1. Introduction

The functional properties of NiTi shape memory alloys (i.e. the shape memory effect and superelasticity) [1] are of significant interest in a wide range of industries including medical [2], aerospace [3] and seismic damping devices [1]. In addition to these functional properties NiTi has excellent physical properties and good resistance to fatigue [4], and corrosion [5], that increase its desirability in these applications. Titanium alloys are desired to be part of these same applications because of their remarkable strength, toughness, fatigue resistance, corrosion resistance and biocompatibility [6], Ti6Al4V is the most widely used Ti alloy with applications found in aerospace, nuclear, civil, chemical and biomedical industries [7]. These highly versatile materials are being integrated into complex multi-component systems, in which overall system performance is optimized by tailoring individual component properties.

Joining NiTi to Ti6Al4V is of great interest for applications in the biomedical and aerospace fields. Despite the importance, no joining techniques have been developed that avoid the formation of brittle intermetallics to produce high strength joints. In this work, Niobium was used as an interlayer to prevent the formation of these brittle phases when joining NiTi to Ti6Al4V. The presence of this interlayer ensured that crack free welds were obtained and no brittle intermetallic compounds were observed. The Niobium interlayer was of a much higher melting temperature than the base materials so the bulk Niobium did not melt during the joining process, acting as a diffusion barrier between the NiTi and Ti6Al4V. The laser was focused on the Ti6Al4V side of the joint, which joined the Ti6Al4V and Niobium by fusion welding. At this interface a (Ti, Nb) region was formed due to dilution of the Niobium and mixing with the Ti6Al4V. At the NiTi–Nb interface a eutectic reaction was responsible for joining. Mechanical testing of the joints revealed that the minimum tensile strength matched the ultimate tensile strength of the weakest material, Niobium. These results highlight new possibilities for the use of high melting point filler materials when joining NiTi to dissimilar materials, so that the formation of undesired phases can be avoided.

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Previous investigations of dissimilar NiTi joining [15,16] offset the laser into one of the base materials to control the degree of mixing; however, the diffusion of the alloying elements was not fully stopped, so brittle intermetallics were still formed. The only reported attempt to use an interlayer to join NiTi and Ti6Al4V has been by Zoeram et al. [10] who studied the use of a Copper interlayer. Use of the Copper interlayer reduced the amount of brittle Ti2Ni intermetallics; however, brittle Cu-based intermetallics, such as Ti5Cu formed. These Cu-based intermetallics were found to be less brittle than the Ti2Ni phase but they still negatively impacted the ductility of the joint.

Use of an interlayer that becomes part of the weld pool has not proven to be sufficient to inhibit the formation of brittle intermetallics when joining NiTi to dissimilar materials [17–19]. Interlayers with a higher melting point than two dissimilar base materials have proven to be successful diffusion barriers that did not allow mixing [20–22]. It is hypothesized that this method could be applied to successfully join NiTi and Ti6Al4V. Selection of an appropriate interlayer for the NiTi–Ti6Al4V joint can be determined using the following criteria:

- No brittle intermetallics are formed with either alloy;
- Crystallographically similar, and miscible with both alloys;
- No detrimental effects to system biocompatibility

With these criteria in mind Niobium was identified as a potential interlayer for the dissimilar joining of NiTi and Ti6Al4V. It is a refractory metal with a melting point of 2477 °C, and, when pure, it is malleable and ductile so can conform easily to any joint configuration [23,24]. The melting point of Niobium is significantly higher than that of NiTi (1310 °C [25]) and Ti6Al4V (1660 °C [26]), so Niobium would be an excellent diffusion barrier between NiTi and Ti6Al4V; with previous proven use as a diffusion barrier between Ti and stainless steel [27]. Niobium has been successfully laser welded to Ti6Al4V [28], and joined with a eutectic reaction to NiTi [23] without the formation of brittle intermetallics, which are not present in these systems [29]. It is hypothesized that if Niobium is used as an interlayer for joining NiTi and Ti6Al4V that the laser can be offset into the Ti6Al4V so that fusion joining occurs on the Ti6Al4V–Nb side of the joint, while eutectic bonding occurs on the NiTi–Nb side of the joint. The relatively high conductivity of Niobium (52.3 m−1 K−1 [24]) to NiTi (18.0 m−1 K−1 [30]) and Ti6Al4V (6.6 m−1 K−1 [31]) would make it a good conductor of heat from the laser heated Ti side to the NiTi side and enable the eutectic reaction to form a joint.

