Formation of β-Ti phase during L-PBF processing of martensitic NiTi

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ABSTRACT

Shape memory activations in martensitic NiTi are highly influenced by the processing technique used. Laser Powder Bed Fusion (L-PBF) is a metal additive manufacturing method being investigated for NiTi processing. The rapid transient thermal effects involved in L-PBF processing are found to cause microstructural anomalies which can result in unfavourable mechanical and functional properties. In this paper, anomalous hard protrusions observed in L-PBF processed NiTi microstructure were investigated in detail. The spatial distribution and cause of these protrusions were analysed. Studies were conducted using EDX, BSE, EBSD, TEM, DSC, AFM and nanoindentation, to identify the compositions, crystal structures, thermal characteristics and nanomechanical properties of these protrusions. The protrusions were identified to be hard β–Ti phase.

1. Introduction

Processing of polycrystalline nitinol (NiTi) shape memory alloys via metal additive manufacturing (AM) has gained high research interest over the last decade [1–9]. The Laser Powder Bed Fusion (L-PBF) technique has been found effective in processing metallic alloys such as Ti64, stainless steels and Ni-base super alloys for specific applications [10–14]. L-PBF of NiTi is still in the early stages of development, due to the challenges faced in achieving a suitable microstructure for tailored phase transformations [5,8,9,15,16]. For a Ti-rich composition with martensitic phase at room temperature, the material is referred to as martensitic NiTi featuring shape memory effect [17]. Since L-PBF is associated with high thermal energy, the samples often get exposed to overheating and Ni evaporation during processing. This rapid transient processing nature can result in formation of porosity, impurities and precipitates, including Ti2Ni2Ox, TiC and Ti2Ni in martensitic nitinol, causing adverse effects on phase transformations and physical properties [18–21].

In this work, a microstructural anomaly found in NiTi samples printed via L-PBF technique was investigated in detail. After thorough metallurgical specimen preparation, the samples were found to contain considerable numbers of small hard particles protruding from the polished surfaces. To date, there have been several reports of Ti2Ni precipitate formations in martensitic NiTi during L-PBF processing. However, the formation of hard β – Ti phase protrusions, found and investigated in this study, has not previously been reported and was found to present novelty in terms of the resulting shape memory response as well as the phase structure resulting from the L-PBF processing of NiTi.

2. Material and methods

NiTi samples of cuboidal dimensions (10 × 10 × 55 mm) were 3D printed using a Aconity MINI (GmbH) L-PBF machine, equipped with IPG Photonics Nd:YAG fibre laser system having a wavelength of 1068 nm. The NiTi powders were supplied by Inugus GmbH from Germany with a nearly equiatomic composition of Ni (49.9) – Ti (50.1) at%. The powder particles were spherical in shape and were produced by electron induction melting gas atomisation (EIGA) process with a particle size distribution of $D_{10} = 12.3 \pm 0.8 \mu m$; $D_{50} = 28.1 \pm 2.2 \mu m$; $D_{90} = 57.3 \pm 7.7 \mu m$; $D_{[3,4]} = 34.0 \pm 3.1 \mu m$.

Multiple NiTi samples were printed using a combination of L-PBF parameters under constant layer thickness (40 µm) and laser spot size (50 µm). Laser parameters included three laser powers (120, 150 and

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180 W), three levels of scan speeds (600, 900 and 1200 mm/s) and three levels of hatch spacings (40, 55 and 70 µm). A Box-Behnken design of experiments (DoE) was followed to print the samples (Table S1 is supplementary). The samples were printed in horizontal (longest axis of the cuboid parallel to build plate surface) and vertical (longest axis of cuboid perpendicular to build plate surface) orientations, following a simple stripe scanning strategy with 90° rotation between each subsequent layer. The volumetric energy density (VED) of L-PBF processing was calculated as: \( \frac{P}{v \cdot h \cdot t} \), where \( P \) is laser power; \( v \) is scan speed, \( h \) is hatch spacing and \( t \) is layer thickness. The VED varied between 44.64 and 156.25 J/mm³, following the combination of the above-mentioned laser parameters. The samples were arranged on the build plate at an angle of 45° for vertical orientation build, and 30° for horizontal build. The build chamber ambient temperature was 20 ± 1 °C for all builds.

