In situ absorption synchrotron measurements, predictive modeling, microstructural analysis, and scanning probe measurements of laser melted Ti-6Al-4V single tracks for additive manufacturing applications

Nicholas Derimow¹*, Edwin J. Schwalbach², Jake T. Benzing¹, Jason P. Killgore¹, Alexandra B. Artusio-Glimpse³, Nikolas Hrabe³, Brian J. Simonds⁴

¹Applied Chemicals and Materials Division, National Institute of Standards and Technology, 325 Broadway, Boulder, CO 80305, USA
²Materials and Manufacturing Directorate, Air Force Research Laboratory, Wright-Patterson Air Force Base, OH 45433 USA
³RF Technology Division, National Institute of Standards and Technology, 325 Broadway, Boulder, CO 80305, USA
⁴Applied Physics Division, National Institute of Standards and Technology, 325 Broadway, Boulder, CO 80305, USA

Abstract

In this work, the fundamental processing-structure-property (PSP) relationships that govern laser-based additive manufacturing were investigated with the Ti-6Al-4V alloy. X-ray synchrotron imaging carried out in conjunction with in-situ integrating sphere radiometry enabled real-time energy absorption measurements for a range of melting conditions that varied laser power and velocity. A thermal conduction model that incorporated the in-situ absorption data and final melt pool geometry was used to predict the thermal histories and diffusion distances along the heat-affected zone (HAZ) in the Ti-6Al-4V alloy to provide insight into the solid-state phase transformations that occurred in the unmelted regions adjacent to the melt pool. Resulting microstructural features were quantified using scanning electron microscopy techniques to elucidate changes in solidification behavior. Significant changes to α/β-Ti phase fractions were measured in the unmelted HAZ, across all test cases. Nanoindentation and scanning probe microscopy revealed differences in the hardness, modulus, and Volta potential across the resolidified melt pool, HAZ, and wrought base material. These measurements and simulations can be used to predict how processing changes lead to differences in the as-built performance of titanium parts that are used in aerospace and biomedical applications. This work demonstrates the utility of coupling in-situ absorption data with a conduction-only high speed model, which leads reasonable agreement with the synchrotron imaging measurements and microstructural transformations observed herein.

Keywords: Additive Manufacturing, Ti-6Al-4V, X-ray Synchrotron, Heat Affected Zone, Thermal Modeling

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1. Introduction

The application of laser technology towards metal melting has led to significant advancements in metal additive manufacturing (AM), particularly in directed energy deposition (DED) and powder-bed fusion (PBF) AM technologies [1]. With the development of metal AM, parts with complex geometries can be fabricated using computer-aided design (CAD), which require significantly less feedstock material compared to traditional fabrication methods. Titanium alloys are very desirable materials for AM applications in the aerospace [2] and biomedical [3] industries due to its high strength-to-weight ratio and good corrosion resistance. Therefore, the burgeoning field of research into Ti-6Al-4V alloy in particular, is aimed at understanding the processing-structure-properties (PSP) relationships as influenced by the many AM processes that are being developed. That is, due to the complex nature of AM with respect to the many variables inherent to the process, there is a need for a complete understanding of how processing affects the material structure, and how the subsequent structure affects material properties.

A recent investigative thrust towards understanding the PSP relationships in Ti-6Al-4V involves the application of high-speed X-ray imaging to capture the melting and solidification events of laser melting in real time [4]. In one such study, Zhao et al. [5] used the techniques described in Ref. [4] to probe the melt pool dynamics, vapor depression characteristics, and solidification rates of laser-melted Ti-6Al-4V alloy with high spatial and temporal resolutions at the 32-ID-B beamline of the Advanced Photon Source (APS) at Argonne National Laboratory. Leung et al. [6] characterized and quantified dynamic movements of both the melt pool and spatter through X-ray synchrotron imaging during laser melting of Invar 36 powder to justify the conclusion that Marangoni convection dominates the liquid metal flow. Parab et al. [7] further developed the in-situ X-ray synchrotron imaging technique to utilize the system for powder melting in order to characterize the melt pool and spatter for laser PBF applications. Investigative synchrotron studies by Bobel et al. [8] into 4140 steel elucidate that small and spherical porosity in the build layer originates from entrapped gas in the gas atomized powder, while much larger pores are created due to keyhole vapor cavity necking (from increased power density). Bobel et al. also characterize the microstructure resulting from the 60 mm/s – 80 mm/s average speed of the solidification front, revealing fine pockets of martensitic phase in the AISI 4140 [8]. Correlative synchrotron imaging and diffraction studies on the DED process of Inconel 718 suggests that the cooling rates can significantly alter the ductility of the alloy due to the formation of non-equilibrium microstructures [9].
During melting, there exists a threshold energy deposition dependent on scan speed/dwell time, that determines either conduction mode or keyhole mode melting. The latter being marked by a deepened melt pool, increased vapor depression, and pore formation [10]. Work by Chen et al. [11] utilized X-ray imaging to study multi-layer laser melting (five layers) of Ti-6Al-4V powder, and revealed the melt pool oscillation stages of keyhole initiation, keyhole development, and melt pool recovery. Li et al. [12] were able to model the dynamic evolution of the molten pool and powder behavior of Ti-6Al-4V through a combination of computational fluid dynamics and Lagrangian particle tracking techniques, and paired with experimental validation with X-ray synchrotron imaging. These phenomena were further studied by Calta et al. where they investigated the dependence of the liquid-vapor interface as a function of ambient and oxygen partial pressures of several industrially relevant alloy systems (Ti-6Al-4V, Al 6061, Ni 400, and 316L steel) [13]. Zhao et al. [14] reveal that a critical keyhole instability generates acoustic waves in the melt pool and can drive pore formation. Recent studies by Simonds et al. [15] successfully quantified the absorbed energy of an evolving melt pool of Ti-6Al-4V alloy during laser melting in both air and argon, while simultaneously imaging the melt pool in real time. This was accomplished via integrating sphere radiometry [16], where the laser power absorption of the metal was quantified in real-time during simultaneous X-ray imaging and melting of Ti-6Al-4V at the 32-ID-B beamline at the APS [15]. This time-resolved absorption data paired with radiographic imaging of the melting provides a clearer look into the absorbed energy and corresponding geometry of the melt pool as a function of power density in this alloy system. Recent work by Khairallah et al. [17] utilize the in-situ X-ray absorption paired with the X-ray imaging to characterize melt pool oscillations that could be used as a detection window for porosity formation. Oh et al. [18] make use of X-ray synchrotron imaging to study the phase evolution in Ti-6Al-4V, and characterized a threshold cooling rate for martensitic, $\alpha'$ phase, to be 2900 °C/s to 6500 °C/s. For further reading, a recent review by An et al. [19] discusses the state-of-the-art of X-ray synchrotron imaging and diffraction for additive manufacturing applications, and summarizes the defects, microstructures, and mechanical properties of the materials studied in the literature to date.