In the current study, a Niobium interlayer was used for pulsed laser joining of NiTi to Ti6Al4V. Defect-free joints were produced, that matched the ultimate tensile strength of the Niobium interlayer.

2. Materials and methods

The NiTi shape memory alloy used in this study was purchased from Memory, had a nominal composition of 50.8 at. % Ni–49.25 at. % Ti, a thickness of 1 ± 0.05 mm, and was superelastic at room temperature. The Ti6Al4V, had a thickness of 1.1 ± 0.05 mm and was purchased from Titanium Joe. A pure Niobium interlayer (99.99 at. %) with a thickness of 50 μm, was purchased from ESPI Metals. Plates of NiTi and Ti6Al4V, with dimensions of 30 × 30 mm, were prepared using a Struers Accutom 50 precision cutting machine. The faying surfaces were ground to 1200 fine grit SiC paper to ensure proper joint fit-up and then cleaned with acetone and ethanol to completely remove impurities.

2.1. Laser welding

A Miyachi Unitek LW50A pulsed Nd:YAG laser system, with a wavelength of 1064 nm, a top-hat spatial profile and a spot size of 400 μm was used. The pulse profile had a peak power of 3.0 kW and a width of 20 ms, including a 3 ms upslope and a 15 ms downslope. The laser spot welds were overlapped by 25% to obtain a continuous weld. NiTi, Ti6Al4V, and Niobium oxidize in air and are prone to hydrogen pickup and embrittlement so a protective atmosphere is required when joining at higher temperatures. Argon was used as shielding gas at a flow rate of 0.99 m³/h.

Preliminary welding tests were performed without filler material to determine the welding power intensity required. As expected from previous work [9], cracking upon solidification occurred due to the formation of brittle intermetallics and residual thermal stresses. In order to overcome the solidification cracking, a Niobium interlayer was introduced between the materials as a diffusion barrier. Fig. 1 depicts a schematic of the set up used for the laser welding procedure. The laser was positioned on the Ti6Al4V side of the joint (250 μm from the joint interface), so that 60% of the beam was positioned on the Ti6Al4V top surface. The Ti6Al4V was preferentially heated because NiTi suffers a degradation of properties at high temperatures. Furthermore, a eutectic mixture is formed between NiTi and Niobium [32], which requires a lower amount of energy to promote joining than between the Niobium and Ti6Al4V. Finally, focusing the laser on the NiTi did not form a joint to the Ti6Al4V side.

2.2. Microstructural analysis

Transmission electron microscopy (TEM) was performed on the joint interfaces between Niobium and both base materials. Focused Ion Beam (FIB), using a Zeiss NVision 40 was used to obtain 10 × 10 μm specimens from the region of interest. TEM analysis was performed in a JEOL 2010F TEM/STEM operated at 200 kV. The electron microscope was equipped with an Oxford Inca Energy Dispersive X-ray (EDS) system and a Gatan imaging filtering (GIF) system for the acquisition of the electron energy loss spectra (EELS). Spectrum imaging technique was used to acquire an energy loss spectrum at each pixel of a selected area. Scanning TEM (STEM) EDS maps were obtained with a 1 nm probe diameter.

2.3. Mechanical testing

Test samples from the welds were prepared with an overall gauge length of 30 mm and a cross-section of 2 mm². Three welded specimens were analyzed. Tensile tests were performed according to the ASTM F2516-07 standard, at room temperature using an Instron model 5548 microtensile tester with an accuracy of ±0.5 μm at a displacement rate of 0.5 mm/min. Tensile strength and elongation up to fracture average values were obtained. Scanning electron microscopy (SEM) of the fracture surfaces was performed.
using a Zeiss Leo 1550 Field Emission SEM with an accelerating voltage of 10 kV.