Optical images of microstructures were obtained using Keyence VH2000E 3D Digital microscope. Prior to etching, the chemical composition of the samples was analysed through an Aztec Live System from Oxford Instruments NanoAnalysis EDS module attached to a Zeiss EVO LS-15 SEM. Backscattered electron (BSE) imaging was achieved by plugging in a CZBSD semiconductor detector (with four diode segments) to the SEM. Differential Scanning Calorimetry (DSC) thermal analysis was followed using Netzsch DSC 214 equipment to analyse the phase transformation temperatures. Thermal cycling was conducted from −60 to −130 °C and back to −60 °C maintaining a ramp rate of 10 °C/min. The crystal structure of martensitic NiTi was analysed at the Open University, using an Electron Backscatter Diffraction (EBSD) detector (Oxford Instruments Symmetry S2) on a Zeiss Crossbeam 550 FIB-SEM. Atomic Force Microscopy (AFM) equipment Bruker Dimension Icon was

![SEM images](image-url)
was also conducted to confirm the composition. Heavier elements to the matrix surrounding it, which further confirms the Ti-rich the BSE image (Fig. 1 d), the protrusions can be seen as darker, compared to the horizontally built (H-built) samples. However, all of the H-built samples showed a large number of these protruded particles randomly distributed in the NiTi matrix. More images of other H-built and V-built samples are shown in Table 1.

The specimen cross-sections for scanning/transmission electron microscope (S/TEM) analysis were prepared using a focused ion beam (FIB) instrument with a Gallium source (Zeiss Auriga, Carl Zeiss AG, Germany). Final polishing was performed using a Fischione 1040 Nano-Mill Argon ion beam polisher. To obtain selected-area electron diffraction (SAED) patterns, TEM images and high-resolution annular dark-field (HAADF) TEM images, a S/TEM FEI Titan 80 – 300 kV (Thermo Fisher Scientific, USA) with Schottky field-emission gun (operated at 300 kV) was used. A camera length of 380 mm was used to determine the SAED patterns. These were then analysed in the Single Crystal 4 software package.

3. Results and discussion

Raw powders having higher Ti content were used to ensure higher phase transformation temperatures and a stable martensitic phase at room temperature. This ultimately favours shape memory property in the L-PBF processed samples. In phase composition analysis, the powders were found to contain fully martensitic phase with no precipitate phases, and near equiatomic composition with higher Ti content (refer Fig. S1 in supplementary). Hard protruding particles (Fig. 1a) were found scattered within the NiTi matrix after L-PBF processing. During fine vibro-polishing, these protrusions were detected due to being hard and more resistant to polishing than the surrounding matrix (NiTi). Therefore, the protruded particles indicated phases with an unyielding hard mechanical property, different from the surficial NiTi matrix. As seen in Fig. 1a-b, the vertically built (V-built) samples showed no, or significantly less, traces of protrusions on the polished surface compared to the horizontally built (H-built) samples. However, all of the H-built samples showed a large number of these protruded particles randomly distributed in the NiTi matrix. More images of other H-built and V-built samples in the DoE can be seen in Fig. S2 in supplementary. To study these protrusions in detail, the H-built samples H2, H6, H8 and H11 from DoE are presented in this paper. The L-PBF processing parameters of these samples are shown in Table 1.

The protruding particles seen in the highly polished samples were revealed to be Ti-rich (98.6–99.5 at%) from EDX analysis (Fig. 1e-f), so these particles are referred to as Ti protrusions for discussion. BSE imaging was also conducted to confirm the composition. Heavier elements (higher atomic number) appear brighter in BSE mode as they deflect incident electrons more strongly compared to the lighter elements. From the BSE image (Fig. 1d), the protrusions can be seen as darker, compared to the matrix surrounding it, which further confirms the Ti-rich composition in the protrusions. Through image analysis, the area fractions of Ti protrusions with respect to the total areas were analysed; Fig. S3 in supplementary. The area fractions were found to be between 0.5% and 2% for H-built samples. No correlation was found between the extent of the area fractions and the L-PBF parameters. Also, the morphology of these particles was found to be irregular throughout the microstructure.

TEM analysis was conducted to substantiate the crystallographic details of Ti protrusions found through EBSD. The boundary of one of such Ti protrusions was located, and a specimen cross-section was prepared. In Fig. 3a, the HAADF TEM image is presented with darker shade representing the Ti protrusion, and lighter shade representing the NiTi matrix. Using the software package and previously reported [22] Ti crystal structures as a reference, SAED analysis was performed. The analysis confirmed BCC structure with a zone axis of [310] for the Ti protrusion; indexed region named P1. Fig. 3b shows the SAED patterns.