The present work systematically studies the PSP relationships in the Ti-6Al-4V specimens from Ref. [15]. That is, the same laser melted Ti-6Al-4V specimens from their study were analyzed in this work via thermal modeling, scanning electron microscopy (SEM), electron backscatter diffraction (EBSD), nanoindentation, and scanning probe microscopy. This was done in an effort to elucidate the PSP relationships via the postmortem solidification microstructures and resulting crystallography. In this work, we utilize a thermal conduction model paired with the time-resolved absorption data collected from the Simonds study to make
predictions of the thermal histories, temperature gradients, and diffusion distances based on the varying laser power density. We report on the microstructural evolution of these alloys, and make comparisons to the microstructural features with respect to the predicted thermal histories. Lastly, we investigate the mechanical properties and Volta potential differences between the microstructural features by means of nanoindentation, and two scanning probe microscopy (SPM) methods: contact resonance force microscopy (CRFM) and scanning Kelvin probe force microscopy (SKPFM).

2. Materials and Methods

The techniques used to elucidate the PSP relationships are summarized in Fig. 1. Processing of the Ti-6Al-4V material involved simultaneous high-speed X-ray imaging, laser melting, and in-situ laser power absorption measurements as part of the Simonds et al. study [15]. These samples were then metallographically prepared for microstructural analysis (SEM/EBSD), which helped guide the thermal modeling to understand the structure. The properties were then investigated by nanoindentation, followed by CRFM and SKPFM.

Figure 1: Flow chart of the experiments detailing the types of techniques used to probe the PSP.

2.1. High-speed X-ray Imaging, Laser Melting, and Integrating Sphere Radiometry

High-speed X-ray imaging, laser melting, and integrating sphere radiometry experiments were carried out at the 32-ID-B beamline of the Advanced Photon Source at Argonne National Laboratory as per Ref. [15]. Test specimens of Ti-6Al-4V plate (NIST Standard Reference Material 654b [20]) were machined to 300 µm thickness prior to X-ray imaging (Fig. 2). The process laser was a 1070 nm wavelength Yb-doped fiber laser with a measured spot size of 49.5 µm ± 5 µm (1/e² value). The Ti-6Al-4V samples were melted
in an environment that had been vacuum pumped and backfilled with argon. Beamline-specific methods and integrating sphere radiometry techniques are described in full detail in Ref. [15] and Refs. [16, 21], respectively. The laser melting was carried out at a velocity of 700 mm/s via sky-write strategy, such that the velocity was constant when the laser was turned on.

The setup in Fig. 2 allowed for real time X-ray imaging of the laser melting with time-resolved absorption data of the melt pool from the integrating sphere apparatus. This enables high resolution spatial and temporal data of the melt pool geometry to be paired with high-fidelity absorption data. This time-resolved absorption data has a combined standard uncertainty between 1.8 % and 2.5 %, depending on input laser power. These powers were measured with a NIST-traceable detector with a 1.3 % uncertainty (coverage factor = 1).

2.2. Metallography

Microscopy specimens were prepared from the laser melted pieces of Ti-6Al-4V by mounting in a conductive resin, followed by polishing using an automatic grinder/polisher. As the spots and laser tracks were near the center of the 300 µm machined plates, the thicknesses of the plates were measured with a micrometer to determine an approximate center for exposing the side-view of the solidification microstructure relative to the laser scanning direction. The Ti-6Al-4V plates were then hot mounted in conductive phenolic resin powder and abraded to half the thickness of the plate (thickness of mount minus 1/2 thickness of the plate) in order to view the spot melt and achieve the side view of the laser scanned microstructures (Fig. 3).
the appropriate depth was met to expose the center of the melt, careful abrading was performed with fine
grit SiC pads as to not remove significant amounts of material, followed by polishing with 1 µm diamond
suspension. The mounted samples were then vibratory polished for approximately 24 h in 0.05 µm colloidal
silica. The axis labels in Fig. 3 pertain to beam normal direction (BND), laser scanning direction (LSD),
and transverse direction (TD) – [BND, LSD, TD].

Figure 3: Stereo micrograph of a melted laser track into the Ti-6Al-4V substrate, detailing how the specimen was prepared
and polished for microscopy. Pictured: Laser scanned, conduction mode melting test case. Axis labels pertain to beam normal
direction (BND), laser scanning direction (LSD), and transverse direction (TD): [BND, LSD, TD].

Microscopy was performed on a Zeiss LEO 1525\textsuperscript{1} field emission scanning electron microscope (FE-SEM)
equipped with a Robinson backscattered electron (BSE) detector and EDAX Hikari electron backscatter
diffraction (EBSD) detector. Microscopy was also performed on a Zeiss Gemini 300 FE-SEM equipped with
an annular backscatter detector and an EDAX DigiView EBSD detector. The BSE imaging and EBSD was
carried out with an accelerating voltage of 20 kV. The EBSD step size was 0.15 µm for the laser spot melted
specimens, and 0.20 µm for the laser scanned melted specimens.

The four melt conditions and associated laser powers are listed below:

- Laser spot, conduction mode melting – ‘Spot-Con’ (90.0 W)
- Laser spot, keyhole mode melting – ‘Spot-Key’ (201.3 W)
- Laser scan, conduction mode melting – ‘Scan-Con’ (131.9 W)
- Laser scan, keyhole mode melting – ‘Scan-Key’ (201.3 W)

\textsuperscript{1}Commercial names are identified in order to specify the experimental procedure adequately. Such identification is not
intended to imply recommendation or endorsement by the NIST nor does it imply that they are necessarily the best available
for the purpose.
These samples are a non-exhaustive list of the melt conditions and parametric cases studied in Ref. [15]. However, the four present conditions were chosen specifically for this study for their applicability towards industrial melt scenarios.

2.3. Thermal Model

A simple thermal model was used to estimate the size of the molten region and to assess aspects of the time-temperature history in the solid-sate region for both scanning processing conditions. While more complex and capable models could be used for the simple cases analyzed in the present work, the Discrete Source Model (DSM) previously described in Ref. [22] was chosen because it is representative of low fidelity, conduction-only models often used for part-scale calculations and parameter screening. Importantly, it can still handle transient energy input processes and beam trajectories, and has relatively low computational cost. It is of interest to determine if such models can produce useful predictions if provided with appropriate, time-resolved absorption data. This model was employed to identify the maximum spatial extent of both the molten region and the region that experiences a maximum temperature above the body-centered cubic (BCC) $\beta$-transus $T_\beta$ (995 °C) but below the solidus temperature $T_s$ (1650 °C). Additionally, it was used to generate the explicit time-temperature histories, which were subsequently analyzed.

The DSM assumes constant and spatially uniform thermophysical parameters, and treats the thermal conduction problem in the semi-infinite domain $Z \leq 0$. A right-handed Cartesian coordinate system is utilized with the $X$ direction parallel to the LSD and normal BND. The origin is centered on the middle of the LSD in the plane of the top surface of the substrate. Further, it uses a discretized representation of the actual moving energy source. The actual smooth trajectory of the energy source is sampled at a series of discrete times, in this case using a uniform time interval $\Delta t$. The energy input process is then represented by a series of discrete sources located and timed to coincide with the sampled positions. This formulation easily allows for arbitrary beam trajectories as well as time-dependent power or spot size. While it does not directly account for convective transfer due to fluid flow in the melt pool, the DSM employs a volumetric heat source. With appropriate calibration information, this elliptical 3D Gaussian source shape can be altered to mimic more rapid heat transfer due to strong convection in the liquid phase.

