Investigation of the microstructure and phase evolution across multi-material Ni_{50.83}Ti_{49.17}-AISI 316L alloy interface fabricated using laser powder bed fusion (L-PBF)

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HIGHLIGHTS
• Laser-powder bed fusion (L-PBF) fabrication of functionally graded nickel-titanium (NiTi)-AISI 316L material demonstrated.
• Excellent bonding between NiTi and AISI 316L alloys controlled via complex bands of multi-material layers.
• Phase and microstructural evolution controlled through the L-PBF settings.
• Multi-material phase and microstructure formation/evolution mechanisms elucidated.

ABSTRACT
This study evaluates the phase and microstructural evolution of additively manufactured (AM) Nickel Titanium (NiTi) alloy, across the interface with 316L stainless steel build plate, in order to understand the processing parameter (input power, layer thickness and scan speed), composition, and microstructure interrelationships necessary to achieve excellent multi-material bonding between NiTi and 316L. The effect of the process parameters utilised was characterised using the Scanning Electron Microscope (SEM), Electron Backscatter Diffraction (EBSD), X-ray diffraction (XRD), and Energy-dispersive X-ray spectroscopy (EDX). SEM/EBSD results demonstrated, for the first time, that the microstructure and phase close to the interface was complex and comprised martensite, austenite and Fe phases, sequentially arranged in a layered sandwich pattern across the build direction. This complexity was necessary for excellent bonding. The L-PBF process parameters influenced the diffusion behaviour and the concentration of elements found at the interface. The diffusion rate of Fe and Ti across the NiTi-316L interface was 3.05 x 10^{-6} m^2/s and 3.27 x 10^{-8} m^2/s, respectively, representing a 93.27-fold increase. The observed
1. Introduction

Nickel Titanium alloy (NiTi) has found application in many fields today since the discovery of its unique properties in 1959 [1]. The unique properties of NiTi which make it attractive include its superior shape memory ability and pseudoelasticity [2–4]. When changes in either temperature or stress is induced in these materials, the crystalline structure is transformed; resulting in a change of phase [5,6]. The high-temperature, stress-free austenitic phase has a high-symmetry crystal structure based on a cubic lattice. The low-temperature, stress-free martensitic phase has a crystal structure with lower symmetry, such as tetragonal, rhombohedral, orthorhombic, monoclinic, or triclinic depending on the alloy [5]. Martensitic transformations involve diffusionless solid-to-solid phase transformations, resulting in the shape memory effect and the pseudoelasticity observed in shape memory alloys (SMAs) [5,6]. In near-equatomic NiTi, the austenite has an ordered B2 (CsCl) crystal structure. In contrast, the martensitic phase has an ordered B19' crystal structure, where B19 denotes an orthorhombic structure resulting from unequal normal strains relative to the (1 1 0) directions of the austenite structure, and the prime (’) indicates that it has additionally been distorted by a shear strain, resulting in monoclinic symmetry [5,6]. Another intermediate phase that sometimes appears is called the R phase, a rhombohedral distortion of the B2 structure [5,6].

Several conventional methods are utilised in the processing of NiTi. Amongst these methods, ingot metallurgy and powder metallurgy are the two main techniques employed. Among the drawbacks are the difficulty in fabricating complex shapes with these techniques. A recent development in the processing of these alloys is the application of laser-based additive manufacturing (AM) processes such as, Laser Powder Bed Fusion (L-PBF), which promises far greater reliability in the development of near-net shape components of NiTi alloys; especially, when the parts are large or complex in geometry [7,8]. In addition, AM provides a route to tailor the microstructure of components, which in turn impacts the superelastic behaviour and the transformation temperatures (TTs) of the alloys through process parameters selection [2,9,10]. The powder bed fusion (PBF) process in metal AM involves using feedstock in the form of powders to fabricate components through laser or electron beam melting. Usually, a thin powder layer (<100 μm) is deposited over a previously melted layer and then melted to form a new top layer. The underlying previous layer is remelted and re-solidifies in the process; and thus, bonds the two layers. This cycle of remelting and re-solidification of layers usually leads to a build-up of residual thermal stresses, changes in the morphology and chemistry of all phases, and a high density of dislocations [11–14]. These effects are very pronounced at the interface region between an AM component and a build plate; especially if dissimilar materials are involved because of the difference in the thermal expansion coefficient and chemistry of the two materials. This could result in warping and debonding during printing. NiTi and 316L are both important alloys in many sectors such as biomedical, automotive, aerospace, telecommunication, gas, oil, and petrochemical industries because of their excellent properties which include superior shape memory ability, pseudoelasticity, excellent formability, corrosion-resistance as well as good weldability [2,3,15,16]. The possibility of joining NiTi and 316L alloy would improve their applicability, since most components found in these sectors require joining [17]. Also, the NiTi component cost would be reduced if a stainless steel alloy could be used as the build plate instead of a NiTi alloy during AM. Thus, the ability to tailor the phase and microstructure through the L-PBF process is important for multi-material fabrication and joining applications/sectors.