3. Results and discussion

Positioning of the laser beam on the assembly was of major importance to forming the joint. Positioning of the laser on the NiTi base material was found not to promote joining at the Ti6Al4V—Nb interface. Only with the laser focused on the Ti6Al4V side were sound joints obtained. In this configuration a good fit-up between the NiTi/Nb/Ti6Al4V interface. Only with the laser focused on the Ti6Al4V side were sound joints obtained. In this configuration a good fit-up between the NiTi/Nb/Ti6Al4V was required to prevent gaps and ensure adequate heat transfer to form a joint. No joint would form if the beam was too far from the Ti6Al4V—Nb interface because insufficient heat was delivered to the NiTi—Nb side of the joint. Positioning the laser too close to the Ti6Al4V—Nb interface would also lead to no joint forming because the laser was reflected off by the Niobium interlayer.

A cross section of a weld captured during FIB milling is shown in Fig. 2. The interlayer formed defect-free interfaces with both the NiTi and the Ti6Al4V (Fig. 3). The pores observed in Fig. 2 were created during milling of the sample for transmission electron microscopy; there was no observed porosity of the specimens prior to milling. As discussed above, the laser was positioned over the Niobium and Ti6Al4V side of the joint, but the significant differences in the melting points of materials resulted in only the Ti6Al4V and NiTi melting while the bulk of the Niobium interlayer remained solid. Necking was observed in the fusion zone on the Ti6Al4V side of the joint. Similar non-symmetrical weld pools were observed during laser and electron-beam welding of Ti6Al4V to Niobium alloys [28,33]. The high melting point and thermal conductivity of the Niobium has been cited as the cause of asymmetry in weld pools. Wetting of the Niobium by the Ti6Al4V, as shown in Fig. 2, is another factor that contributed to the necking. Finally, positioning of the laser beam on the Ti6Al4V can cause a loss of material through vaporization which can also contribute to the observed necking [34].

3.1. Ti6Al4V—Nb Interface

As a result of the good wettability of the liquid Ti on the Niobium surface, the liquid phase incorporates Niobium and promotes its diffusion due to convection currents. However, as both elements have full solubility in one another, solid state diffusion of Ti into Niobium also occurs, as observed in Fig. 4. A (Ti, Nb) region formed at the interface of the Niobium interlayer and the fusion zone as shown in Fig. 4. The (Ti, Nb) region had a width of 30 nm, and additional Niobium diffused into the liquid to a distance of at least 200 nm, mixing thoroughly in the melt by convection currents and the Marangoni effect [35].

The content of Ti, Al and V in the (Ti, Nb) region decreased compared to the Ti6Al4V base material. Point EDS in the (Ti, Nb) region revealed an overall composition of 47.7Ti-46.2Nb-2.9Al-3.3V (in wt. %). Some TiNb-based alloys have similar compositions to this region [36,37]. The addition of Nb to these alloys results in both powerful β-stabilization and solid-solution strengthening [38]. A minimum of 36 wt. % Nb is required to stabilize the high temperature β phase at room temperature [39]. Computing the Al and Mo equivalency [39] of the (Nb,Ti) region indicated that it should be β metastable at room temperature.

Electron energy loss spectroscopy (EELS) provided a finer spatial distribution of the elements at the interface as shown in Fig. 5. The lack of mixing of Niobium with the Ti6Al4V at the Nb—Ti6Al4V interface, with the (Ti, Nb) region identified. The red line represents the EDS line scan. Below: Results for EDS line scan. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

![Fig. 2. Scanning electron microscopy image of the dissimilar joint.](image)

![Fig. 3. Scanning electron microscopy image of the interface between the Niobium and both the Ti6Al4V and the NiTi. The white squares mark the areas prepared by FIB and used for TEM analysis, shown in Figs. 4–6.](image)

![Fig. 4. Above: (Region A from Fig. 3) STEM image and EDS line scans across the Nb—Ti6Al4V interface, with the (Ti, Nb) region identified. The red line represents the EDS line scan. Below: Results for EDS line scan. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)](image)
for diffusion to occur [40]. The difference in composition and the high heating and cooling rates of the pulsed laser welding process contributed to the lack of mixing of the (Ti, Nb) region with the bulk of the fusion zone [14]. At the interface between the (Ti, Nb) region and the Niobium interlayer there was a sharp discontinuity in the Titanium spectra, which indicated no elements had diffused into the interlayer, due to the short time of the joining process.