The DSM typically employs an efficiency factor, $\eta$, to account for energy loss mechanisms that are computationally expensive to include directly. Mechanisms that are active in a manner spatio-temporally coincident with the incident energy source can be roughly accounted for by simply decrementing the nominal power $P$ to get an effective power $P_{eff}$ according to $P_{eff} = \eta P$. These losses are often assumed to be dominated by reflection of some portion of the incident laser energy, however the calibration procedure
Table 1: Parameters used in the discrete source model and associated isotherm identification process.

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Value</th>
<th>Unit</th>
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<tbody>
<tr>
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<td>kg m(^{-3})</td>
</tr>
<tr>
<td>( \kappa )</td>
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<td>W m(^{-1}) K(^{-1})</td>
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<td>( c_p )</td>
<td>678.2</td>
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<td>°C</td>
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<tr>
<td>( T_s )</td>
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<td>°C</td>
</tr>
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<td>( T_\beta )</td>
<td>995</td>
<td>°C</td>
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<td>m</td>
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<tr>
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<td>µm</td>
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<tr>
<td>( \Delta r_{\text{tol}} )</td>
<td>0.01</td>
<td>µm</td>
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also implicitly accounts for all losses that occur in the immediate vicinity (i.e. one beam diameter) of the incident beam such as evaporative cooling or radiative losses. Typically, \( \eta \) would be adjusted such that modeled width and depth of a single track matches those observed experimentally. However, in the present case no such calibration was performed. Instead, the measured, time-resolved absorption data measured in-situ \( \alpha (t) \) was employed directly as the efficiency: \( \alpha (t) \approx \eta (t) \). We expect this to be an upper bound on the actual efficiency, as other loss mechanisms could be present that further reduce \( \eta \).

As mentioned earlier, the DSM source shape is typically calibrated using the empirical information. The extent of the volumetric source in the build plane is characterized by \( \sigma_x \) and is typically set to match an experimentally measured beam diameter, with \( \sigma_x \) set equal to 1/4th of the 1/e\(^2\) diameter. The value \( \sigma_z \) determines the extent of the source in the direction normal to build plane. Often, this value is calibrated to match an experimentally observed single track width-to-depth ratio. For conditions where significant keyholing is present, large values of \( \sigma_z \) are employed to mimic the enhanced thermal transport in the direction normal to the plate. In the present work, we employ the model in an uncalibrated fashion and instead fix \( \sigma_z \) at a small value of 1 µm, effectively converting the volumetric source into a flux.

The input parameters used by the model are described in Table 1. Typically, the DSM employs both a spatial cutoff distance \( R_{\text{cut}} \) as well as temporal cutoff \( t_{\text{cut}} \) to control computational burden at the expense of accuracy as described in detail in Ref. [22]. Because the beam trajectories in this work consisted of a single pass of 1.4 mm in length, the computational expense is extremely modest. To avoid any concern about loss of accuracy, both cutoffs were set at infinity, i.e. no cutoff was used.
2.4. Nanoindentation and Scanning Probe Microscopy

Nanoindentation was performed on a representative cross section of the Scan-Con specimen using a Bruker Hysitron TI 950 TriboIndenter with a Berkovich indenter tip. A total of 625 indentations (25 by 25 square grid) were performed across a region of the sample, encompassing the main areas of interest (melt pool, heat affected zone (HAZ), and wrought microstructure). A trapezoidal load function was used with a loading rate of 250 µN/s up to 5000 µN, held for 2 s, and unloaded at the same rate of 250 µN/s per indentation. Initial testing revealed an indentation depth for the specimens to be approximately 220 nm, therefore a spacing of 5 µm was chosen as it is approximately 20 times the indentation depth [23].

The Young’s modulus and surface potential of the Spot-Key specimen were characterized CRFM [24] and SKPFM [25], respectively. Both measurements were performed on an MFP-3D (Asylum Research, Santa Barbara, CA) atomic force microscope.

CRFM was performed with a relatively stiff (spring constant 38 N/m) ultra nanocrystalline diamond cantilever and tip. The measurement was performed in contact mode at a set point force of ≈ 2.5 µN ± 0.5 µN. A dual alternating current (AC) modulation was applied to the customized damped “shake” piezo of the cantilever holder. The resonance frequency of the surface coupled cantilever was measured by dual AC resonance tracking (DART) [26] while scanning the surface in contact mode, producing a 90 µm x 90 µm surface map with 90 nm pixel resolution. The DART frequency map was corrected for feedback lag by fitting amplitude and phase data to a damped harmonic oscillator model. The corrected frequency map was then converted to a contact stiffness map by modeling the cantilever as an Euler-Bernoulli beam with the tip offset back from the cantilever end. To convert the contact stiffness map to modulus, Hertzian contact mechanics with a hemispherical tip were assumed. To determine the tip radius, which is unknown, the radius value was adjusted until the mean value of Young’s modulus in the melt pool region - the most mechanically uniform region of the image – determined by CRFM was equal to the mean value obtained by nanoindentation arrays of similar regions. Topographic data acquired simultaneously with the frequency data are also presented.

SKPFM was performed with an electrically conductive cantilever with titanium/iridium coating. The nominal cantilever spring constant was 2.8 N/m. SKPM was performed in a dual pass method wherein the first pass maintained amplitude modulated intermittent contact feedback with the sample to map topography and the 2nd “lift” pass used a feedback loop to determine the DC bias that nulled the electrostatically driven AC cantilever oscillation. The AC bias was 3 V for the lift pass and the lift height was -90 nm, indicating that the mean tip-sample distance was smaller than during the topographic pass.
3. Results

3.1. X-ray Synchrotron Imaging

The high-speed X-ray synchrotron imaging of the laser melting was acquired in tandem with the in-situ absorption measurements for the four test conditions [15]. A representative data set from the experiments in Ref. [15] is presented in Fig. 4 (Power = 201.3 W), where the absorption versus time plots correspond (combined uncertainty = 1.8 %) to the radiographs on the right side of the figure at those moments in time as the laser scanned across the surface. Note that the tilted radiographs were due to a 7° angle of incidence of the laser to the normal surface to maximize the amount of directly-scattered-light captured by the integrating sphere.

The data set in Fig. 4 is of the Scan-Key condition. The initial keyhole that is formed is relatively deep and has a correspondingly high absorption. This phenomenon has been explained previously [15] and is common start-of-scan behavior. Once a steady-state is reached, a relatively stable vapor depression is observed until the laser power is cut, leading to solidification. The absorption data presented on the left side of Fig. 4 shows that the absorption also stabilizes in this regime.

The Spot-Con and Spot-Key modes, as well as the Scan-Con mode display the following absorption behavior. The Spot-Con has relatively stable absorption, whereas the Spot-Key generated during the laser
exposure is much more dynamic due to the effect that the keyhole vapor depression has on absorption. The Scan-Con melting shows relatively stable absorption from the beginning to the end of the melt track, with no increase in absorption, like that for the Scan-Key test case presented in Fig. 4. The data sets for these three test cases can be found in the Supplemental Information as videos.