In the joining of similar and dissimilar materials, an understanding of the relationship between phase equilibrium, microstructural changes and properties is important as has been demonstrated in previous studies [16–20]. Previous studies which have been carried out to address bonding and weldability using laser can be grouped into two categories; namely, those which investigated the conventional laser welding of NiTi/other alloys to stainless steel (SS) and those related to the bonding of a build plate to NiTi during AM processing [17,20–23]. Pouquet, et al., investigated the effect of laser welding process parameters on the weldability of a 0.34 mm thick NiTi foil to a 0.47 mm thick 316L [17]. They reported extensive cracking in the samples. One key result; however, was that the weld pool composition determined the strength of the joint. It could be concluded that process parameters such as pulse duration, material placement sequence prior to welding as well as the presence of a filler affected their results. LÜ, et al., used a combination of tungsten inert gas (TIG) welding and laser spot welding processes, to join NiTi to a stainless steel pipe [20]. They reported that there was the occurrence of interdiffusion between NiTi and SS within a short distance at the fusion boundary. This resulted in the formation of intermetallic compounds (Ni3Ti + (Fe,Ni)Ti) in agreement with Pouquet, et al. [17]. Recently, Hellberg, et al., investigated the microstructural and mechanical properties of NiTi and SS wire joints produced by micro electron beam welding without a filler material [21]. Based on mechanical test results, they concluded that the strengths of the joints were very similar to those obtained by laser welding using a nickel filler material. The obvious advantage here was the absence of a nickel filler which reduced the risk associated with a nickel release, and thus, could be used in medical applications. To study element diffusion during AM processing, Liu, et al., utilised a selective laser melting (SLM) process to fabricate multi-material components composed of mainly 316L stainless steel and C18400 copper alloy [24]. Good metallurgical bonding was reported as evidenced by the substantial amount of diffused Fe and Cu element found at the bond interface. Cracks were also observed at the interface between the intermixing zone and the SS. This was attributed to the physical property mismatch and the pressure exerted in the austenitic steel grain boundaries by the presence of diffused copper. Thus, it is useful to optimise the processing conditions in order to achieve good bonding. The work of Obeidi, et al., demonstrated the importance of process parameters optimisation when they concluded that printing NiTi parts on a different substrate material such as 316L was feasible once the process parameters were optimised [23]. They reported that the use of a low volumetric energy density (VED), which comprised high scanning speed and low laser power, resulted in delamination and non-weldability of a NiTi part to a 316L substrate.

Although it has been observed by several researchers of the occurrence of interdiffusion activities among the constituent elements in dissimilar materials during AM processing, to the best of the authors’ knowledge, not much detail has been provided so far. A recent study carried out to investigate the effect of the L-
PBF process parameters on the Ni loss, phase TTs, and transition enthalpies during metal AM processing of NiTi demonstrates that one major area which needs addressing is the mechanism of formation and evolution of phases and the microstructure which mitigates warping/debonding during L-PBF processing [25]. The ability to bond NiTi to SS via metal AM has not previously been demonstrated within the literature. Typically, when producing metal AM components, the same base plate material is used as per the metal powder utilised for component fabrication. This enables good bonding due to the match of thermal expansion coefficient and mechanical properties. If SS could be used as a base plate material, this would significantly lower the cost of metal AM processing with NiTi powder due to the high cost of the thick NiTi plate material required for the base plates. The ability to control the bond quality and strength between NiTi and SS is also required in order to be able to manufacture composite NiTi-SS components. For actuator applications with shape memory NiTi, being able to combine NiTi with the non-shape memory SS would enable the integration of such actuators into conventional system designs and infrastructures. The production of NiTi components on SS plates within one process furthermore reduces the number of manufacturing steps and hence cost for manufacture. However, to date, no study has investigated the possibility of how NiTi to SS bonding within the metal AM process can be achieved.

This investigation is therefore focused on filling this knowledge gap through the evaluation of the bonding of NiTi to a stainless steel build plate using L-PBF. This work presents an in-depth examination and understanding of the phase and microstructural evolution at the NiTi-316L interface required to achieve this as well as the processing parameters. In addition, this study presents the phase and microstructural evolution at the NiTi-316L interface during metal AM as evaluated using metallurgy, XRD, SEM, EBSD and EDX characterisation. A main novel outcome of this work is the presentation of the influence of the process parameters on this multi-material bonding and an understanding of the phase evolution at the interface.

2. Materials and methods

2.1. Materials

In this investigation, gas atomised Ni$_{50.83}$Ti$_{49.17}$ (NiTi) powder (Ingulis GmbH, Germany) with good sphericity (Fig. 1(a)) was utilised for the L-PBF process. The NiTi powder’s particle size distribution (PSD) analysis was carried out using a Malvern Mastersizer 3000 particle size analyser which showed: D$_{10}$ = 16.7 μm, D$_{50}$ = 31.5 μm and D$_{90}$ = 56.6 μm.

2.2. L-PBF AM processing

An Aconity MINI (GmbH) metal 3D printer equipped with a 200 W fibre laser (IPG Photonics) with a wavelength of 1068 nm was utilised in the fabrication of NiTi samples on an AISI 316L stainless steel build plate (140 mm diameter), under an argon gas atmosphere (purity – grade 5). The oxygen level in the printing chamber was maintained at less than 20 ppm during processing. 51 NiTi samples of approximately 0.3 mm × 10 mm × 10 mm (Fig. 1(b)) were fabricated according to the Design of Experiment (DoE) parameters given in Table 1 by utilising a Box–Behnken design. A constant spot size and hatch spacing of 50 μm and 70 μm, respectively, was utilised in all processed samples. The utilised process parameters resulted in input volumetric thermal energy density (VED) in the range of 25.92 to 116.67 J/mm$^3$ for the various processing conditions. The VED represents the average energy applied per volume of material during a powder bed fusion process. The VED was calculated according to the equation [23,25]:

$$\text{VED} = \frac{P}{\nu \sigma t} (J/mm^3)$$

where:

$\text{VED}$ = Volumetric energy density in J/mm$^3$

$P$ = Power in W

$\nu$ = Scan speed in mm/s

$\sigma$ = Laser beam diameter (spot size) in mm

$t$ = Powder bed layer thickness in mm

The processing parameters, levels and VED employed in the fabrication of the eight NiTi samples which successfully bonded to the build plate are given in Table 2. A powder supply factor of 2 (twice the layer thickness) was used during the entire build to ensure that sufficient powder was delivered after each layer. To ensure optimum powder coverage during processing, a powder re-coater speed of 50 mm/s was applied during powder deposition. To reduce the powder re-coater impact, the cuboidal samples were oriented at 45 rotation with respect to the re-coater blade motion as previously demonstrated to be effective [23]. Thus, to ensure a 90 angle rotation between layers, a 45 starting angle for the hatching was utilised. The simple and alternative hatching strategy was applied during processing, from which the laser beam reversed direction after each consecutive track.

