Melt pool geometry and microstructure of Ti6Al4V with B additions processed by selective laser melting additive manufacturing

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HIGHLIGHTS

- Boron-added Ti6Al4V-xB alloys processed by selective laser melting (SLM) were evaluated by a powder-free approach.
- Justification for the powder-free approach was presented using data from Ti6Al4V.
- Influence of laser power, scan speed and B wt.% on Ti6Al4V-xB melt pool geometry and microstructure were presented.
- Promising compositions for further study were 2–5 wt% B. Acceptable laser power-scan speed combinations were identified.

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ABSTRACT

This paper documents an investigation into the microstructures and melt pool geometry features of Ti6Al4V + (0, 1, 2, 5, 10, wt%) B alloys processed by selective laser melting (SLM). Single laser-deposited tracks were made on powder-free surface of arc-melted Ti6Al4V-xB buttons. The applicability of powder-free results was supported by evaluation of Ti6Al4V melt pool geometry deposited with and without powder. For each Ti6Al4V-xB composition, melt pools were produced over wide ranges of laser beam power (P) and scan speed (V), with melt pool geometry and microstructure information gathered into mapping in P-V space to develop P-V process window. By varying wt% B and P-V parameter, a variety of microstructures were produced. A promising microstructure consisted of a TiB network with submicron spacing. Melt pool microhardness was characterized, showing evident enhancement from arc-melted baseline for all Ti6Al4V-xB composition. This work identified Ti6Al4V-xB with 2–5 wt% B as a promising composition range for SLM processing and showed the powder-free methodology can provide melt pool scale information for trial alloy composition evaluation.
1. Introduction

The application of additive manufacturing (AM) technologies to metals is rapidly growing because it enables fabrication of geometrically sophisticated parts with minimal material waste [1,2]. There are several different metal AM processes, generally classified as directed energy deposition (DED) or powder bed fusion (PBF) processes. This work focuses on alloy development for laser powder bed fusion (LPBF), also known as selective laser melting (SLM). SLM is one of the most popular metallic AM technologies since it enables accurate control over part dimensions and fabrication of high-resolution features [1,2]. However, the relationships between microstructure, processing, properties, and performance are only available for a limited number of alloy compositions [3], leaving a huge metallic material space unexplored for SLM processing.

The primary obstacle to experimental SLM alloy development is powder availability. SLM powder feedstocks generally have strict requirements [4–6], including uniform size, good flowability, and low porosity. It is impractical and costly to produce small-scale powder batch for all the trial compositions of interest. Computational modelling is an important part of the solution and there are currently many efforts on the macro-scale ($10^{-3}$–$1$ m) and meso-scale modelling ($10^{-5}$–$10^{-3}$ m) [9–14]. Although model sophistication is continually increasing, AM processes remain complicated and challenging to fully describe. Experimental data are still needed to benchmark SLM computational models.

There have been several studies that employ single-track laser scan to create melt pools on substrate with and without a powder layer addition. These single-track studies have been used to survey melt pool geometry and microstructure for Ti6Al4V [15], Inconel 625 [16,17], Ti-Nb alloys [18], and 304 stainless steel [19]. They observed similarity between melt pool geometry for solid tracks made with and without powder [15,16]. This shows that single-track deposition directly on solid alloys can provide helpful information to predict in-situ melt pool behavior for SLM part fabrication. Besides, the single-track experimental results have provided guidance for constructing melt pool heat transfer modelling [16,17,19] and solidification microstructure modelling [17,18], which help to inform SLM part build process parameter selection. This study examines how single tracks to be used for initial SLM trial composition assessment when powder batches are not available, which might provide some experimental guidelines for SLM alloy development.

The base alloy Ti6Al4V was chosen for this study because of its prevalence in AM. Composition modification by B additions was chosen because they have led to significant property enhancements (tensile strength, wear resistance, fatigue, etc.) for Ti-alloys processed by various conventional production routes, including casting, arc-melting, and powder metallurgy [20–25]. The reason for these enhancements was mainly considered to be the formation of TiB precipitates in Ti-matrix. From the pseudo-binary Ti6Al4V-B phase diagram (shown below in Fig. 1), B has a negligible solid solubility ($<0.001$ at.%) in both β-Ti and α2-Ti phase [26], indicating that almost all the added B would be in TiB at B levels $<10$ wt%. Over 10 wt% B, both TiB and TiB2 precipitates form. TiB is well-known as a reinforcement phase for titanium alloy. It shows unique advantages over other reinforcing particles such as TiC and SiC [22,27], including (1) higher modulus; (2) similar thermal expansion coefficient as Ti; (3) excellent chemical and thermal stability. However, conventionally processed Ti6Al4V-xB was reported to show rapidly degraded ductility and fracture toughness if its B level increased to hypoeutectic range ($>1.5$ wt% B) [28,30]. The possible reason for this was formation of coarse primary TiB precipitates in Ti-matrix. SLM process might be a solution to TiB coarsening considering its rapid solidification characteristics.