3.2. Electron Microscopy

A backscattered electron (BSE) image and associated crystallographic information for the Spot-Con melting case is presented in Fig. 5. The microstructure of the spot melt evolved after 2 ms of laser exposure at 90.0 W. After the beam was switched off, the solidification occurred rapidly, leading to the microstructure in Fig. 5a. The microstructure of the cross section has three distinct regions: the solidified melt pool, followed by the heat affected zone (HAZ), and finally wrought base material that was unaffected by the process. Based on the observable moving solid/liquid interface and the frame rate used during X-ray imaging, the average solidification velocity was calculated to be approximately 107 mm/s. The depth of the melt pool was measured at center to be approximately 32 µm from the postmortem image in Fig. 5a consisting of acicular, hexagonal closed packed (HCP) α, whereas the HAZ was on the order of 40 µm (sides) to 50 µm (maximum depth). The BSE image in Fig. 5a of the HAZ has a slightly higher brightness when compared to the brightness/contrast of the wrought material, which may be due to either internal chemistry differences (Z-contrast) or electron channeling (EC) from changes in crystallography [27]. Energy dispersive X-ray spectroscopy (EDS) was employed to look for changes in chemistry across the HAZ relative to the wrought material, however there were no clear differences from mapping across the wrought and HAZ (not shown). However, EBSD was carried out on all three microstructures, in the region highlighted by the white square in Fig. 5a, which revealed a transformed microstructure in the HAZ, shown in Fig. 5b. Unlike the large α grains present in the wrought microstructure, the inverse pole figure (IPF) map (oriented in [BND] for all IPF maps herein) displays much finer, acicular α grains in the HAZ when compared to the wrought microstructure. The phase map present in Fig. 5c corresponds to the same location outlined in Fig. 5a, with a significant amount of BCC β present in the HAZ highlighted in green. The β phase is present in the wrought microstructure as well, but the phase fraction of β is much larger in the HAZ.

The Spot-Key microstructure is presented in Fig. 6, with similar microstructural features to that of the Spot-Con case. The postmortem micrograph in Fig. 6a however, contains a deepened melt pool region corresponding to the keyhole melting mode from increased laser power. The depth of the keyhole is approximately 290 µm from the surface, whereas the width of the keyhole is on the order of 150 µm. After 2 ms of laser exposure, the liquid solidified with an average velocity of 136 mm/s. The thickness of the HAZ ranges
from 40 µm to 56 µm, with the smallest thickness occurring near the bottom of the keyhole. The melt pool solidified into the acicular α/α’, whereas the wrought phase was assumed to be relatively unaffected and is assumed to be mostly α. The IPF and phase maps, in Fig. 6b–c correspond to the highlighted region in Fig. 6a. The acicular grain structure of the HAZ differs in the same manner in this case as the conduction mode melting microstructure, with an increase in volume of the β phase inside of the HAZ. The β phase fractions were measured to be approximately < 1 % for the melt pool, 29.3 % for the HAZ, and 3.1 % for the wrought region. Texture analysis was carried out on each of the regions in Fig. 6b, shown as pole figures in Fig. 7. There is a relatively strong fiber texture due to rolling that transitions to a weak texture/mixed distribution of grain orientations due to a single solidification event. The grain sizes were approximated from the EBSD analysis, and are on the order of 0.37 µm – 0.54 µm α thickness for the HAZ and melt pool, and 6.54 µm equivalent spherical diameter for the wrought grains.

The Scan-Con specimen is presented in Fig. 8, similarly to the spot melting cases. Fig. 8a is the entire field of view of the elongated melt track. The beam direction moved from the left of the image to the right, with no keyhole formation. The nominal length of the melt track was 1400 µm, whereas the depth of the melt pool varied slightly across the length of the scan: Approximately 45 µm at the beginning to of the scan, leveling out to about 35 µm – 40 µm during the middle, and ending with a depth of 18 µm. The thickness of the HAZ was on the order of 20 µm across the length of the scan, with the thinnest regions (5
Fig. 6: Spot-Key case (201.3 W), a) BSE image of the microstructure, b) IPF map of the highlighted region in the BSE image, c) phase map of the highlighted region. Note that beta phase legend is the same as Fig. 5.

Fig. 7: α-phase pole figures of the three microstructure regions of the Spot-Key test case in Fig. 6b.

μm – 15 μm) occurring at the beginning and end of the laser scan (average values in Table 3). The labels in Fig. 8 represent the melt pool, HAZ, and wrought regions similarly to the single spot melt condition. Two highlighted squares at the center and end of the melt track were studied via EBSD. Fig. 8b, c correspond to the center box and Fig. 8d, e correspond to the box at the end of the laser scan. The IPF maps (Fig. 8b, d) display a transformed HAZ such that the wrought α microstructure has become acicular. The phase maps (Fig. 8c, e) display increased β phase fraction within the HAZ compared to the melt pool or wrought regions.

The Scan-Key specimen (Fig. 9) had markedly similar microstructural features as the conduction mode case in Fig. 8. The microstructure is annotated in the same fashion as the conduction mode case, however now with the presence of a deep keyhole that was formed at the beginning of the scan (Fig. 4). The nominal scan length was 1400 μm whereas the depth of the keyhole was measured to be approximately 140 μm. This
depth remained consistently between 65 \( \mu m \) and 70 \( \mu m \) until the end of the melt track, which had a reduced depth of 40 \( \mu m \). The average thickness of the HAZ was measured to be approximately 23.5 \( \mu m \) (Table 3).

Like the conduction mode melting schema in Fig. 8, the microstructural features are essentially the same. That is, the major morphological features were of the melt pool region, HAZ, and unaffected wrought base microstructure. However, like the Spot-Key scenario, a deep keyhole is observed. The IPF maps in Fig. 9b,d are of the highlighted regions in the BSE image. Similar to the previous cases, the HAZ microstructure is transformed into internal acicular \( \alpha \) from the larger wrought \( \alpha \) grains. The \( \beta \) phase is more visible in the IPF maps in the 111 direction than the other test cases. The phase maps in Fig. 9c,e show the \( \alpha \) and \( \beta \) phases represented in blue and green, respectively with the presence of the \( \beta \) phase within the HAZ.

Higher magnification images of the Scan-Con test case are presented in Fig. 10, where the micrographs are of the central region of the melt track. The micrograph in Fig. 10a displays all three morphological regions of the microstructure; the melt pool, HAZ, and base wrought microstructure. Towards the bottom of the melt pool just above the HAZ, there is a wavy morphology, consisting of partially dissolved and resolidified \( \alpha \) and \( \beta \) that follow the direction of the beam path. The micrograph in Fig. 10b is of the rapidly solidified melt pool region, displaying acicular \( \alpha/\alpha' \) morphology. The HAZ (Fig. 10c) and wrought grain morphology (Fig. 10d) appears at first glance to be similar, however closer inspection of the wrought phase reveals that the HAZ is drastically different, such that there is transformed acicular \( \alpha \) within the prior \( \alpha \) grains in the HAZ.
3.3. Thermal History Calculations

The longitudinal cross-section images of the Scan-Con and Scan-Key cases (Figs. 8a and 9a, respectively) were manually analyzed to determine the depth of the melt pool and HAZ, as well as the height of the liquid-vapor interface with respect to the initial substrate surface. First, images are rotated 7° such that the substrate plane is horizontal, and then a regular grid of vertical lines spaced 50 µm along the X direction is overlaid on the image. The locations where grid lines cross the boundary between the top surface of the melted material, the extent of the molten region, and the HAZ were manually identified and their positions recorded using Fiji [28]. Profiles of these regions are shown as dotted lines in Fig. 11.