2.3. Sample preparation

In order to effectively investigate the properties of the successful prints, these samples were cut using the electrical discharge machining (EDM) process to include approximately a distance of

![Fig. 1.](image-url)
0.3 mm normal to the NiTi-SS interface from the NiTi side (thickness of the as-fabricated AM NiTi); and a distance of 0.89 mm normal to the interface from the 316L side, giving approximately a total sample thickness of 1.2 mm (see Fig. 4). The samples were further sectioned into four pieces each to give a final sample size of 5 mm × 5 mm × 1.2 mm using a precision cutter (IsoMet 1000) under continuous lubrication. Samples perpendicular to the z-build direction (top view) and parallel to the build direction (cross-section view) were mounted using a two-part resin mixture whose exothermic temperature was about 40°C to avoid heating effect which could result from the use of hot-press resin mounting technique. The samples were prepared and analysed using the ASTM E3-11(2017) and E407-07(2015) standards as guide [26,27]. For easy identification, these samples have been designated ‘top-view’ and ‘cross-section’ in this investigation.

Samples for EBSD characterisation were prepared using P320, P600, P1200, P4000 SiC papers followed by a 3 μm diamond suspension on a patterned polishing plate and finished with a silica suspension mixed with hydrogen peroxide on a chemical cloth. After mechanical polishing, the samples were finely polished using a 0.06 μm colloidal silica on a multi cloth for 16 hours at 110 Hz using a Saphir-Vibro vibropolisher from MetPrep®. Final polishing using colloidal silica removed any damage resulting from mechanical polishing and provided a homogeneous surface for EBAD analysis. After polishing, the samples were immediately rinsed with deionized water and placed in an ultrasonic bath for 5 min to remove any colloidal silica particles left on the surface. After the polishing process, the samples were coated with a carbon film (5 nm) to avoid any electrical charging effects during the electron beam’s interaction with the non-conductive sample surface. Samples used in optical microstructural and elemental composition analyses were first ground using a P320 SiC paper followed by the use of a 9 μm, 3 μm and 1 μm diamond suspension for polishing. A mixture of colloidal silica (0.4 μm) and 30% hydrogen peroxide was used finally to achieve a mirror-polished surface before rinsing. Subsequently, cleaning in an ultrasonic bath for 5 min was performed. Etching was carried out using a freshly prepared mixture of 1 mL HF, 1 mL HNO3 and 18 mL H2O chemical etchant (approx. 20 to 60 s depending on samples) to reveal the various zones of interest in the cross-section as well as in the top view samples.

2.4. Material characterisation

2.4.1. Optical microscopy and SEM/EDX characterisation

A combination of Keyence-2000 optical microscope and a Zeiss EVO LS-15 SEM (equipped with Oxford Instruments® EDX) system was used for morphology, microstructure, and elemental composition analyses of the samples. For the EDX analysis, an accelerating voltage of 20 kV and a current of 600 pA was utilised. Elemental composition was acquired using the Oxford Instrument® Aztec software.

2.4.2. XRD characterisation

XRD phase analysis were carried out on the samples (top view direction) using a triple-axis Jordan Valley Bede D1 high resolution XRD system with Cu-Kα (λ = 1.5405 Å) radiation source operated at 45 kV and 40 mA. The scan wavelength for this system was in 2θ mode with a scanning range from 15° to 100°, a step-size of 0.1° and steps of 0.01° per second. Phase identification was carried out using JCPDS-ICDD card numbers 00-035-1281, 03-065-0145, 01-075-0878, 00-018-0898, 00-049-1614 and 018–899).

2.4.3. EBSD characterisation

A cross-section and top view sample EBSD characterisation was performed using a Zeiss Crossbeam 550 equipped with Oxford Instruments® Symmetry S2 CMOS detector; at an accelerating voltage of 20 kV and a current of 5 nA. The samples were mounted on a conventional sample holder and tilted to 70°. The EBSD patterns were acquired using automatic indexing in a rectangular grid mode; a step size between 1 μm and 0.1 μm. The crystallographic parameters used to index the NiTi phases were acquired from the literature, and the database diffraction files reconstructed using an Oxford Instrument software, ‘Twist’. Table 3 provides the crystallographic parameters of the phases used. After acquisition, the EBSD results were processed using an Oxford Instrument HKL Channel 5 software. The datasets were cleaned by performing the routine single wild spike removal, followed by an eight-point iterative nearest neighbour zero solution, and a seven-point nearest neighbour zero solution for three cycles [28]. The wild spike replaced individual isolated indexed pixels with zero solutions. The eight-point and the seven-point nearest neighbour processing infilled zero solutions with a computed solution/orientation based upon adjacent indexed pixels.

