. A438-440, 589-592.

Kundu, S., Sam, S., Chatterjee, S., 2011. Interface microstructure and strength

 properties of Ti-6Al-4V and microduplex stainless steel diffusion bonded joints.

 Mater. Des. 32, 2997-3003.

Ma, Y., Li, H., Yang, L., Hu, A., 2018. Reaction-assisted diffusion bonding of Ti6Al4V

 alloys with Ti/Ni nanostrctured multilayers", J. Mater. Proc. Tech. 262, 204-209.

Miranda, R.M., Assunção, E., Silva, R.J.C., Oliveira, J.P., Quintino, L., 2015. Fiber

    laser Welding of NiTi to Ti-6Al-4V. Int. J. Adv. Manuf. Technol. 81, 1533-1538.

Oliveira, J.P., Panton, B., Zeng, Z., Andrei, C.M., Zhou, N., Miranda, R.M, Braz

    Fernandes, F.M., 2016. Laser Joining of NiTi to Ti6Al4V using a Niobium

    interlayer. Acta Mater. 105, 9-15.

Oliveira, J.P., Miranda, R.M., Braz Fernandes, F.M., 2017. Welding and Joining of NiTi

    Shape Memory Alloys: A Review. Progress in Mater. Sci. 88, 412-466.

Oliver, W.C., Pharr, G.M, 1992. Improved technique for determining hardness and

    elastic modulus using load and displacements sensing indentation experiments. J.

    Mater. Res. 7, 1564-1583.

Otsuka, K., Ren, X., 2005. Physical metallurgy of Ti-Ni-based shape memory alloys.

    Progress in Mater. Sci. 50, 511-678.

Ramos, A.S., Vieira, M.T., Simões, S., Viana, F., Vieira, M.F., 2009. Joining of

    Superalloys to Intermetallics Using Nanolayers. Adv. Mater. Res. 59, 225-229.

Senkevich, K., Knyazev, M., Runova, Y., 2013. Special features of formation of a

    TiNi–VT6 diffusion joint. Metal Science and Heat Treatment 55 (7-8), 419-422.

Shiue, R-H., Wu, S-K., 2005. Infrared brazing Ti50Ni50 and Ti-6Al-4V using the Bag-

    8 braze alloy. Mater. Trans. 46, 2057-2066.

Simões, S., Viana, F., Ramos, A.S., Vieira, M.T., Vieira, M.F., 2013. Reaction zone

    formed during diffusion bonding of TiNi to Ti6Al4V using Ni/Ti nanolayers. J.

    Mater. Sci. 48, 7718-7727.

Simões, S., Viana, F., Koçak, M., Ramos, A.S., Vieira, M.T., Vieira, M.F., 2011.

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

    Mater. Chem. Phys. 128 (1-2), 202–207.

Zoeram, A.S., Mousavi, S.A.A.A., 2014. Laser welding of Ti-6Al-4V to nitinol.

   Materials and Design 61, 185-190.