Examination of the longitudinal cross-section profiles in Figs. 8a and 9a shows transient behaviors near both the beginning and ending of each track in the solidified state. Near the start of the track, the solidified top-surface protrudes above the plane of the substrate in both cases, and in the case of Scan-Key melting scenario the depth of the initial melt pool is substantially deeper than in the central portion of the track. Near the end of the track, the solidified top-surface is observed to be below the plane of the substrate and the extent of this feature in terms of both length and depth is more significant in the case of the Scan-Key versus the Scan-Con mode melting.

As the HAZ remains in the solid-state for the duration of processing, conduction is most likely the only
thermal transport mechanism active within the region, unlike the liquid phase, which is also subject to convection. For Ti-6Al-4V as temperature increases, the equilibrium volume fraction of the body-centered cubic (BCC) $\beta$ phase increases in relation to the hexagonal close-packed (HCP) $\alpha$ phase. At the $\beta$-transus temperature ($T_{\beta} \approx 995 ^{\circ}C$) the equilibrium volume fraction of $\alpha$ phase is zero. In reality, dissolution of the $\alpha$ phase and growth of the thermodynamically favorable $\beta$ phase does involve diffusion, so consideration of irradiance time is also critical.

Several approaches with different thermal criteria were considered to describe this HAZ. The first, and simplest approach is to identify the locus of points that achieve a maximum temperature that is equal to $T_{\beta}$. This locus surrounds all points that would, if the transformation occurred instantaneously, completely transform to $\beta$ during processing. They are denoted by solid blue lines in the panes of Fig. 11. Table 3 shows the average depth of the HAZ boundary as measured from within the steady state. In the second approach, both the maximum temperature achieved at any time during processing was captured as well as the total cumulative time spent above $T_{\beta}$ (including both heating and cooling portions of the trajectory). In the final
Figure 11: Calculated maximum temperatures (°C), time above $T_\beta$ (µs), and diffusion distance (µm). Solid red and blue lines are the modeled bottoms of the melt pool and HAZ, respectively. Dotted red and blue lines are the empirically observed bottoms of the melt pool and HAZ, respectively. Solid black line is the modeled surface of the substrate, whereas the dotted black line is the empirically observed surface. Scan-Con plots pertain to a), c), and e), whereas Scan-Key pertain to b), d), and f).
Table 2: Average and standard deviation of the empirically observed and uncalibrated model predictions for the Scan-Con and Scan-Key specimens melt pool width $\bar{W}_m$, depth $\bar{D}_m$, and cross-sectional area $\bar{A}_m$ within the central 700 $\mu$m portion of the tracks.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Source</th>
<th>$W_m$ [µm]</th>
<th>$\Delta W_m$ [%]</th>
<th>$D_m$ [µm]</th>
<th>$\Delta D_m$ [µm]</th>
<th>$A_m$ [µm$^2$]</th>
<th>$\Delta A_m$ [%]</th>
<th>$W_m/D_m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scan-Con</td>
<td>Expt.</td>
<td>119.0, 1.8</td>
<td>36.5, 0.7</td>
<td>49.9, 0.4</td>
<td>36.6</td>
<td>3415</td>
<td>22.0</td>
<td>2.13</td>
</tr>
<tr>
<td>Scan-Con</td>
<td>Model</td>
<td>106.3, 0.7</td>
<td>-10.7</td>
<td>49.9, 0.4</td>
<td>36.6</td>
<td>4167</td>
<td>22.0</td>
<td>2.13</td>
</tr>
<tr>
<td>Scan-Key</td>
<td>Expt.</td>
<td>174.6, 5.2</td>
<td>70.4, 2.2</td>
<td>70.4, 2.2</td>
<td>36.6</td>
<td>9649</td>
<td>14.2</td>
<td>2.48</td>
</tr>
<tr>
<td>Scan-Key</td>
<td>Model</td>
<td>164.5, 2.1</td>
<td>-5.8</td>
<td>80.3, 1.1</td>
<td>14.2</td>
<td>10378</td>
<td>7.6</td>
<td>2.05</td>
</tr>
</tbody>
</table>

approach, an effective diffusion distance for Al in a BCC Ti matrix was computed by numerically integrating the time-temperature history and using the temperature-dependent diffusion coefficient [29]. The details of this integration procedure are described in the Appendix.

Considering the cross sections of both tracks, the central 700 $\mu$m of length has approximately constant depth and the solidified top-surface is coincident with the original substrate plane. This region was therefore selected as being representative of steady-state behavior, and the arithmetic average of experimentally observed depth $D_m$ and width $W_m$ (width measured from top-down light microscope images; see Fig. 3) were computed over this region. Additionally, an approximate measure of $XY$ cross-sectional area $\bar{A}_m$ is defined as

$$\bar{A}_m = \frac{\pi}{4} W_m D_m.$$  (1)

Similar averages were calculated from uncalibrated model predictions, and all measures of steady-state geometry are shown in Table 2, including differences between the predicted and experimentally observed values, normalized by the appropriate empirical value.

Examination of Table 2 shows that while the model produces melt pool dimensions on the same order of magnitude as the empirical observations, there are some systematic discrepancies. The model consistently under-predicts the steady-state width of the melt pool by 10.7 % in the conduction mode, and 5.8 % in the keyhole mode. The predicted depths are systematically too large by 36.6 % in the conduction case and 14.2 % in the keyhole case. While the directions of the width and depth errors are opposite, the net effect is an over-prediction of the molten area in a transverse cross-section by 22.0 % in the conduction case, and 7.6 % in the keyhole case. One final consideration regarding sizes is the change in molten area between the two conditions. The empirical results indicate an increase in molten area by a factor of 2.83 on moving from the laser scanning conduction to laser scanning keyhole parameters, whereas the model predicts this increase to be only 2.49, 11.9 % lower than the actual observed change.
Table 3: Average and standard deviation of the heat affected zone dimensions within the central 700µm portion of the tracks.
For the empirical cases, the HAZ extent is the observed extent of microstructural modification. For the modeled case, this is the depth of locations that experience \( T_{\text{max}} = T_0 \).

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Source</th>
<th>( D_{\text{HAZ}} ) [µm]</th>
<th>( D_{\text{HAZ}} - D_{m} ) [µm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scan-Con</td>
<td>Model</td>
<td>66.7, 0.4</td>
<td>16.8</td>
</tr>
<tr>
<td>Scan-Con</td>
<td>Expt.</td>
<td>56.9, 1.3</td>
<td>20.4</td>
</tr>
<tr>
<td>Scan-Key</td>
<td>Model</td>
<td>105.5, 1.5</td>
<td>25.2</td>
</tr>
<tr>
<td>Scan-Key</td>
<td>Expt.</td>
<td>93.9, 2.3</td>
<td>23.5</td>
</tr>
</tbody>
</table>

Table 4: Average values of the hardness and modulus from nanoindentation across the entire regions.