3. Results and discussion

3.1. Phase characterisation

XRD characterisation was carried out with the beam normal to the as-built top-down view plane, on the NiTi side (see Fig. 3 and labelled ‘A’ on the schematics in Fig. 4). It could be observed from Fig. 2 that the various process parameters affected the phase(s) of the NiTi obtained when compared to the original powder used in the L-PBF processing. One clear observation was the huge difference in peak intensity and FWHM of the sample processed at 66.67 J/mm³ compared to the rest. Also, the peak shape at the 2θ angle of between 42° and 47° of the sample processed at 33.33 J/mm³ (in red circle) clearly was different. Among the possible reasons for the observed difference, strain as well as the presence of mixed phases are the two factors that could lead to the observed differences [31,32]. The result demonstrates that it was possible

Table 1

<table>
<thead>
<tr>
<th>AM processing parameters and set levels examined.</th>
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<tbody>
<tr>
<td>Power (W)</td>
</tr>
<tr>
<td>Low</td>
</tr>
<tr>
<td>Med</td>
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<tr>
<td>High</td>
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</table>

Table 2

<table>
<thead>
<tr>
<th>S/N</th>
<th>Power (W)</th>
<th>Layer thickness (µm)</th>
<th>Scan speed (mm/s)</th>
<th>VED (J/mm³)</th>
</tr>
</thead>
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<tr>
<td>1</td>
<td>120</td>
<td>60</td>
<td>1200</td>
<td>33.33</td>
</tr>
<tr>
<td>2</td>
<td>160</td>
<td>90</td>
<td>1000</td>
<td>35.56</td>
</tr>
<tr>
<td>3</td>
<td>140</td>
<td>90</td>
<td>800</td>
<td>38.89</td>
</tr>
<tr>
<td>4</td>
<td>160</td>
<td>60</td>
<td>1200</td>
<td>44.44</td>
</tr>
<tr>
<td>5</td>
<td>120</td>
<td>60</td>
<td>800</td>
<td>50.00</td>
</tr>
<tr>
<td>6</td>
<td>160</td>
<td>60</td>
<td>800</td>
<td>66.67</td>
</tr>
</tbody>
</table>
to control the NiTi phase by using the L-PBF process parameters. For example, using a VED of 44.44 J/mm³ and 66.67 J/mm³ resulted in the formation of a martensite and austenite NiTi phase, respectively. Intuitively, a higher VED should generally result in increased Ni depletion. This is not always the case since the exact extent of Ni evaporation is dependent also on the exact process parameters used to achieve that VED [33–35]. The resulting phase structure was also dependent on the residual stress, discussed in further detail below.

3.2. Effect of L-PBF processing parameters on residual stress

Fig. 3 shows the typical surface morphology of the AM NiTi samples (top-down), produced with different process parameters when inspected in detail using the SEM. The presence of sintered as well as partially-melted adjacent powder particles can be observed on the surfaces of the samples. The differences in their morphology which has been attributed to the difference in their process parameters, can be observed clearly. For example, the processing conditions for samples in Fig. 3 (a) & (d) were similar except for the scan speed of 800 mm/s and 1200 mm/s, respectively. This resulted in higher surface porosity and roughness in Fig. 3 (a) compared to Fig. 3 (d). This is as a result of the difference in the energy imparted to a particular spot per unit time during processing. Sample processed with higher VED generally resulted in less surface roughness.

The L-PBF process involves repeated deposition and laser irradiation during which each spot in the build experiences multiple cycles of melting and solidification such that it becomes the heat-affected zone (HAZ) when its adjacent locations has been deposited. This generally results in residual stress in samples and thus cracks [36–38]. As shown in Fig. 3, the presence of longitudinal cracks and microcracks was observed on the surface of some of the samples. These cracks were thought to be a direct result of the residual stresses induced by the differing amount of energy imparted to the melt pool during laser processing, and the high cooling rate inherent in a L-PBF process. A typical example of the microcracks is given in Fig. 3 (c-f). For example, in Fig. 3 (c), cracks could be observed running across the entire surface of the sample processed at 66.67 J/mm³, which was not the case for other samples. The melt-pool lines were not able to prevent the microcrack propagation in these samples; however, no macroscale cracks were evident (Fig. 3 (d)). The cracks observed in Fig. 3 did occur via two mechanisms: solidification and liquidation cracking [39]. Solidification cracking would occur in the fusion zone during a partial laser melting of NiTi such that the non-solidified liquid part when entrapped, induces tensile residual stresses upon solidification. Liquidation cracking, on the other hand, does occur in the heat-affected zone where phases with low melting points, such as regions with chemical segregation as well as the eutectics, are usually found [35,40].

In order to understand the role of residual stresses in the formation of the observed cracks, an analysis based on the Young’s modulus and coefficient of thermal expansion (CTE) for samples processed using VED of 44.44 J/mm³ and 66.67 J/mm³, for instance, might illustrate the typical thermal stresses developed during the L-PBF processing. Thus, thermal stress ($\sigma$) was estimated by the equation [22]:

$$\sigma = E \alpha \Delta T$$

### Table 3

<table>
<thead>
<tr>
<th>Crystal System</th>
<th>NiTi - Austenite</th>
<th>NiTi - Martensite</th>
<th>Fe-FCC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Laser Group</td>
<td>Cubic-High</td>
<td>Monoclinic</td>
<td>Cubic-High</td>
</tr>
<tr>
<td>Space Group</td>
<td>11 (P 3 3 m)</td>
<td>2 (I 2 1 m)</td>
<td>11 (P 3 3 m)</td>
</tr>
<tr>
<td>a (Å)</td>
<td>2.9930</td>
<td>2.8980</td>
<td>2.9315</td>
</tr>
<tr>
<td>b (Å)</td>
<td>2.9930</td>
<td>4.1080</td>
<td>2.9315</td>
</tr>
<tr>
<td>c (Å)</td>
<td>2.9930</td>
<td>4.6460</td>
<td>2.9315</td>
</tr>
<tr>
<td>$\alpha$ (°)</td>
<td>90.00</td>
<td>90.00</td>
<td>90.00</td>
</tr>
<tr>
<td>$\beta$ (°)</td>
<td>90.00</td>
<td>97.80</td>
<td>90.00</td>
</tr>
<tr>
<td>$\gamma$ (°)</td>
<td>90.00</td>
<td>90.00</td>
<td>90.00</td>
</tr>
<tr>
<td>Composition</td>
<td>50%Ni, 50%Ni</td>
<td>50%Ni, 50%Ni</td>
<td>100%Fe</td>
</tr>
</tbody>
</table>

Fig. 2. XRD profile of L-PBF processed samples showing possible effects of strain and the presence of mixed and amorphous phases.
where $E$ is the Young’s modulus, $\alpha$ is the CTE and $dT$ is the temperature gradient.

For the sample processed at 44.44 J/mm$^3$, XRD results indicated that the phase was mostly martensite. Therefore, $E_{44.44} = 34.02$ GPa and $\alpha_{44.44} = 6.6 \times 10^{-6} / ^\circ C$ [41,42] were employed for the analysis. For the sample processed using a VED of 66.67 J/mm$^3$, the XRD results showed that it was in the austenite phase; thus, $E_{66.67} = 83$ GPa and $\alpha_{66.67} = 11.0 \times 10^{-6} / ^\circ C$ [42,43]. Since it has been reported previously that there was little or no relative variation in the mean layer surface temperature of the L-PBF samples during processing for the first few layers [23]; therefore, a constant temperature gradient for both samples was assumed. Thus,

$$dT_{44.44} = dT_{66.67} = dT$$

(3)

Therefore, $\sigma_{44.44} = 2.25 \times 10^{-4} dT$ and $\sigma_{66.67} = 9.13 \times 10^{-4} dT$ (where, $\sigma$ values are in GPa).

Thus, $\sigma_{66.67} \approx 4\sigma_{44.44}$ and implies that the thermal stress developed in the samples processed at 66.67 J/mm$^3$ was approximately 4 times as much as that developed in 44.44 J/mm$^3$ samples (assuming that the effect of any other phase present is negligible). This explains the observed crack size and propagation differences among samples. This is in agreement with previous studies which showed that residual stresses increased with increasing energy density in AM parts [44,45]. In order to have complete information on the microstructural and phase evolution of the AM samples, it was necessary to examine the cross-section of the samples, in addition to the surface examination discussed in this section. This is detailed in subsequent sub-sections.

3.3. Microstructural analysis

Etching revealed that the samples were not simply composed of NiTi alloy on a 316L substrate, rather a complex microstructure comprising various layers (zones) with distinct properties. Fig. 4 shows the schematics of a typical sample comprising NiTi alloy on a 316L (top image) along with the optical and SEM micrographs.
of the etched sample cross-section (bottom) revealing the various possible zones and phases. In Fig. 4, Zone 1 is the region considered the unaffected bulk in the 316L. Zone 2 represents the 316L region closest to the interface zone. Zone 3 is designated as the interface zone, zone 4 is the NiTi region nearest to the interface zone, zone 5 is the austenite region whereas zone 6 is the topmost part comprising mixed phases of martensite, austenite, NiTi2, etc. The dominant phase obtained at zone 6 suggested dependence on the processing parameters utilised as will be discussed in subsequent sections.

In this investigation, two types of microstructures were observed on the cross-section samples depending on the L-PBF process parameters utilised, which for simplicity have been represented by the calculated VED during processing. One type represents where the VED used produced an interface zone (interlayer) between the NiTi alloy and 316L parts. In the other type, the VED did not lead to the presence of an interface zone in the microstructure. Samples, where the VED were below 50 J/mm³ resulted in the absence of an interface layer, whereas samples processed with ≥ 50 J/mm³ resulted in the interface zone. This behaviour was observed to be independent of the phase(s) of the sample and layer thickness during printing. In general, above the interface zone, the microstructure of the NiTi was a complex one. For example, Fig. 5 compares the microstructures of two samples. The phases of the samples in Fig. 5 (a) & (b) were martensite and austenite, respectively. The presence of needle-like and plate microstructure; indicative of the martensite phase of NiTi, was predominantly present. These martensitic structures were a combination of fine and coarse needle-like and plate microstructures and have been observed previously by several researchers [46,47]. It could be observed in Fig. 5 (c) that the fine structures were predominantly found at the region close to the interface layer. Coarse structures were observed as one moved away from the interface region. It has been reported that during L-PBF processing of NiTi with similar chemical composition, the melt pool temperature was higher at the first layer (that is, the region closest to the 316L build plate) when compared to the top layer of the build [23]. It was further reported that these differences in temperature across the layers, resulted in obtaining fine martensitic microstructures at higher melt pool temperature zone, and coarse martensitic microstructures at low temperature level zone in their samples [23]. As such, it could be assumed that the zones close to the interfaces as well as the interface zone in the samples used in this investigation would be at a higher temperature compared to the rest. This would explain the presence of fine martensitic microstructures close to the interface zone (Fig. 5 (c)). In order to confirm the phases present at the different zones of the samples, EBSD analysis results is presented in the next subsection.