The random distribution of Ti protrusions is independent of the locations of the pores. Further microstructural analysis revealed via optical microscope images (Fig. 4a-b) that these protrusions are formed in regions of overlapping scan tracks and epitaxial melting (deep in the melt pool overlapping the previous scanned layer). Either way, it is certain that these regions are exposed to continuous high thermal energy. From examination of the thermographs of middle layer of the L-PBF samples (Fig. S4 in supplementary), it can be seen that the effect of the same L-PBF parameters was much less for the V-built samples. In the V-built samples (samples V2, V6, V8 and V11 in Fig. S4), the temperature profiles are similar with only slight variations between samples, however, in the case of H-built samples, the effect of the different VED can be clearly seen to have resulted in more variation in the global average temperatures (samples H2, H6, H8 and H11).

The H-built samples also exhibited several regions of high temperature or hotspots across the layer, and higher intralayer thermal gradients. The surface area for heat build-up and for heat dissipation, as well as inter-layer laser scanning delays, can affect the thermal profiles of L-PBF samples produced in the different orientations. These temperature profiles would produce higher local cooling rates in the H-built samples which can be seen to have caused the more precipitation and the significant number of Ti-rich protrusions found in the H-built samples compared to V-built samples.

In NiTi system, high Ni evaporation is possible, which could lead to precipitate formations or change in functional properties [9,18,23–25]. The formation of nearly pure Ti particles has not previously been reported. From EBSD band contrast maps and IPF-Z maps (Fig. 2a-d), and microscopic images (Fig. 4a-b), it was also noticed that these protrusions occur mostly in regions of very fine martensitic grains. Regions with large grain size rarely showed the presence of these kind of protrusions. The formation of small martensite grains is often caused due to high energy exposure [26]. This was also confirmed from pyrometric IR data where localised high temperatures were detected. The melt pool temperatures are significantly high in L-PBF and the process itself is susceptible to high cooling rates (10² °C/s) [9,27]. At times, the melt pool temperature can go severely high in the range of 3000 – 5000 °C, depending on material, laser power and scan speed. The boiling point of Ni (2730 °C) is lower compared to that of Ti (3287 °C). When the Ni content is higher (> 50.5 at%), Ni₄Ti₃ and Ni₃Ti precipitates are often formed. However, in martensitic NiTi, where the Ti content is marginally higher, high temperatures can lead to Ti₂Ni (Ti-rich) precipitate

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Laser power (W)</th>
<th>Scan speed (mm/s)</th>
<th>Hatch spacing (μm)</th>
<th>VED (J/μm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2/V2</td>
<td>120</td>
<td>600</td>
<td>55</td>
<td>90.91</td>
</tr>
<tr>
<td>H6/V6</td>
<td>150</td>
<td>900</td>
<td>55</td>
<td>75.76</td>
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<td>H8/V8</td>
<td>180</td>
<td>900</td>
<td>70</td>
<td>71.43</td>
</tr>
<tr>
<td>H11/V11</td>
<td>150</td>
<td>1200</td>
<td>70</td>
<td>44.64</td>
</tr>
</tbody>
</table>
formations. Such precipitates, as well as dislocations or other local stress fields can alter the phase transformation temperatures (TTs) of L-PBF NiTi [9,15,28–30]. These Ti$_2$Ni formations can also occur due to a eutectoid reaction between Ni and Ti, which overcomes the influence of Ni evaporation, and thereby decreases the TTs overall. A similar trend was observed in Fig. 4c, where the H-built samples exhibit lower TTs. The Ni reductions are high for these samples compared to V-built ones, and this should

![Fig. 2. Microstructure of H11 through EBSD: (a) Band contrast map, (b) phase map showing martensitic B19$^\prime$ NiTi (blue) and Ti-rich BCC phase (yellow), (c) IPF Z map showing grain orientations (index maps shown right), (d) 50 µm close-up image of white-border region in IPF map showing random twinned structures; AFM scans showing protrusions: (e) sample H6, (f) sample H11.](image)

![Fig. 3. (a) High-angle annular dark-field (HAADF) TEM image showing boundary between Ti protrusion (darker shade) and NiTi matrix (lighter shade); (b) selected area electron diffraction (SAED) pattern acquired in TEM at point P1 along with analysed zone representation.](image)
generally induce higher TTs in H-built samples. However, a reduction in TTs along with an overlapping Ms – As transition region (indicated by darker peach shade) are observed, where the As temperature lies below the Ms temperatures. This coinciding martensite – austenite phase transition can result in better shape memory activation and fatigue resistance [31]. A better shape memory capability in H-built samples transition can result in better shape memory activation and fatigue temperature for Ti samples (Table S2 in supplementary data).