<table>
<thead>
<tr>
<th>Region</th>
<th>Hardness (GPa)</th>
<th>Modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melt pool</td>
<td>4.25 ± 0.22</td>
<td>99.85 ± 8.28</td>
</tr>
<tr>
<td>HAZ</td>
<td>4.25 ± 0.42</td>
<td>99.98 ± 9.13</td>
</tr>
<tr>
<td>Wrought</td>
<td>4.39 ± 0.52</td>
<td>108.79 ± 10.60</td>
</tr>
</tbody>
</table>

3.4. Material Properties

Nanoindentation was performed on the Scan-Con melting case in order to assess the hardness and modulus as influenced by the resultant microstructure of the laser scan. The indentation pattern, as described in the methods, consisted of a 25 by 25 square grid with 5 µm spacing between each indent (125 µm by 125 µm area), totaling 625 indentations. Fig. 12 displays the typical microstructure of melt pool, HAZ, and wrought phases with their respective indentations. The bar chart in Fig. 13 was constructed using an average of the indentations that are in representative areas of the microstructure (i.e., not along the interfaces between the regions). The values were averaged for 16 indentations in the melt pool (not including the wavy boundary), 16 indentations in the HAZ, and 16 indentations in the wrought microstructure. The 16 indentations were chosen in the HAZ and wrought portions of the regions such that each indentation was inside of a grain, as to avoid grain boundary effects as well as \( \alpha/\beta \) interfaces. The bar chart in Fig. 13 is an average of the indentations for the aforementioned indentations with error bars representing one standard deviation from the mean value (±1σ).

The BSE image in Fig. 12 is cropped to show the three areas of interest (Bottom 150 indentation points into the wrought region not shown). As previously mentioned, the indentations into the HAZ and wrought regions are located within \( \alpha \) and \( \beta \) grains, grain boundaries, and along interface between the \( \alpha/\beta \) grains. The data presented in Table 4 represents the average hardness/modulus of the indentations in each region, as opposed to the granular indentation data in Fig. 13.

The variability in hardness and modulus values measured with nanoindentation was compared to a complimentary set of hyper-maps generated with multiple techniques based on scanning probe microscopy. Fig. 14 shows an example of an SPM data set recorded across all three distinct microstructure zones in the.
Figure 12: BSE image of the Scan-Con melted cross section with the nanoindentation grid across all three regions of interest: Melt pool, HAZ, and wrought microstructure.

Figure 13: Bar chart summarizes the average hardness and modulus data from within singular grains of the HAZ and wrought regions. Error bars are $\pm 1 \sigma$.

Spot-Key sample. Results from contact mode mapping (Fig. 14) indicates minimal topographic variations that are on the order of $\pm 5$ nm in height variation, with the local deviations being spatially correlated to phase boundaries in the microstructure. In Fig. 14c, a modulus map is shown with variations based on the mean Young’s modulus of the melt pool since this microstructural zone contained the least amount of spatial variation in phase content, whereas the wrought zone exhibited the highest variation in modulus when comparing to the melt pool and HAZ. When compared to the EBSD-based phase map in Fig. 6, (the same sample analyzed in Fig. 14), the variations in modulus do not correlate spatially with differences in phase fraction. Rather we see specific grains in the wrought with higher modulus than similarly appearing grains in the HAZ. These high-modulus grains are attributed to grain orientations aligned with the highest stiffness. Further, SKPFM measurements were performed on this region to determine what differences in Volta potential could be measured across the three zones, with the wrought microstructure exhibiting the
Figure 14: Scanning probe microscopy data from the Spot-Key melting sample. a) BSE image displaying where the SPM data was taken. b) Contact mode height image. c) Flattened modulus map, calibrated to average modulus of the melt pool. Color scale is GPa variation. d) SKPFM surface potential map, 0th order flattened. Dotted curved lines represent the boundaries of the HAZ.

The greatest range (≈ 40 mV total range) and the melt pool exhibiting the smallest range (≈ 20 mV total range). Large differences in Volta potential were observed across the different phase boundaries for the wrought portion of the material and encompassed the entire range of measured potential.

4. Discussion

4.1. Processing

The HAZ is what is referred to as a region of unmelted material affected by the heat transfer from a weld zone or melt pool during processing. Depending on the synthesis, processing, or overall material diffusivity, resultant property changes in the HAZ can vary. In each of the four melting scenarios described herein (Spot-Con, Spot-Key, Scan-Con, and Scan-Key), all instances led to HAZs with significant phase transformations.
present in the postmortem micrographs of the microstructures. This is due to the high temperatures of the melt pool causing the HAZ to exceed the β-transus temperature of \( \approx 995 ^\circ C \). A equilibrium phase diagram of Ti-6Al as a function of V content in wt.% was digitized and replotted for this work from Ref. [30]. Due to the rapid cooling process, the potential for martensitic, \( \alpha' \) is considerable.

The melt pool regions of all of the microstructures displayed in the BSE images in Figs. 5, 6, 8, and 9 are all consistent with the rapidly solidified, possibly martensitic, acicular \( \alpha/\alpha' \) phase resulting from the high cooling rates \( (10^3 \text{ K/s} - 10^6 \text{ K/s}) \) associated with laser surface melting in metals [31]. However, transmission electron microscopy (TEM) would need to be employed to state definitively whether or not this phase is indeed \( \alpha' \), and is outside the scope of the present investigation. However, a recent study by Oh et al. [18] revealed through TEM analysis that fully martensitic, \( \alpha' \) microstructures are found in laser fusion zones that solidified from the melt pool. Therefore based on the morphology of the acicular phases and laser melting cooling rates employed in this work, it is reasonable to assume that this phase is the martensitic \( \alpha' \). The wavy melted zone near the boundary between the melt pool and HAZ in the laser scanning experiments (Fig. 10), is likely the result of the rapid quenching of a mushy zone during the experiment. The EBSD analysis across the regions displayed in the BSE images of the aforementioned figures all reveal \( \beta \) phase throughout the HAZ. The HAZ is typically defined as a region that undergoes solid state property changes resulting from heat exposure. To what extent, however, depends on the material system and temperature. Studies of laser welding of Ti-6Al-4V show that HAZ width varies as a function of welding speed, such that an increase in welding speed leads to a reduction in HAZ width [32]. Zhang et al. [33] characterize the microstructure of the HAZ in electron beam welded Ti-6Al-4V, and found that there was a decrease in primary \( \alpha \) and an increase in \( \beta \) along the HAZ, as well as a secondary \( \alpha \) phase transformation. Both of these observations from literature support the microstructural observations from this work: increased \( \beta \) phase fraction (Figs. 5 – 9) and secondary alpha phase transformation in the HAZ.

4.2. Structure

A systematic investigation of the effect of cooling rates and heat treatment temperatures in Ti-6Al-4V by Shaikh et al. [34] reveal that with fast quenching near \( T_\beta \), there can be a phase transformation of the wrought \( \alpha + \beta \) into martensitic \( \alpha' \), acicular \( \alpha \), and transformed \( \beta \) depending on the method of quenching and temperature of the heat treatment. Given the high-cooling rates associated with laser surface melting of metals, it is reasonable to assume that the cooling rates in the present experiment are consistent with the martensitic, \( \alpha' \) phase transformation observed in Ref. [34] as EBSD analysis cannot distinguish the difference between \( \alpha \) and \( \alpha' \). Thus, the microstructure of the HAZ in Fig. 10c might possibly be a transformed primary
\( \alpha \) to \( \beta \) when the HAZ temperature passed the \( \beta \)-transus temperature followed by a martensitic \( \alpha' \) upon cooling. In the present investigation, the Ti-6Al-4V alloy \( \beta \)-transus temperature, \( T_\beta \approx 995 \, ^\circ\text{C} \) must have been surpassed (Fig. 15) in some regions that remain in the solid state during the laser melting leading to a microstructure consistent with previous studies of the HAZ as influenced by heat treatment above \( T_\beta \) and rapid quenching.