3.4. Electron backscatter diffraction (EBSD) characterisation

As regards the EBSD investigation, the cross-section and top view of three samples processed using VED of 33.33 J/mm³, 50.00 J/mm³, and 66.67 J/mm³ were evaluated. Firstly, the dominant phases obtained in the samples were confirmed using EBSD maps, as shown in Fig. 6 (a), (b) & (d); for samples processed at 50.00 J/mm³, and 66.67 J/mm³, respectively. As can be observed, the phase was predominantly austenite above the interface; however, sandwiched between this austenite phase and the interface zone, a layer comprising the martensitic phase and those from 316L are found. The GROD map in Fig. 6 (c) shows the level of deformation in the samples (see horizontal colour code for reference). The deformation within the grains was mostly observed on the austenite phase. This indicates that the formation mechanism of the austenite phase was related to the thermomechanical history generated during L-PBF processing. This is understandable given the nature of the L-PBF process which involved using a highly localised laser heat source to repeatedly scan a surface, and thus, induce large thermal gradients. In order to provide an understanding of the phase formation and evolution, an analysis of the mechanisms is presented in subsequent sub-sections.

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**Fig. 4.** Schematics of a typical sample (top), where ‘A’ – top view & ‘B’ – cross-section; optical microscope of the sample cross-section (bottom left) as well as the SEM micrograph of the sample (bottom right) revealing the various possible zones and phases obtainable across the NiTi-stainless steel sample.
3.5. Phase formation and evolution

The presence of alloying elements as well as nickel depletion/surplus in NiTi alloys have varying effects on both their mechanical and functional properties as has been reported by several researchers. The most common effect is usually the change in the martensitic transformation temperature and path [48,49]. For example, for Ni-rich NiTi and binary NiTi alloys, it is possible to change the martensitic transformation type from $\text{B2} \rightarrow \text{B19}^\text{0}$ simply by the addition of Fe, heat treatment at the correct temperature to induce $\text{T}_3\text{Ni}_4$ precipitates or through cold-working followed by annealing (for example, at 673 K). These would result in high density of rearranged dislocations in a sample [2,6,49]. EBSD results of the preceding sub-section indicated that Fe contributed to the phase formation and evolution of the interface layer and the subsequent zones above the interface layer, since Fe was found in those zones. It would be assumed that other elements such as Cr, Ti, and Ni can be found also in those zones in proportions different from their original parent concentrations and compositions. Here, EDX line scan was used to investigate the diffusion of Ni, Ti, Fe and Cr across the samples’ cross-section in order to understand their effect on the phase and microstructural formation and evolution, as a function of the L-PBF process parameters (VED) utilised in their fabrication. Figs. 7, 8, & 9 show the elemental concentration variation across a line drawn from the 316L part of the sample to the NiTi part (yellow horizontal line). In the Figures, Zone 1 to 6 has been used to give the reader a visual perspective of the diffusion in the different layers of the sample cross-section as was shown in Fig. 4. The various colour codes show regions (zones) with distinct diffusion behaviours for clarity. A study of the diffusion profiles of these samples, led to the following observations and, thus, influenced the strategy adopted for the diffusion analysis in this work: (1) Utilising energy (VED) of 38.89 J/mm$^3$ resulted in the absence of an interface layer whereas using a VED of 50 or 66.67 J/mm$^3$ produced an interface layer of of thickness 51 μm and 62 μm, respectively; (2) In all the samples examined, the chemical composition varied over the range of the diffusion zone. Distinct diffusion behaviours could be observed at each zone in the samples (zones are highlighted in colours for clarity in the Figures). Therefore, it should be expected, that the diffusing atoms would experience different chemical environments; and thus should possess different diffusion coefficients. This explains why the diffusing elements shown in Figs. 7–9 showed approximately the S-profiles usually associated with interdiffusion [50]; (3) The diffusion profiles of Ni and Ti indicated similar trend. Similar trends could also be observed for the Fe and Cr profiles. Therefore, Ti and Fe were utilised for the diffusion analysis for simplicity; (4) There appeared to be a correlation between the utilised VED and the diffusion-affected-zone width which was 194 μm, 195 μm and 260 μm; for samples processed using 38.89 J/mm$^3$, 50 or 66.67 J/mm$^3$, respectively (See Figs. 7–9). This indicates that the diffusion processes favoured higher energy input; (5) In Figs. 8 & 9, as regards the interface zone, the concentration level of Fe was higher than that of Ti. In contrast, the level of concentration of these elements at the extremes of the samples was almost similar. This indicates that the Fe and Cr’s contribution to the formation of the interface layer was higher than that from Ti and Ni. Thus, the chemical and mechanical properties of the interface zone would be expected to be somewhat similar to that of the 316L SS substrate; and (6) The concentration profiles of Ni, Ti, Fe and Cr within the range of the interface zone (as one moved from the 316L zone towards the NiTi zone and vice versa) was reasonably constant in the 50 and 66.67 J/mm$^3$ samples, indicating a steady-state diffusion. This implies also that the diffusion rates of the elements at this zone was identical. Thus, diffusion occurred via an exchange mechanism in which atoms crossed the interface in pairs. It is generally difficult to study diffusion in multicomponent interdiffusion processes because of the multiple hopping possibil-

![Fig. 5. Optical micrographs of L-PBF processed samples exhibiting different phases: (a) sample processed with 50 J/mm$^3$ showing a predominantly martensitic phase; (b) sample processed with 66.67 J/mm$^3$ showing the austenite phase of NiTi alloy; (c) magnified image of (a) where fine and coarse needle-like and plate martensitic structures can be observed; (d) magnified view of (b) showing the austenite phase microstructure.]
ties of each atom [50]. Therefore, for simplicity, the analysis in the zones were considered as a diffusion couple in order to give insight into the phase formation and evolution mechanism. Samples processed with the VED levels at 50 and 66.67 J/mm², were used for these analyses as presented below, since both contained an interface layer. Moreover, this enabled a reasonably similar distance of diffusion to be examined while still enabling analysis of the effect of the VED on the extent of diffusion.