Extensive studies on Ti6Al4V have been conducted to optimize process variables such as laser beam power ($P$), laser scan speed ($V$), scan strategy, and layer thickness [15,29,31]. Limited studies have focused on composition modifications. Titanium matrix composite (TMC) fabrication by SLM processing has been studied using powder mixture of pure Ti mixed with Mo [22,23], Cu [32], and TiB2 [34,35]. The results showed promising grain refinement and property enhancement (yield stress, wear resistance, corrosion resistance) compared to the SLM-fabricated commercially pure Ti. In addition, B-modified Ti6Al4V alloy with B% from 0.1 to 0.25 wt% was investigated with wire-feed laser directed energy deposition (L-DED) AM process, with prior-β grain refinement and mechanical property enhancement observed [25,36]. Ti6Al4V modified by Mo [37], Cu [38], Zr [39], were also investigated for wire or powder-feed L-DED process, all showing the benefits of composition modification to achieve better properties than L-DED processed Ti6Al4V. Compared to L-DED, SLM could achieve higher cooling rate during solidification, which might enable microstructure refinement at higher B alloying levels with further enhancement to properties.

This work employed a powder-free experimental methodology to identify Ti6Al4V-xB compositions suitable for SLM processing by evaluating four different Ti6Al4V-xB compositions over a wide composition range from 0 to 10 wt% B, with each composition tested over a large $P$-$V$ space. The high-B Ti6Al4V-xB selected in this study might show the capability of SLM to fabricate metal matrix composite (MMC). The Ti6Al4V-xB candidate compositions were produced by making arc-melted buttons, which are much easier to produce than lab-scale powder batch, especially for a series of commercially unavailable compositions in this case. The reliability of “powder-free” result was supported by evaluation of single-track melt pools made on solid Ti6Al4V and on one powder layer deposited over solid Ti6Al4V. High level of similarity was observed between the former and the latter. A model for laser absorptivity was developed as function of laser power ($P$), scan velocity ($V$) and material state (powder/solid). Then, the powder-free method was adopted to evaluate the trial compositions by making single tracks over a range of $P$ and $V$. 70 different combinations of B wt% composition and $P$-$V$ process parameter were investigated in this study, resulting in melt pools with very different geometries, microstructures & hardness. Characterization of geometry and microstructure features for these melt pools provided information on the SLM process window and the influence of $P$ and $V$ on microstructure. Some unique microstructures were observed, such as sub-micron-size TiB cellular networks. From current result, a few promising $P$-$V$, B% composition combinations were identified, which would be considered for future powder production and further investigation.

2. Materials and experimental methods

Five Ti6Al4V-xB compositions ($x = 0.1, 2, 5, 10$, wt% B) were selected for evaluation. The pseudo-binary phase diagram for the

Fig. 1. Pseudo-binary phase diagram of Ti6Al4V-B system: trial compositions of this study indicated by red dashed line.
The EOS M290 machine was used to perform single-track laser scan experiments on the buttons, as schematically shown in Fig. 2(c). The EOS M290 machine was equipped with diode-pumped Yb laser with fixed beam focus diameter of 100 μm and maximum power output of 400 W. The customized button holder as shown in Fig. 2(b) was used to position and fix the Ti6Al4V-xB button samples on the build plate of the EOS M290 machine and to ensure the button surfaces were maintained at the same level. The holder could be flipped so that laser scans could be made on both sides of the button. Experiments were conducted under Ar atmosphere. Seven individual tracks (length: 13 mm, 2 mm spacing between tracks) were made on each button surface, so there were fourteen tracks made per button. Each track corresponds to a different P-V setting as listed in Table 1.

Selection of the 14 P-V settings was guided by processing map approach [43] where the cooling rates for the P-V settings were first estimated from the Rosenthal solution in Eq. (1) [44], using the data for the Ti-Al-V-B quaternary system. The diagram was generated by Thermo-Calc [40], using data for the Ti-Al-V-B quaternary system from the COST507 light metal database [41]. All alloys selected were expected to form only TiB, except for Ti6Al4V-10B, for which some primary TiB2 was expected. The compositions were selected to compare hypo- and hyper-eutectic alloys, and to assess melt pools containing various TiB precipitate vol%, as shown later in Fig. 6.

The test materials were fabricated by arc-melting charges of B powder (supplier: Alfa Aesar) and bulk pieces of Ti6Al4V (supplier: ATI) under Ar atmosphere, holding in a well stirred molten state for 50–60s before cooling. For each trial Ti6Al4V-xB compositions, multiple alloy ingots (approximately 35 g each) were fabricated. Each ingot was re-melted 4–5 times to ensure composition homogeneity. The B content of the alloy buttons, especially their local B content at the near surface region, was confirmed by examining the vol% of TiB precipitates measured by image processing with SEM/EDS and XRD analysis (Panalytical X’Pert Pro). In addition, nano-indentation experiments were carried out to assess melt pool hardness using an MTS Nano Indentation instrument. Indentation tests were carried out at five to seven locations in each melt pool with indentation depth of 1000 nm. The melt pool dimension, microstructure and micro-hardness results presented in Section 3 were the average results summarized from all three cross sections per track.

3. Results & discussion

3.1. Evaluation of absorptivity and melt pool size for tracks with and without powder

Initial work was conducted to quantitatively assess the level of dimensional similarity for melt pools generated by laser scan on a solid alloy and on one layer of powder. It was expected that laser absorptivity would vary with P, V, and material state (powder/bulk) [45]. Thus, an empirical laser absorptivity model for Ti6Al4V was developed. Single-track laser scan tests were conducted on Ti6Al4V with three different material states: (i) on Ti6Al4V arc-melted buttons, (ii) on Ti6Al4V alloy baseplate (referred to as the no-powder test), and (iii) on one 30 μm thick layer of Ti6Al4V powder spread across Ti6Al4V baseplate (referred to as the powder-added test). The tests of state (i) were conducted as part of this study and those for (ii) and (iii) were part of a previous study with details reported in [15]. Melt pool width measurements were then summarized into three different datasets:

1. Width (W) of 48 melt pools from no-powder test & their corresponding P-V sets [15];
2. width of 48 melt pools from powder-added test & their corresponding P-V sets [15];
3. width of 14 melt pools made on arc-melted Ti6Al4V button & their corresponding P-V sets (this work, Table 1).