### 3.2. NiTi–Nb Interface

A eutectic NiTi and Niobium microstructure was observed at the NiTi–Nb interface as shown in Fig. 6 (which corresponds to insert B of Fig. 3). This microstructure was previously observed by Grummon et al. [41] when brazing NiTi to pure Niobium. It was suggested that a quasibinary eutectic isopleth exists between the intermetallic NiTi and pure Niobium [32, 41]. The eutectic isotherm is 140°C below the congruent melting temperature of NiTi (1310°C). Spontaneous melting occurred with the pure Niobium being in intimate contact with NiTi at the high temperatures, and upon solidification two phases were formed: austenitic NiTi and bcc-Nb [42].

From the quasi-binary phase diagram it can be determined that the interface between NiTi and Niobium will spontaneously melt at temperatures above 1170°C. It is expected that, in conditions close to equilibrium, the first liquid to form has a composition similar to the eutectic point at Ni15Ti3Nb34. However, in the fast heating and cooling of pulsed laser welding the equilibrium condition does not occur [43]. In zone A of Fig. 6, was identified as the un-melted NiTi base metal. A proeutectic zone (zone B), which terminated in bulbous projections, was observed near the non-melted NiTi.

Selected area diffraction (SAD) was performed in these NiTi regions as marked in Fig. 7a). Indexing the SAD image in Fig. 7b) confirmed that these regions were the austenitic phase of NiTi.

The majority of the joint was composed of a lamellar eutectic solidification region as observed in zone C of Fig. 6. Using STEM in High Angle Annular Dark Field (HAADF) mode it was possible to distinguish between light (i.e. NiTi) and heavy (i.e. Nb) elements [44], as shown in Fig. 8. EDS mapping of these regions confirmed the dark regions were Niobium lean and the light regions were Niobium rich regions of a eutectic structure as shown in Table 1.

On the left side of Fig. 6, Niobium-rich regions were observed, which were identified as the un-melted Niobium grains. Significant grain boundary penetration around these Niobium grains is shown in Fig. 9 [45]. The faster diffusion along these paths resulted in the eutectic reaction propagating along the grain boundaries instead of through the bulk. In the Ni–W eutectic system the Tungsten has a significantly higher melting point than Nickel which resulted in grain boundary penetration of Ni–W eutectic along the W grain boundaries [46]. In the present work, similar behavior is observed by eutectic reaction of the NiTi–Nb system due to the significant difference in melting temperatures between Nb and NiTi.

Two different joining mechanisms were identified for the NiTi/Nb/Ti6Al4V joint. Fusion welding was used to join Ti6Al4V to Niobium. Niobium experienced dilution and was incorporated into the Ti6Al4V weld pool. A (Ti, Nb) region was formed upon solidification as a thin layer along the Niobium interface due to minimal mixing with the bulk fusion zone. The Niobium interlayer acted as a heat sink due to its high thermal conductivity absorbing a significant amount of energy from the Ti6Al4V side of the joint and transferring it to the NiTi side. This enabled this interface to reach temperatures of at least 1170°C so that contact melting between NiTi and Niobium occurred and a joint between these two materials was formed. Dissimilar joint between NiTi and Ti6Al4V did not form when no interlayer was present, further suggesting that the eutectic reaction was responsible for joining at the NiTi–Nb interface. As expected from the NiTi–Nb phase diagram, no intermetallic compounds were observed in the solidified joint. The high melting point of the interlayer ensured that the bulk of the Niobium remained in the solid state during welding, successfully stopping...
mixture of the two base materials.

3.3. Mechanical behavior of the welded joint

Tensile tests were performed on the joints made with the Niobium interlayer, with the laser offset into the Ti6Al4V. The stress–strain curve of the welds is shown in Fig. 10. As discussed in previous sections dissimilar joints between NiTi and Ti6Al4V were not formed without the interlayer, or with the laser offset into the NiTi.