In order to study the mechanical properties of the protrusions, nanoindentation was performed. Nanoindentation has been widely used to understand the localized functional and mechanical property changes in NiTi system [35–38]. To evaluate the associated deformation response of these Ti protrusions, the nanoindentation response was measured. Fig. 5a highlights the indentation points where measurements were taken from the Ti protrusions and the surrounding NiTi matrix. As presented in Fig. 5b, the P-h characteristics acquired under the same load specifications, show that the depth of indentation achieved in the protrusion was three times lower compared to the NiTi matrix (Fig. 5d). Using Oliver and Pharr method (OPM) [39],
nanohardness values of the martensitic NiTi matrix and Ti protrusion were calculated. The Ti protrusions were found to be nearly 9 times harder than the martensitic NiTi matrix. Previous studies show β – Ti as a hard material with a ferritic iron-like BCC structure having a ductile-brittle transition temperature. This temperature in generally above room temperature, which can result in cleavage fracture at ambient conditions [40]. Along with low penetration, the indents on Ti protrusion were seen to undergo a sudden plunge (conventionally termed as pop-in) after certain depth of indentation (Fig. 5b). These pop-ins can be due to this cleavage fracture in brittle and hard β – Ti. It can also be due to an underlying porosity (beneath the protrusion) that is created during drastic Ni evaporation. The variation in P-h curve of indents made on Ti protrusions was found to be negligible, while the variation in NiTi matrix was found to be considerable. Nanoindentation is well-known for its high sensitivity to microstructural inhomogeneity [36,41]. Therefore, these variations in P-h curves can indicate a high heterogeneity in NiTi martensitic matrix, whereas the Ti protrusions are more homogeneous. This further supports the premise of these protrusions being a single entity of β – Ti. All of the above characterisations help to summarise that the protrusions are a hard β – Ti phase. A comparative study based on some previous studies shows that β – Ti exhibits a higher hardness than the NiTi system [42,43]. However, based on processing conditions and formation mechanics this can vary in each scenario. Also, during processing or indentation, a martensitic transformation can occur inside β – Ti resulting in α’– Ti which further leads to increased hardness characteristics. These small fractions of α’– Ti are generally not indexed in EBSD [43–45].

4. Conclusions

The formation of hard protrusions in NiTi caused by L-PBF processing has been investigated in detail. These protrusions were found in as-fabricated NiTi samples after fine polishing. The entities were significantly present in horizontally built samples, whereas they were scarce/not seen in samples built in the vertical orientation. Further investigation revealed these to be nearly pure Ti phases which precipitated in the regions of high-temperature exposures such as melt pool boundaries, scan track overlaps and epitaxial melt region. Localised high melt pool temperatures can also locally eliminate Ni from fine grained martensitic regions, promoting the formation of Ti-rich precipitates. Upon detailed analysis, these particles were found to be β – Ti. Even though the presence of precipitates and secondary phases in L-PBF NiTi has been reported in the past by several researchers, the presence of a β – Ti phase observed in the current study is novel from the metal additive manufacturing route. A suggestion for future investigation is a systematic analysis of how the powder properties, L-PBF parameters and scanning strategies affect the formation of the β – Ti phase in L-PBF processed NiTi.

CRediT authorship contribution statement

Josiah Cherian Chekotu: Conceptualization; Methodology; Data curation; Investigation; Formal analysis; Validation; Project administration; Writing – original draft, Writing – review & editing. Sujith Kumar S: Methodology; Data curation; Formal analysis; Validation; Writing – review & editing. Giulia Degli-Alessandrini: Methodology; Data curation; Formal analysis; Validation; Writing – review & editing. Muhammad Zeeshan Mughal: Methodology; Data curation; Formal
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.

Data availability

Data will be made available on request.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mtcomm.2023.106668.

References