The absorptivity model was developed from datasets (1) and (2), with dataset (3) kept for validation. First, datasets (1) and (2) were filtered to remove melt pools with keyholing geometry. This was because the model fitting used Rosenthal model (Eq. (2)) as a basis, which often fails to provide accurate prediction for keyhole melt pool dimension [45–48]. The experimental data W, P, V was processed by Eq. (2), which is a Rosenthal-based relation [46], to derive a “predicted” absorptivity ($\eta_{\text{pre}}$) for each melt pool.

$$T = 2\pi k(T_{\text{solid}} - T_0)(T_{\text{liq}} - T_0) \frac{V}{\eta P}$$

where $T$ is cooling rate at melt pool solid/liquid boundary, $T_{\text{solid}}, T_{\text{liq}}$ are solidus & liquidus temperature, $T_0$ is temperature far from melt pool, taken as 35°C in this study (machine chamber temperature), $k$ is thermal conductivity, $V$ is laser scan speed, $P$ is the laser output power, $\eta$ is absorptivity, which was obtained from an absorptivity model discussed later in this paper.

The obtained laser-scanned tracks were then sectioned normal to laser scan direction at three locations well away from the two ends of the tracks to examine melt pool cross-sections. The sectioned surface was ground, polished and etched with Kroll’s etchant. Melt pool dimension and geometry were measured using melt pool cross section images taken by a Zeiss optical microscope. Melt pool microstructure characterization was conducted by SEM/EDS characterization (FEI Quanta 600) in both backscatter electron mode (BSE) and secondary electron mode (SE). Un-laser treated microstructure (i.e., arc-melted microstructure) was also characterized by SEM/EDS and XRD analysis (Panalytical X’Pert Pro). In addition, nano-indentation experiments were carried out to assess melt pool hardness using an MTS Nano Indentation instrument. Indentation tests were carried out at five to seven locations in each melt pool with indentation depth of 1000 nm. The melt pool dimension, microstructure and micro-hardness results presented in Section 3 were the average results summarized from all three cross sections per track.

Fig. 2. Schematic diagram of (a) Ti6Al4V-xB alloy button; (b) button holder in the EOS M290 machine; (c) single-track scan pattern.
\[ h_{\text{pre}} = \frac{\pi k(T_m - T_0)W + 0.125e\rho C(T_m - T_0)VW^2}{P} \]  

(2)

where \( W \) is melt pool width, \( \rho \) is density, \( C \) is heat capacity, \( T_m \) is melting temperature (average of liquidus temperature & solidus temperature), \( e \) is Euler’s number. The value for alloy properties used in Eq. (2) were listed in Table 2.

The open-source code go-eureqa [49], an automated model generation tool, was used to find the best function that would describe the variation in \( h_{\text{pre}} \) with \( P \) and \( V \). The following relation was obtained

\[ \eta = K P^a V^b \]  

(3)

where \( K, a, b \) are fitting parameters, with two sets generated: one for melt pools made with powder, the other for melt pools made without powder. Table 3 shows the final optimized values of these parameters.

Two points should be emphasized: first, the fitting of no-powder absorptivity model (with dataset(1)) and powder-added absorptivity model (with dataset(2)) were independent from each other. Second, none of the data from dataset (3), the model validation dataset, were included as data input of model fitting, and the 14 \( P-V \) settings selected for dataset (3) did not overlap with any of the 48 \( P-V \) settings for dataset (1) and (2).

Fig. 4 presents the melt pool width comparison for these three datasets. The x-axis in Fig. 4 is the square root of the absorbed power density, \( Q/V \). The absorbed power (Q) is related to the laser beam power (P) by \( Q = \eta P \). \( \eta \) is the absorptivity, calculated by the absorptivity model in Eq. (3).

Fig. 4 shows that similar widths were achieved across all three datasets if they have same \( Q-V \) combination, except for two situations:

1. Melt pools with keyhole geometries, as indicated by the black hollow circle in Fig. 4. This was expected since the laser absorptivity changes significantly when deep keyholes form, which was difficult to be accurately assessed by Eq. (2), a Rosenthal-based relation.

2. Melt pools generated at \( P = 370 \) W, as indicated by the dashed-line circled point in Fig. 4 (labeled as “outlier”). This was close to the power output limit of the EOS M290 machine (400 W) and under these conditions there were possible deviations between actual and programmed laser power output.

The validity of this absorptivity model was supported by the observation in Fig. 4 that melt pool widths from dataset (3), which was the validation dataset not used in fitting, not only followed the same linear trend with \( (Q/V)^{0.5} \), but also show overlap with the data points from both dataset (1) and (2). Based on Eq. (3), \( \eta \) varied from 0.29 to 0.52 and from 0.25 to 0.44 for scans with and without powder. This range was also within Ti6Al4V absorptivity measured from other studies (0.28 to 0.48) [50,51].