In an attempt to model this temperature history along the HAZ, the DSM from Section 2.3 was employed to generate the temporally-dependent thermal histories presented in Fig. 11 that make use of the time-resolved absorption data of the actual melting event (Fig. 4). Using the time-resolved absorption data from the integrating sphere, the DSM values presented in Fig. 11 are consistent with the observed phase transformations in the HAZ resulting from the temperatures above \( T_\beta \). Fig. 11a-b display the maximum temperatures for the conduction and keyhole mode melting as a function of position for the simulated process. The solid blue lines in Fig. 11 are the loci of points whose maximum temperature at any time is equal to \( T_\beta \), as resulting from the input heat source. Figs. 11c-d and 11e-f represent the time above \( T_\beta \) and diffusion distance of Al, respectively. The modeled HAZ thicknesses computed using the difference in the maximum depths of \( T_\beta \) and \( T_s \) presented in Table 3 agree with the experimental HAZ observations to within less than 5 \( \mu\text{m} \). Similar to Liang et al. [35] where the authors use a computational fluid dynamics framework paired with CALPHAD, the DSM is used to simulate spatial temperature profiles that predict the presence of a HAZ in the temperature regions that can lead to phase transformation in Ti-alloys.

When used in a calibrated manner, the model efficiency factor \( \eta \) is adjusted to bring the modeled and observed melt pool sizes into agreement, and effectively captures all energy losses that are coincident
with the molten pool (Appendix, Fig. 17). However, in the present case only the reflection of laser energy is contributing to \( \eta \) which could over-estimate the energy actually available for subsequent thermal conduction. The direction of the deviation between predicted and observed dimensions is therefore as expected, but it is somewhat surprising that the thermal model produced values closer to the empirical behavior for the keyhole case than the conduction since it is assumed that some of these loss mechanisms are more intense in the keyhole regime, particularly evaporative cooling.

In addition to the absolute dimensions of the pools, the width-to-depth aspect ratio is another important geometric indicator of the active transport mechanisms. In previous work, it was shown that with appropriate calibration of the source shape, in particular the ratio of \( \sigma_x \) to \( \sigma_z \), the DSM can produce a range of melt pool aspect ratios [22]. However, in the present uncalibrated application of the DSM \( \sigma_x \) has been set to match the empirically measured energy distribution, and \( \sigma_z \) has been left at a small value to act as a surface flux rather than a volumetric source. With these settings, the model results exhibit width-to-depth ratios close to 2 in the steady-state region, essentially a circular cross section. The observed results for both conditions indicate substantially higher width-to-depth ratios, over 3 in the case of the conduction-mode condition. This substantial widening of the pool relative to its depth is consistent with a Marangoni flow in the liquid carrying hot fluid from the center line laterally towards the edges of the pool. This is consistent with a material where surface tension decreases as temperature increases [36], which is indeed expected for titanium [37]. In contrast, the formation of the keyhole transports energy vertically downward into the substrate at a rate much faster than conduction alone. Indeed, while the empirically observed aspect ratio is still larger than 2, it is substantially reduced in the keyhole case compared to the conduction only case indicating that both of these thermal transport mechanisms are relevant and their relative importance changes with processing parameters.

The discussion above focused on behavior in the steady-state region, but both the empirical and model data also describe the pool geometry in the transient regions at both the start and end of tracks. The DSM does not include the physics governing displacement of the free-surface between the liquid and vapor phases, and therefore it cannot capture the transient increase in height of solidified material above the substrate at the beginning of the track, nor the depression left at the end of the track. However, the DSM can capture features dictated by transients in the thermal field caused by changes in laser power input, beam trajectory, or absorptivity. The present trajectories are simple, but the measured absorptivity shows a marked transient in the keyhole case, with an enhanced absorptivity within the first 0.5 ms. The cross-sections exhibit a significant depth transient in this same region, with the molten zone extending down to
124 μm approximately 150 μm from the start of the track. Using the measured transient absorptivity as an input to the DSM, the modeled depth transient is 93.9 μm at 188 μm from the start of the track. The DSM underpredicts the extent of the depth transient by 24.2%, significantly more than the margin of error for the steady-state depth for the same track. Not surprisingly, the complex physics governing the initial formation of the keyhole are not captured by a conduction-only model, though a portion of this increased depth attributable to enhanced absorptivity is accounted for.

Fig. 16 shows the impact of adjusting the source diameter σₓ away from the value established by empirical beam characterization σₓ Expt. As noted in the text, modification of the source shape via the parameters σₓ and σᵧ has previously been utilized to match the modeled and observed melt pool aspect ratio. Justification for this calibration process is that the DSM does not contain all appropriate transport mechanisms in the liquid phase and artificial spreading of the energy source can be used to mimic the more rapid transport of energy via convection.

Specifically, Fig. 16a shows that increasing σₓ systematically increases the ratio of the predicted width to depth. It was noted in the main text that this ratio begins around 2, essentially a circular transverse cross-section. For conduction mode parameters C, a value σₓ/σₓ Expt. = 2.3 is necessary to match the observed Wm/ Dön, whereas for the keyhole mode parameters σₓ/σₓ Expt. = 2.75 is required to reproduce the observed ratio.

Alternately, Fig. 16b shows the absolute errors in both the width and depth dimensions, as well as the root-mean square error of the combination of width and depth. As σₓ/σₓ Expt. is increased, the tendency to overpredict depth monotonically decreases. The trend of width underprediction is reduced, though at more extreme values of σₓ/σₓ Expt. width is ultimately over-predicted. Considering the RMSE metric which combines both melt pool dimensions, Fig. 16b indicates a minimum value of 10.2 μm with σₓ/σₓ Expt. ≈ 1.75, and for keyhole model the RMSE drops to 5.4 μm at σₓ/σₓ Expt. = 2.5. Fig. 17 shows the depth profiles and associated details of the thermal histories for both the conduction and keyhole conditions when σₓ/σₓ Expt. has been calibrated to minimize the RMSE of width and in each case. The agreement between the modeled and experimental cases is clearly closer than in Fig. 11. While not shown in this figure, consideration of the individual error components shows that the overall RMSE values are dominated by the depth error. Upon calibration, the width errors are driven to less than 1 μm, though the depths are still overestimated by 10 μm and 5 μm for the conduction and keyhole modes respectively.

The significant increase in σₓ beyond the experimentally observed value necessary to optimize various metrics of the melt pool shape suggests that, not surprisingly, transport mechanisms beyond conduction are
important within the melt pool. Additionally, the fact that different values of $\sigma_x/\sigma_{x\text{Expt.}}$ are necessary to match the observed aspect ratio and to reduce the overall error between the conduction and keyhole cases suggests a different degree of convective transport is present for these two cases.