An average tensile stress of 300 MPa and an elongation to fracture near 2.0% were measured. This was a significant improvement on joints made without the interlayer, which were unable to be tested because they fractured during removal from the welding fixture. The tensile strength of pure Niobium ranges between 250 and 350 MPa, so the joint strength matched the maximum theoretical strength of the interlayer. Similar values of tensile strength were obtained by Zoeram et al. [10], despite using a Copper interlayer, which has better mechanical properties than

Fig. 7. a) HAADF image of the NiTi–Nb interface with a region analyzed with SAD indicated; b) Indexed SAD image of NiTi that was performed on the marked area of the NiTi region.

Fig. 8. HAADF image of the eutectic microstructure with EDS analysis points indicated. The black spots were identified as impurities.

<table>
<thead>
<tr>
<th>Point</th>
<th>Atomic content (%)</th>
<th>Ni</th>
<th>Ti</th>
<th>Nb</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>51.7</td>
<td>38.1</td>
<td>10.2</td>
<td></td>
</tr>
<tr>
<td>P2</td>
<td>12.5</td>
<td>22.8</td>
<td>64.7</td>
<td></td>
</tr>
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Fig. 9. –Grain boundary penetration of NiTi into the Niobium grains.

Fig. 10. Stress-strain curve of NiTi to Ti6Al4V weld with Niobium interlayer.
Niobium. However, the tensile strength of the Niobium interlayer joints was below the critical value for stress induced martensite formation in NiTi. The joint strength may be improved through further optimization of joining parameters including joint fit-up, laser peak power, and pulse width. This study has proven that a high melting point interlayer can be used to achieve a defect-free joint between NiTi and Ti6Al4V. If a similar interlayer was identified that had higher ultimate tensile strength, then the joint strength could be increased to accommodate the superelastic effect.

The fracture surfaces of the welded specimens exhibited mostly brittle fracture morphology from the Ti6Al4V fusion zone as shown in Fig. 11. The 50 μm thick interlayer was torn during fracture leading to the Ti6Al4V and NiTi fracture surfaces having both the fusion welded and eutectic bonded regions of the joint. The NiTi side of the joint had more ductile dimples from the eutectic phases formed, while the Ti alloy side had more brittle cleavage features from the fusion zone. Hydrogen or oxygen pick-up by the Ti6Al4V weld pool could contribute to the brittle characteristics of the fracture surfaces [47,48]. The grain boundary penetration of the Niobium interlayer by the eutectic reaction with the NiTi can reduce the ductility of this region, which can also contribute to the observed brittle crack formation [45].

4. Conclusions

Defect-free, dissimilar laser welding of NiTi to Ti6Al4V was achieved using a Niobium interlayer. This opens up the possibility to join these materials in more complex configurations. The following are the major conclusions that can be drawn from the study:

1. Niobium acted as a barrier to mixing of the two base materials, which prevented the formation of brittle intermetallics, while ensuring joining at both interfaces. Dissimilar joining between NiTi and Ti6Al4V did not occur when the interlayer was not used.
2. The average tensile strength and elongation of these interlayer joints was 300 MPa and 2%, respectively. This ultimate tensile strength matched that of the Niobium interlayer.
3. At the NiTi–Nb interface, intimate contact between NiTi and Niobium promoted joining due to a eutectic reaction.
4. At the Ti6Al4V–Nb interface, dissolution of the Niobium into the liquid Titanium occurred. A thin (Ti, Nb) region with an average chemical composition of 47.7Ti–46.2Nb–2.9Al–3.3V (in wt.%) was identified at the interface of the Niobium interlayer and the fusion zone.

5. Precise control of the position of the laser with respect to the interlayer was crucial to obtain a sound weld. If the beam was positioned far away from the interlayer, eutectic melting in the NiTi–Nb interface did not occur. When the beam was placed too close to the interlayer, no joint formed because it was reflected by the Niobium.

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References


Fig. 11. Fracture surface on the Ti6Al4V side (a) and on the NiTi side (b) of the joint.