For the samples processed using 50 and 66.67 J/mm², the concentration of the elements was measured under the diffusion-affected zone at the starting points designated A and B in Fig. 8; and C and D in Fig. 9. For example, 1 → 2 indicates that the start of diffusion is at point 1 and ends at point 2. This convention was used for the diffusion analysis presented in this work. Fick’s second law diffusion equation was applied. It is given as [51]:

$$\frac{\partial C}{\partial t} \approx D \frac{\partial^2 C}{\partial x^2}$$  \hspace{1cm} (4)

where, \( \partial \) is the atomic concentration of Fe or Ni in (at\%)
\( t \) is time in second (s)
\( D \) is the diffusion coefficient in m²/s

\( x \) is the position in metre (m)

Considering the horizontal nature of the concentration profiles prior to point 1, 5 (opposite direction to 1), 6 and 11 (opposite direction to 6) in Figs. 8 and 9, respectively, the elements concentration was assumed to be constant. Therefore, the adopted solution to the above equation was of the form [51]:

$$\frac{C(x,t) - C_0}{C_s - C_0} = 1 - \text{erf} \left( \frac{x}{2\sqrt{Dt}} \right)$$  \hspace{1cm} (5)

where, \( \text{erf} \) is the error function.

\( 2\sqrt{Dt} \) is the diffusion length.

Based on Eq. (5), the diffusion rate of Fe and Ti across the various zones (1 → 2, 2 → 3, …10 → 11) for the two samples, were computed. Starting with the sample processed at 50 J/mm² (Fig. 8), the initial L-PBF process started with the NiTi powder’s deposition on the 316L build plate. Thus, at that stage, there was zero diffusion across the 316L into the NiTi powder. Therefore, the initial Fe concentration in NiTi was zero; thus, \( C_0 = 0 \). For Fe diffusion from point 1 to 2 to occur, the NiTi powder was radiated with laser of energy 50 J/mm² which led to the melting, and the subsequent solidification of both substate and NiTi powder. From Fig. 8, it was assumed that the initial concentration of the Fe in 316L was constant and given as \( C_s = C_1 = 2400\text{cps} \). At point 2, the Fe concentration, represented as \( C(x,t) = C_s = 2085\text{cps} \). The diffusion distance, \( x = 50 \mu m \). It is well known that the solidifica-

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Fig. 6. (a) Phase map of the cross-section of 50 J/mm² sample, 60 μm scan; (b) Phase map of the cross-section of 66.67 J/mm² sample, 60 μm scan; (c) GROD map of a magnified region from (a) showing deformation in the austenite phase of NiTi; (d) Phase map of the magnified section in (b) showing a mixture of martensitic phase of NiTi and that from 316L close to the interface.
tion process of L-PBF is very rapid, therefore, 300 s was assumed as the time it took the sample to cool down to room temperature after fabrication. Hence, the diffusion coefficient $D$ of Fe in the interface layer ($1 \rightarrow 2$), was computed as $3.05 \times 10^{-6} \text{m}^2/\text{s}$. A similar procedure was utilised to arrive at the $D$ values of Fe and Ti across the various zones of the rest of the samples (Table 4). As can be

Fig. 7. Diffusion profiles of Fe, Cr, Ti and Ni across the various zones of a sample processed using 38.89 J/mm$^2$. An SEM micrograph of the line scan region is also shown for visualisation.

Fig. 8. Diffusion profiles of Fe, Cr, Ti and Ni across the various zones of a sample processed using 50 J/mm$^2$. An SEM micrograph of the line scan region is also shown for visualisation.
observed in zone 3 (see Figs. 8 and 9, as well as Table 4), a difference was also observed on the diffusion behaviour of the two samples at the interface layer. For samples processed using 66.7 J/mm², the diffusion behaviour suggests that there was a breakdown of Fick’s second law, and therefore, not applicable. In contrast, the other sample showed an approximate result. It is to be noted that a slight change in the boundary conditions of the latter sample would have equally led to a breakdown of Fick’s second law. This, therefore, suggests a reaction–diffusion mechanism in this layer, where the diffusion of Fe, Cr, Ni and Ti competed with the formation of the interface layer through a chemical reaction. This usually results in a competition between the localisation and the homogenisation of dislocation densities; and leads to material deformation.

There was no significant difference observed in the $D$ values of Fe and Ti when the entire diffusion-affected-zone width was used for the analysis (that is, $D_{1-5} = D_{5-1}$ and $D_{6-11} = D_{11-6}$ for 50 & 66.7 J/mm² samples, respectively). However, it could be observed that the Fe diffusion rate was higher than that of Ti in the two samples when considering the first few layers. A particular effect of this could be seen in the phase formation and evolution in the samples as was shown in the EBSD images in Section 3.4.