The absorptivity model was also compared to the assumption of a constant absorptivity in Fig. 5, which was reported in [50]. In this figure, the \( Q-V \) combinations that result in a constant melt pool width are indicated (the label shape distinguished the type of laser scan test (powder-added/no-powder), the color distinguished the resulting melt pool width). Absorbed power (Q) in Fig. 5(a) adopts the empirical absorptivity model described above and in Fig. 5(b) adopts the constant absorptivity (\( \eta = 0.48 \)) from [50]. Melt pool dimension is essentially determined by absorbed power density, represented by \( Q/V \). Based on this, if the absorptivity properly accounted for the presence of powder, the bulk- and powder-symbols would overlap for each melt pool width. This was the case for Fig. 5(a), while there was more scatter in Fig. 5(b). From this point of view, the absorptivity model in Eq. (3) gave a more accurate

<table>
<thead>
<tr>
<th>Laser P-V settings tested for single bead laser scan test.</th>
<th>Track</th>
<th>#1</th>
<th>#2</th>
<th>#3</th>
<th>#4</th>
<th>#5</th>
<th>#6</th>
<th>#7</th>
<th>#8</th>
<th>#9</th>
<th>#10</th>
<th>#11</th>
<th>#12</th>
<th>#13</th>
<th>#14</th>
</tr>
</thead>
<tbody>
<tr>
<td>V (mm/s)</td>
<td>800</td>
<td>1200</td>
<td>1600</td>
<td>2200</td>
<td>580</td>
<td>800</td>
<td>1200</td>
<td>580</td>
<td>800</td>
<td>580</td>
<td>1200</td>
<td>1600</td>
<td>1600</td>
<td>1050</td>
<td></td>
</tr>
</tbody>
</table>
estimation than an absorptivity constant to P-V space and material state.

This initial work suggested that, with the proposed laser absorptivity model in Eq. (3), the assumption of bulk/powder melt pool similarity was valid for melt pool geometry across a large P-V space except when keyholing occurred or the maximum laser power was approached. For actual SLM part build at certain P-V setting, one could adopt this absorptivity model to estimate its Q-V combination and predicted its melt pool behavior using the no-powder melt pool information at same Q-V combinations.

3.2. Assessment of Ti6Al4V-xB buttons

Example microstructures from the arc melted Ti6Al4V-xB buttons are shown in Fig. 6. The TiBw precipitates (TiBw; TiB, TiB2 or Ti3B4) exhibited 2 morphologies: high-aspect-ratio whiskers and highly-faceted rods with hollow centers filled with Ti-matrix or a different TiBw precipitate. XRD analysis confirmed that only TiB is present for the alloys with wt% B ≤ 5%. In the Ti6Al4V-10wt%B material, XRD detected TiB, TiB2 and Ti3B4. This result was in line with the prediction from the pseudo-binary Ti6Al4V-xB phase diagram (Fig. 1).

To ensure consistency, the region that was going to be laser-scanned was examined. This region was defined from button surface to 50 °C isotherm boundary during laser scan predicted by Rosenthal model (approximately 1000 μm from button surface). For each button, seven to ten images were taken at different locations from this region and then processed by Imagej software [42] to quantify the local area fraction of TiB precipitate, which was assumed equal to the vol% of TiB precipitate [20,52]. The result was shown in Fig. 6(e). The small error bar (standard deviation) in Fig. 6(e) indicated small variation in vol% of TiB at different locations of this region, showing that TiB precipitates were uniformly distributed across the whole button surface. Fig. 6(e) also shows that, the average measured TiB vol% in this to-be-scanned region in each button was in line with the corresponding vol% TiB predicted by Thermo-Calc software [40] for all four B-containing trial compositions.

3.3. Ti6Al4V-xB melt pool dimensions

Fig. 7 shows the comparison of single-track melt pool width measurement for each trial Ti6Al4V-xB compositions. The melt pool widths were average values measured from melt pool cross section at three locations along each laser track. The laser absorptivity developed for bulk Ti6Al4V alloy (Eq. (3)) were adopted for the four Ti6Al4V-xB trial compositions to calculate Q in Fig. 7. From suggestion by Section 3.1, dimensions for melt pools with keyholing geometry features were not included in Fig. 7.

Fig. 7 showed an approximately linear relationship between \( \frac{Q}{V} \)0.5 and melt pool width for all five trial compositions. For same Q-V combination, increasing B addition up to 5 wt% did not lead to evident melt pool dimension variation compared to that of Ti6Al4V. However, a significant decrease in melt pool width was observed at 10 wt% B. Since the melt pool dimension is essentially determined by Q and V, the small melt pool dimension variation indicated that B addition up to 5 wt% might not influence laser absorptivity and that the absorptivity model in Eq.(3) obtained for Ti6Al4V might reasonably estimate Ti6Al4V-xB with 8%≤5 wt%. Larger B additions at level of 10 wt% appeared to decrease absorptivity. The potential problem of this evident melt pool dimension deviation between Ti6Al4V and Ti6Al4V-10B is further discussed in Section 3.7.

3.4. Melt pool geometry P-V mapping

With 5 different Ti6Al4V-xB material and 14 different P-V sets, the single-track test in this work generated melt pools with 70 different [8% levels, P, V] combinations. Their melt pool geometries were categorized into five types based on width (W), depth (D), cap height (H) and track stability observed from both cross-section and top-down views. The five melt pool geometry types were: (1) normal, characterized by D/W ratio around 1/2; (2) keyholing, characterized by D/W much >1/2; (3) balling, characterized by a sufficiently large H value and evident variations in H along length of the track; (4) under-melt, characterized by D less than nominal powder layer thickness(30μm) for SLM Ti6Al4V build, i.e., D < 30μm; (5) melt pool with defects, characterized by porosity & cracks observed in melt pool. Example images of these categories are shown in Fig. 8.