4.3. Properties

The nanoindentation measurements were processed using analysis of variance (ANOVA) techniques, and displayed statistically significant differences in hardness across all three regions for the intragranular data used to produce Fig. 12. There was also statistical differences in the modulus between the melt pool and wrought regions, as well as the HAZ and wrought sections for this same data. There was no statistical differences in modulus between the melt pool and HAZ regions. The microstructure of a two-phase material like Ti-6Al-4V has granular scale anisotropic properties depending on the crystallographic orientation of $\alpha$ [38], whereas the effects of the $\beta$ phase are not currently fully understood.

The small grain size of the rapidly solidified melt pool would typically result in a harder material, in line with the Hall-Petch relationship. However, the wrought base metal consisted of NIST SRM 654b [20] (Ti-6Al-4V), and was thermomechanically processed (hot forged) into rods during historical production, prior to sectioning into the smaller pieces of material that were used for this study. This historical processing of the material could have led to residual stresses which can be dependent on the cooling rates of post hot-forging heat treatments [39], and therefore granular variability in the measured mechanical properties based on prior-$\beta$ grain Burgers orientation variant selection and $\alpha$ texture inheritance. The HAZ resulted
in lower hardness/modulus values when heated above the $\beta$-transus temperature, which may be due to the phase transformation and resultant new crystallographic texture and/or stress relief. The hardness and modulus values per region of microstructure (melt pool, HAZ, wrought) measured via indentation correlate with phase fraction and grain orientation but not grain size in this particular case.

When examining the averaged data from all of the indentations (Table 4), i.e., not just those within grains, ANOVA revealed no statistical significance between the regions except for the melt pool and wrought indentations. The melt pool and HAZ have similar hardness and modulus values as opposed to the wrought base metal, which had overall larger standard deviation among the measurements used to calculate the average values. This is likely due to the scale of the probing mechanism (Berkovich indenter) in comparison to the scale of the microstructural features. Therefore caution should be exercised when choosing a representative data set based on the sampling of the microstructural features. In order to account for this, the scanning probe microscopy data can provide a clearer picture on a granular basis.

Since the variation in CRFM-based modulus is greatest for the wrought zone and the $\beta/\alpha$ phase ratio is lower than in the HAZ, the variation is thus attributed to differences in crystallographic orientation of the alpha phase and the larger grain size. These results are consistent with nanoindentation measurements performed by Zhang et al. [33]. Interestingly, the SKPFM measurements of changes in Volta potential indicate the potential for Galvanic corrosion to occur (the larger the range, the greater the thermodynamic propensity) is least likely for the melt pool zone and most likely for the wrought microstructure where the widest variation in crystallographic texture and phase fraction can occur. The crystallographic orientation and phase fraction dependence of Volta potential in $\alpha-\beta$ titanium alloys have been previously reported to depend on local misorientation and atomic packing fraction in a given crystallographic plane [40]. Notably, the differences in Volta potential measured in this work on a laser-melted titanium alloy are approximately half of the range measured by Benzing et al. on an electron-beam melted Ti-6Al-4V alloy subjected to a sub-$\beta$-transus hot isostatic pressing treatment [40].

5. Conclusion

Laser exposed Ti-6Al-4V specimens were simultaneously imaged and melted, along with in-situ power absorption measurements and metallographically prepared for microstructural and mechanical characterization. Four melt scenarios were studied: laser spot conduction mode melting, laser spot keyhole mode melting, laser scan conduction mode melting, and laser scan keyhole mode melting. A thermal model was then employed that utilized the time-resolved absorption data gathered in Ref. [15] to model the thermal
histories and diffusion distances of the laser scanned conduction and keyhole mode melting experiments. Lastly, the material properties of the melt pool, HAZ, and wrought base metal were investigated via nanoin- dentation and scanning probe microscopy. Several summary points from the present work are presented below:

- All four melt scenarios (spot/scan and conduction/keyhole) studied via electron microscopy and backscatter diffraction techniques reveal a significantly β-transformed heat affected zone (HAZ) (≈ 30 \% β phase fraction) resulting from spending time with $T_β < T < T_s$.

- The microstructural changes of the HAZ is consistent with a primary α to β to mixed acicular α/α'/β transformation as a result of the elevated temperatures paired with the rapid cooling inherent to laser surface melting.

- Using the time-resolved absorption data, the Discrete Source Model was used to model the laser scanned conduction and keyhole mode melting experiments. The model demonstrates reasonable agreement in the steady-state region between the overall relative depths of the HAZ for each test case with respect to depths greater than or equal to the β-transus temperature for Ti-6Al-4V. The uncalibrated model predicts molten width and depth to within 11 \% and 37 \% respectively of observations, and the depth of the locus of $T_{max} = T_β$ is within 4 \(\mu\)m of the observed HAZ thickness.

- The Discrete Source Model (DSM) underpredicts the transient depth of the keyhole when compared to the steady state melting depth, however this discrepancy may be accounted for with additional underlying physics not represented in a conduction-only model. However, the DSM may be employed as a low-cost alternative to resource-intensive models in order to quickly gain an understanding of the thermal histories to a reasonable degree of accuracy.

- The melt pool and HAZ had smaller hardness values when compared to the wrought base metal and reduced intergranular mechanical heterogeneity. The modulus values for the melt pool and HAZ were similar, however, much lower than that of the wrought base metal.

In summary, laser-based metal manufacturing of Ti-6Al-4V alloys shows promise for a wide variety of biomedical and aerospace applications. One of the overarching goals of additive manufacturing is aimed at reducing post-processing, such that as-built parts will one day be service-ready. It is crucial to obtain a full understanding of the PSP relationships involved in every step of the manufacturing process. In the present work, it is shown that the heat affected zone resulting from the high temperatures of the melt pool
result in significant crystallographic phase transformations, which may or may not be a desirable outcome if trying to additively manufacture parts that are service-ready. Note that in built-up part, the microstructure will be as-solidified, and therefore the HAZ of the previously solidified layer adjacent to the new melt pool may exhibit different behavior. It appears that at this stage, homogenization heat treatments [41] may be required for Ti-6Al-4V alloys produced via laser melting in order to account for the periodic layers of phase transformed heat affected zones across an entire built part.

6. Appendix

6.1. Diffusion Distance

The diffusion distance \( l_{j,q} \) at location \( j \) for component \( q \) is computed according to

\[
l_{j,q} = \sum_{i=1}^{N-1} \sqrt{4D_q (\bar{T}_{i,j}) \Delta t_i}, \tag{2}
\]

where the effective temperature for each time step is

\[
\bar{T}_{i,j} (\vec{r}_j, t_i) = 0.5 \left[ T(\vec{r}_j, t_{i+1}) + T(\vec{r}_j, t_i) \right], \tag{3}
\]

and the duration of the step is

\[
\Delta t_i = t_{i+1} - t_i. \tag{4}
\]

The diffusivity of component \( q \) is given by

\[
D(T) = D_0 \exp \left( \frac{-Q}{RT} \right) \tag{5}
\]

where \( R \) is the ideal gas constant and \( T \) is in expressed as an absolute temperature. Values of \( D_0 \) and \( Q \) for components \( q = \text{Al} \) are given in Table 5.
Figure 17: Comparison of the experimental and modeled depth profiles and details of thermal histories in the calibrated case for Conduction mode a), c), and d), as well as the keyhole mode b), d), and f).
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