In order to visualise the role of Ni content across the sample, the Ni-Ti ratio across the various zones is presented in Fig. 10. For

![Fig. 9. Diffusion profiles of Fe, Cr, Ti and Ni across the various zones of a sample processed using 66.67 J/mm². An SEM micrograph of the line scan region is also shown for visualisation.](image)

![Fig. 10. A plot of the variation of Ni-Ti ratio across the various zones of L-PBF samples. Note: $n = 4$; error bars shown for each result are 95% CIs.](image)
example, tracing from the 316L part (a region on the 316L immediately before the start of the interface layer) towards the NiTi part for the sample fabricated using a VED of 50 J/mm³, the Ni-Ti ratio was (1.74 ± 0.05) to (0.93 ± 0.00) indicating the presence of Ni-rich and slightly Ti-rich regions at the extremes, respectively. The implication is that the Ni-rich region (region closer to the interface) would exhibit a lower TT compared to the NiTi top layer which comprised Ti-rich regions. This is in agreement with the recent report by Chekotu, et al. [25].

3.6. Mechanism of phase formation and evolution

As was shown by the concentration profiles (Figs. 7 - 9), the concentration of the alloying elements (Fe & Cr) decreased from the interface towards the NiTi bulk. The presence of these elements would result in three situations; namely, a reaction to form a new phase or a mixed phase, and the modification of the parent phase through site occupancy, by the alloying elements (Fig. 11). This is in good agreement with what was observed in this investigation.

The EBSD results presented in the previous section demonstrated that the phase at the interface zone (see 1 → 2 in Fig. 7, for example) was neither 316L nor NiTi. An analysis of the EDX results presented previously showed that the likely phases formed were related to Fe_{58.3}Ni_{16.5}Cr_{15.9}Ti_{9.3} alloy; as a result of the interface reaction between 316L and NiTi during processing. Above this layer (that is, in 2 → 3), what was observed from the EBSD result was a mixture of phases, related to 316L as well as that from NiTi. Studies have shown that Fe would preferentially substitute for Ni during diffusion. Also, excess Ni solubility in NiTi is usually high compared to that of Ti under equilibrium conditions as could be observed in the Ni-Ti phase diagram (Fig. 12 (a)). These usually lead to the formation of Fe₂Ti and Ni₃Ti, respectively (Fig. 12 (b)). EDX results suggested that the likely phases on this zone were Fe₂Ti, Ni₃Ti, and martensitic phase of NiTi. Based on the phase diagram in Fig. 12 (c), this is understandable since cooling down the samples from the liquidus at a high cooling rate (as obtainable in LPBF process) after processing, would result in the formation of phases immediately below the solidus. This implies that alloys with a composition slightly rich in iron would solidify as γ phase, in addition to a high concentration of the brittle phase, Fe₂Ti because of the high cooling rate. Further formation of Fe₂Ti in the subsequent layer was largely suppressed by the presence of excess Ni [17,52]. The formation of Fe₂Ti would explain the extensive cracks found on this region (see Fig. 4), when compared to the other layers as this phase is known to lead to cracking in laser welded NiTi-SS joints [17]. The austenite phase of NiTi was obtained above this layer (that is, in 3 → 4). This layer is believed to have resulted through the site occupancy of the alloying elements in the NiTi matrix. The site occupancy resulted in a significant alteration of the lattice dynamic properties, such that a large change in TT was induced to compensate for the stress developed in the material. This is in agreement with previous studies, where it was shown that alloying NiTi with Fe led to a change in the martensitic transformation temperature. As the sample thickness increased; however, the concentration of the alloying elements (Fe & Cr) decreased; leading to the formation of a slightly Ni-rich layer (4 → 5). This resulted in a decrease in the TT of subsequent layer as would be expected for Ni-rich NiTi alloys [49,53]; and thus, resulted in the retention of austenite phase at room temperature. This process was repeated until a thickness was reached, where the TT was no longer dependent on Ni surplus but on the level of deformation (residual and plastic strain) in the sample; which has been reported affected TTS [6]. Several reports point out that unrecoverable strains at high temperature might not be solely as a result of dislocation slip at the moving habit plane interfaces but as a result of a combination of stress induced B₂ → B₁₉ → B₁₀ martensitic transformation into twinned austenite and dislocation slip [54–57]. At this stage, with excess Ti present, the precipitation of brittle NiTiₙ phase is usually considered favourable; and they usually act as sites for crack initiation. This would explain the level of samples’ microcracks as discussed in Section 3.2. Thus, the thermomechanical history of the samples played a major role in the formation and evolution of the room temperature phase and microstructure of the samples.

Fig. 11. Schematics of phase formation and evolution: (I) Reaction to form interface layer; (II) Formation of layer comprising mixed phases of NiTi (B₁₀), FeTi₂ and Ni₃Ti; (III) Formation and modification of B₂ NiTi phase through site occupancy.
4. Conclusions

This study demonstrates for the first time that the microstructure and phase across the NiTi-316L interface of AM fabricated parts was complex, comprising phases in a sandwiched or more intermixed formations. This complexity was necessary for excellent bonding to occur. The L-PBF process parameters seemed to control the diffusion behaviour and the concentration of elements found at the interface. Subsequently, this dictated whether an interface zone was formed or not. For example, samples processed with VED of $\geq 50$ J/mm$^2$ produced an interface zone. Diffusion across the various sandwiched layers in the samples seemed to approximate Fick’s law of diffusion except at the interface layer. Here a reaction–diffusion mechanism occurred, such that Fe, Cr, Ni and Ti diffusion competed with the formation of the interface layer through a chemical reaction.

EDX analysis gave an insight into the mechanism of formation and evolution of the phases. The L-PBF process induced high plastic strains during the fabrication of parts due to the extremely high solidification rates. EBSD GROD maps provided a clear visual expression of the level of deformation within the grains and was observed mostly on the austenite phase. This indicates that the mechanism of forming the sandwiched martensite and austenite phases is related to the chemistry at the interface and the thermo-mechanical history generated during L-PBF processing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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