Based on this categorization in Fig. 8, melt pool geometry P-V maps were generated for each Ti6Al4V-xB trial composition, as shown in Fig. 9(a)-(e), which reports melt pool geometry information of each P-V data point in Table 1. Fig. 9 also marks the P-V data points if their corresponding melt pool show geometrical change from the B-free Ti6Al4V melt pool generated by same P-V sets, an example of which is presented in Fig. 10 for P-V set #9 (115 W-800 mm/s) tested with Ti6Al4V,Ti6Al4V-1%B and Ti6Al4V-10%B. From Fig. 10, it could be seen that at P-V set #9, as B% increases from 0 wt% to 1 wt% and 10 wt%, melt pool changed from key-holing (Fig. 9(a)) to under-melt geometry (Fig. 9(b)) and under-melt pool geometry with evident defect (Fig. 9(c)).

From Fig. 9, it could be seen clearly that B addition had

### Table 2

<table>
<thead>
<tr>
<th>Material</th>
<th>Absorptivity</th>
<th>Melting temperature (K)</th>
<th>Thermal conductivity (W/m · K)</th>
<th>Density (kg/m³)</th>
<th>Heat capacity (J/kg · K)</th>
</tr>
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<tbody>
<tr>
<td>Ti6Al4V</td>
<td>Eq. (2)</td>
<td>1913</td>
<td>6.7</td>
<td>4430</td>
<td>526</td>
</tr>
</tbody>
</table>

### Table 3

<table>
<thead>
<tr>
<th>Material state</th>
<th>K</th>
<th>a</th>
<th>b</th>
</tr>
</thead>
<tbody>
<tr>
<td>With powder</td>
<td>0.11</td>
<td>0.15</td>
<td>0.07</td>
</tr>
<tr>
<td>No powder</td>
<td>0.06</td>
<td>0.43</td>
<td>-0.09</td>
</tr>
</tbody>
</table>
significant and complicated influences on melt pool geometry. For 1
and 2 wt% B, only melt pool geometry in the low-power $P$-$V$
space were altered from that of Ti6Al4V, while for 5 and 10 wt% B, the
altered melt pool geometry extended to higher power regions.
Keyholing was observed at high $P$, low $V$ range, as expected [47].

However, evidence of keyholing was also observed in Ti6Al4V at
relatively low power range ($P = 115$ W). This observation was in
accordance to recent studies using dynamic x-ray radiography [53]
showing deep and narrow vapor depressions can form at low po-
wer and result in keyholing. When B was present, the lower power
observations of keyholing were shifted to 200 W. This could be
attributed to differences in vaporization behavior between the un-
modified Ti6Al4V and the B-containing alloys, which might be
investigated by future study.

Among the five melt pool geometries, the normal melt pool
geometry (Fig. 8(a)) would be preferred for a part build. This ge-
ometry should result in highest potential for fully dense parts,
while the other four geometries are commonly observed to be
related to part defects including porosity, unfused powder, lack-of-
fusion and cracking [17,44,45,50]. The thresholds for the undesir-
able key-holing, balling- and under-melt geometries could be
derived from Q-V thresholds listed in Table 4, which were obtained
by model fitting as such: Each fitting model in Table 4, was derived
from literature-collected models, with their fitting parameter ($m_1$,$m_2$,$m_3$) depend solely on material properties or on material
properties and powder layer thickness. For the single-tracks of this
study, $m_1$, $m_2$, $m_3$ were constants across Q-V space for each
composition. They were determined by searching boundary using
least squares regression with fitting models in Table 4, to classify
data points of normal-type from keyholing-, balling-, undermelt-
Baseline microstructure in this study was referred to melt pool microstructure. Prior baseline microstructure and Type (i) microstructure were qualitatively shown in Fig. 12(a-1). The TiB precipitates in type (i) microstructure were of a high-aspect-ratio, needle-shape whisker morphology, similar to that of arc-melted eutectic TiB (Fig. 6). Their dimensions were 0.5–1.0 μm for major-axis length and 0.1–0.17 μm for minor axis length, greatly refined from arc-melted TiB. A uniform distribution across prior β-Ti grains was observed, with precipitate spacing 0.5–1.5 μm, as qualitatively shown in Fig. 12(a-1).

**Ti-matrix:** little modification from baseline Ti6Al4V microstructure. Prior β-Ti grains still exhibited a high-aspect-ratio columnar morphology with grain size in the tens of microns. The Ti-matrix still exhibited both lamellar α′ & acicular-α′ martensitic morphology.

### 3.5. Melt pool microstructure P-V mapping

Five distinct melt pool microstructures (referred to as type (i)-(v)) were distinguished for 56 B-modified melt pools with different [B%, P-V] combinations (four B% level, 14 P-V sets), with their typical SEM images presented in Fig. 12. The TiB precipitates identified in type (i)-(v) microstructure were qualitatively confirmed to contain Ti and B by EDS measurements. Their major microstructure features were compared below and summarized in Table 5. The microstructure features were summarized over melt pool cross-sections taken from three locations for each laser track.

#### 3.5.1. B-free Ti6Al4V: baseline microstructure

Baseline microstructure in this study was referred to melt pool microstructure created on B-free Ti6Al4V arc-melted button. For all 14 P-V sets tested, coarse columnar prior β grain with lamellar α′ and accicular α′ martensite were observed, typical of SLM Ti6Al4V [29]. Prior β grains had high-aspect-ratio columnar morphology with widths 10–50 μm and they appeared to extend from the bottom to top of melt pool.

#### 3.5.2. Ti6Al4V-xB: type (i) microstructure

**TiB precipitates:** as indicated by the red arrow in Fig. 12(a-2), TiB precipitates in type (i) microstructure were of a high-aspect-ratio, needle-shape whisker morphology, similar to that of arc-melted eutectic TiB (Fig. 6). Their dimensions were 0.5–1.0 μm for major-axis length and 0.1–0.17 μm for minor axis length, greatly refined from arc-melted TiB. A uniform distribution across prior β-Ti grains was observed, with precipitate spacing 0.5–1.5 μm, as qualitatively shown in Fig. 12(a-1).

**Ti-matrix:** little modification from baseline Ti6Al4V microstructure. Prior β-Ti grains still exhibited a high-aspect-ratio columnar morphology with grain size in the tens of microns. The Ti-matrix still exhibited both lamellar α′ & acicular-α′ martensitic morphology.

#### 3.5.3. Ti6Al4V-xB: type (ii) microstructure

**TiB precipitates:** as indicated by the red arrow in Fig. 12(b-2), TiB precipitates in type (ii) were present as a continuous network that was substantially different from the TiB whisker morphology formed by arc-melting (Fig. 6). The TiB network presents refined sub-micron cell spacing (0.1–0.5 μm) as shown in Fig. 12(b-2).

**Ti-matrix:** There was no evidence of columnar prior β-Ti grains as in unmodified baseline microstructure and Type (i) microstructures. β-Ti grain, combined with the TiB network, was likely to be eutectic solidification product, as further discussed in Section 3.7. The specific α or α′ constituents in the Ti-matrix could not be determined.

#### 3.5.4. Ti6Al4V-xB: type (iii) microstructure

**TiB precipitates:** presented as a discontinuous network morphology, indicated by the dark-contrast boundaries pointed out by white arrow in Fig. 12(c-1). Similar to that of type (ii) microstructure, the TiB network in type (iii) microstructure also present sub-micron spacing was in the range of 0.1–0.5 μm. At high magnification (Fig. 12(c-2)) the discontinuous TiB network appeared to be an agglomeration of isolated, nano scale TiB whiskers. The dimension of each isolated TiB whisker were measured to be 70–120 nm for major-axis length, much finer than that of type (i) melt pool microstructure.

**Ti-matrix:** similar to type (ii) microstructure, no columnar prior β-Ti grains were observed. As with type (ii) the α or α′ constituents could not be determined.

#### 3.5.5. Ti6Al4V-xB: type (iv) microstructure

**TiB precipitates:** present two different size scales and two morphologies. The larger TiB precipitates, as indicated by white
Fig. 9. Melt pool geometry P-V mapping for B-free Ti6Al4V ((a)) and four Ti6Al4V-xB compositions (1%, 2%, 5%, 10%B: (b), (c), (d), (e)).

arrow in Fig. 11(d-1), exhibited a faceted rod morphology. The rods had hollow centers filled with Ti-matrix, similar to the morphology of arc-melted primary TiB (Fig. 6). The smaller TiB precipitates, as shown in Fig. 11(d-2), presented high-aspect-ratio needle-shape morphologies similar to arc-melted eutectic TiB (Fig. 6). These two types of TiB precipitates in this microstructure were considered as primary and eutectic TiB, due to their morphological resemblance to the eutectic and primary TiB precipitates in arc-melted condition (Fig. 6). The typical length scale for primary TiB precipitates was 1–3 μm in major axis and around 0.5 μm in minor axis. Eutectic TiB precipitates showed a much finer size of approximately 75–90 nm in major axis length.

It should be noted that compared to type (i) melt pool microstructure, this microstructure showed not only finer dimensions but also a much denser distribution for eutectic TiB whisker.

**Ti-matrix**: β-Ti grains showed an equiaxed hexagonal morphology with a typical grain size of 1–5 μm. The white dashed line in Fig. 11(d-1) and (d-2) marked the β grain boundaries.

3.5.6. Ti6Al4V-xB: type (v) microstructure

**TiB precipitate**: similar to type (iv), two types of TiB precipitates with different size scales were present. The smaller one presented a needle-shape morphology and larger one a rod morphology with hollow center, which were also considered eutectic and primary TiB. Unlike type (iv) microstructure, the larger primary TiB in type (v) microstructure exhibited dendrite-like features, as shown by Fig. 12(e-2). Besides, compared to type (iv), type (v) microstructures showed much denser distribution and a coarser length scale for primary TiB (major axes: 5–10 μm; minor axes: 1–2 μm), as shown by Fig. 12(e-2). Eutectic TiB precipitates in type (v) microstructure were greatly similar to those in the type (iv) microstructure, presenting a high-aspect-ratio whisker morphology with nano-scale dimensions and a dense distribution. Due to the dense TiB precipitate distribution, it was not possible to determine characteristics of the Ti-matrix microstructure.

Based on above categorization, melt pool microstructure P-V mapping could be obtained for each Ti6Al4V-xB trial composition as shown in Fig. 13. The numbers marked for each data point corresponds to the P-V set in Table 1. Sometimes different microstructures were observed in local regions of one melt pool, and these situations were indicated by overlapping colors, e.g. P-V set #11 in Fig. 13(a). The position of each colour in the semicircle was in accordance with the region in the melt pool cross section where their corresponding microstructure type is observed. Fig. 13 clearly showed that each Ti6Al4V-xB composition not only presented different types of melt pool microstructure but also different trends across P-V space. Some reasons for this are discussed below in Section 3.7.
3.7.2. Melt pool geometry

The melt pool geometry was compared to Ti6Al4V. While for Ti6Al4V-10B, a much narrower normal melt P-V space was observed, as shown both directly and indirectly in Fig. 9 and Table 4. This means the likelihood of producing defect-free parts would be lower for Ti6Al4V-10B or at least there would be less flexibility in SLM process parameter selection.

3.7.3. Melt pool microstructure

Melt pool microstructure P-V mapping (Fig. 13) showed the extent of the microstructural differences across P-V space was low when B levels were 2-5 wt%: Ti6Al4V-2%B and 5%B presented type (ii), (iii) and type (ii), (iii), (iv), respectively, across P-V space. These microstructure types were similar in many ways, containing sub-micron-spacing TiB network for both type (ii) & (iii), and nanoscale TiB whisker for both type (iii) & (iv). While Ti6Al4V-1%B presented type (i) & (ii) melt pool microstructure at different P-V space. As shown in Section 3.5, these two types of microstructure were drastically different in basically all microstructural features discussed for TiB precipitate and Ti-matrix. The same conclusion was reached for Ti6Al4V-10%B, which presented type (iii) & (v) in its microstructure P-V mapping. Substantial microstructure variation in P-V space could complicate the choice of optimal P-V parameters, since SLM builds with slightly different P-V settings might lead to substantial property variations. Based on this, Ti6Al4V-xB with 2-5 wt% B might be preferred.

More importantly, type (ii) and (iii) microstructure (Fig. 12(b-1)–(b-2), Fig. 12(c-1)–(c-2)) show the potential for promising property enhancement. As mentioned in Section 3.5, TiB network distribution in type (ii) and (iii) microstructure suggested eutectic solidification. This was supported by the study of Hidenori et al. [59], who observed the in-situ TiB network microstructure evolution in Ti-B alloy by laser scanning confocal microscopy. From this point, the sub-micron TiB network spacing suggests significant microstructure refinement. Unlike type (iv) and (v), type (ii) and (iii) microstructure showed no presence of primary TiB at 2 wt% B and 5 wt% B, which were typical hyper-eutectic compositions. One

![Diagram](image_url)
possible explanation for this was that rapid solidification altered the behavior from primary TiB growth to either coupled eutectic growth or even primary β-Ti growth, thus leading to type (ii) & (iii) microstructures with all eutectic TiB precipitates [52,56]. Apart from [58], this TiB network architecture has also been observed in wire-feed processed Ti6Al4V with 0.1 wt% B [25] and LENS-processed CP-Ti with 1.6 wt% B [55]. However, it should be noted that the TiB network spacing observed in type (ii) or (iii) microstructures (0.1–0.5 μm) was much finer than the ones in previous studies (25 μm for [25]; 5–10 μm for [55]). This could be attributed to the evidently faster cooling rate of SLM-solidification (10^6-10^7 K/S) compared to that of the other 2 AM processes (around 150 K/S for [25]). The study in [55] also showed that the refinement in TiB network spacing would result in more effective mechanical property enhancement based on a Hall-Petch strengthening mechanism. This suggests the benefits of choosing SLM method for Ti6Al4V-xB fabrication.

TiB network architecture was also intentionally fabricated by

![Typical SEM images of 5 different Ti6Al4V-xB melt pool microstructure observed for 56 tested [Ti6Al4V-xB, P-V] combination, referred to as Type (i)-(v) microstructure, respectively showing uniformly-distributed TiB_{eut} whisker ((a-1), (a-2)), continuous TiB network ((b-1), (b-2)), discontinuous TiB network ((c-1), (c-2)), nano scale TiB_{eut} needle + TiB_{pri} rod ((d-1), (d-2)) and dendritic TiB_{pri} rod + nano-scale TiB_{eut} needle ((e-1), (e-2)). TiB_{eut}: eutectic TiB; TiB_{pri}: primary TiB; (i-2) image on the right: high magnification image of green box in (i-1) image on the left, with i as a, b, c, d, e.](image-url)
Wang et al. [57] using a multi-step powder metallurgy, who reported promising creep resistance and enhanced high-temperature tensile strength. This work showed SLM processing is able to produce similar microstructures.

### 3.7.4. Melt pool hardness variation in Q-V space

From Fig. 14, melt pools of all Ti6Al4V-xB trial compositions showed higher hardness value compared to the arc-melted Ti6Al4V-xB buttons with the same composition. In addition, all B-containing Ti6Al4V-xB alloys were harder than the B-free Ti6Al4V melt pool at the same P-V settings. The higher hardness might originate from the dimension refinement and morphology modification of both TiB precipitate and Ti-matrix. Although the hardness enhancements were highest for Ti6Al4V-10B, the largest hardness variability across the P-V settings tested was also observed at this composition. This might be attributed to dimension variations of the primary TiB rods, which were observed at different P-V settings. Therefore, this large hardness variation across tested P-V range suggests that Ti6Al4V-10wt%B might not be suitable to be processed by SLM route, since there would be large variations in properties with slight changes to P-V parameters.

In summary, Ti6Al4V-xB with 2–5 wt% B was the most promising composition range. This range showed: (1) comparable melt pool dimensions to B-free Ti6Al4V melt pool across wide P-V space, (2) large P-V process window resulting in normal-geometry melt pool; (3) promising microstructures with sub-micron-dimension TiB network architecture and high-vol% of refined-size TiB precipitates; (4) enhanced melt pool hardness with little variation across P-V space.

### 3.7.5. Powder-free method: range of application

In this study, we found three factors that must be considered when adopting the powder-free method for SLM alloy development. The first factor was the dimensional inconsistency of powder/bulk melt pool when keyholing occurs (Section 3.1), since the adopted laser absorptivity model (Eq. (3)) might underestimate the absorptivity when keyholing occurs. However, the P-V threshold for keyholing was easily identified by melt pool geometry P-V mapping and can be excluded from analysis. The second factor was the reliability of absorptivity model as composition changed. In this case, the absorptivity was likely different from Ti6Al4V-10wt%B and Ti6Al4V. This deviation in absorptivity might be distinguished by the melt pool dimension deviation as presented in Section 3.3. The third factor was the melt pool inconsistencies along the laser

<table>
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</tr>
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<tbody>
<tr>
<td>type (i)</td>
<td>Needle-shape</td>
<td>Main-axis length: 0.5–1.0 μm</td>
</tr>
<tr>
<td>type (ii)</td>
<td>Continuous cellular network</td>
<td>Network spacing: 0.1–0.5 μm</td>
</tr>
<tr>
<td>type (iii)</td>
<td>Individual: needle-shape</td>
<td>Individual length: 70–120 nm</td>
</tr>
<tr>
<td></td>
<td>Agglomerate: cellular network</td>
<td>Network spacing: 0.1–0.5 μm</td>
</tr>
<tr>
<td>type (iv)</td>
<td>Primary: highly faceted rod</td>
<td>Primary: 1–3 μm</td>
</tr>
<tr>
<td></td>
<td>Eutectic: needle-shape</td>
<td>Eutectic: 75 nm</td>
</tr>
<tr>
<td>type (v)</td>
<td>Primary: highly faceted rod with dendrite arms</td>
<td>Primary: 5 μm</td>
</tr>
<tr>
<td></td>
<td>Eutectic: needle-shape</td>
<td>Eutectic: 75 nm</td>
</tr>
</tbody>
</table>

Fig. 13. melt pool microstructure P-V mapping for each Ti6Al4V-xB candidate compositions, with Ti6Al4V-1%B, 2%B, 5%B, 10%B shown in (a), (b), (c), (d) respectively. Note: labels with multiple colors (e.g. #11 for Ti6Al4V-13B in (a)) corresponds to different microstructures observed on a single melt pool cross section.

### Table 5

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track length when starting material shows coarse precipitate. In this study, this observation only occurred at 10 wt% B.

As shown in Fig. 15, the arc-melted Ti6Al4V-10B button contained boride precipitates were only partially melted at the bottom of melt pool (Fig. 15(b)), due to its length scale comparable to the laser beam diameter (100 μm for EOS M290). This suggests microstructure and thermal property variation of arc-melted Ti6Al4V-10%B button at the scale of laser beam focused diameter. The inconsistent melt pool behavior for single-track on arc-melted button would complicate its melt pool comparison to single track on powder.

In the context of this study, these limitations only influence the accuracy of Ti6Al4V-10wt.%B composition evaluation and the powder-free method still produced a significant amount of useful information for SLM alloy and process design.

4. Conclusion

A powder-free method to evaluate trial composition tailored for SLM processing was introduced and applied to Ti6Al4V-xB (x = 1, 2, 5, 10 wt.%). The following observations were made:

• Melt pool widths were similar for Ti6Al4V for “no powder” and “powder added” cases. A model for laser absorptivity was developed as a function of material-state (powder/bulk) and P-V variables.
• For each trial Ti6Al4V-xB composition, melt pool geometry and microstructure were mapped across P-V space and preliminary process windows were identified.
• Five different melt pool microstructures were observed for the 56 tested [B%, P-V] combinations. The most promising were microstructures that exhibited continuous or discontinuous cellular TiB network architecture with a sub-micron network spacing, referred to as type (ii) and (iii) microstructure in this paper.
• 2–5 wt% B was identified as a promising composition range for SLM processing route because its corresponding Ti6Al4V-xB alloy presented a large P-V process window, showed promising microstructures (type (ii) and (iii)) with little variation across P-V space, small melt pool dimension deviations from Ti6Al4V, and greatly enhanced and stable hardness across P-V space.
• There are many advantages of adopting SLM processing technology as microstructure engineering tool for Ti6Al4V-xB. Rapid solidification in SLM-condition resulted in significant TiB precipitate refinement even at high-B% and created various TiB morphologies. This work presents initial guidance that could be used for further development of B-modified Ti alloys and the powder-free methodology is applicable to many materials systems.

CRediT authorship contribution statement

Yining He: Project administration, Software, Data curation, Formal analysis, Investigation, Methodology, Writing - original draft. Colt Montgomery: Project administration, Software. Jack Beuth: Conceptualization, Funding acquisition, Resources. Bryan Webler: Conceptualization, Funding acquisition, Resources, Supervision, Writing - review & editing, Validation.

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References

S. Tamirisakandala, R.B. Bhat, J.S. Tiley, et al., Grain re-