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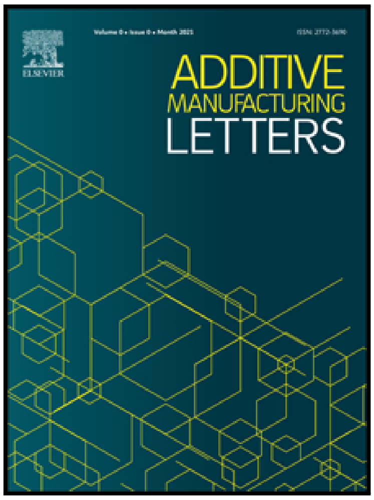

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Highlights

- Virgin Ti-6Al-4V feedstock was shown to have oxygen content variability as a function of build height.
- Powder morphology between low-oxygen and high-oxygen content particles show no differences across singular builds.
- Due to the elevated temperatures in PBF-EB, Ti-6Al-4V may be gettering the build chamber during the initial build layers.

Sintered powder oxidation variation as a function of build height for titanium alloy produced by electron beam powder-bed fusion

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Abstract

It is well-established that titanium alloy (Ti-6Al-4V) powder oxidizes during electron beam powder-bed fusion (PBF-EB) due to the high background temperatures resulting from layer preheating and sintering of the powder bed before melting. However, it is not known if oxidation is homogeneous throughout the entire build area. This work investigates the potential for variation in powder oxidation as a function of build height for PBF-EB Ti-6Al-4V, up to build heights of 35 mm. Thin-walled cylindrical powder capsules were printed in proximity to solid parts in order to capture the sintered powder for controlled chemical sampling. Powders collected from the bottom 3 mm and top 3 mm of the powder capsules show no morphological differences from the virgin powder. Higher oxidation is observed at the bottom of the powder capsules, and decreases with build height to approximately zero at 35 mm height. This magnitude of oxidation and change with build height was consistent across multiple locations in multiple builds, suggesting build height is the main factor in oxidation magnitude. An increase in oxygen content of 0.02 wt.% in a single build is significant when considering the maximum allowable oxygen is only 0.13 wt.% in material specifications (ASTM F3001-14). The predominant source of oxygen must be transient. This helps prioritize some potential sources of oxygen (e.g. powder moisture) over others when developing mitigation techniques. All of these observations from this work motivate scrutiny of powder handling and mixing procedures as well as development of oxidation mitigation techniques.

Keywords: Additive manufacturing, Ti-6Al-4V, Powder oxidation, Powder chemistry, Electron beam powder-bed fusion

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1. Introduction

Electron beam powder-bed fusion (PBF-EB) is a widely used additive manufacturing (AM) technique for 3D printing complex geometrical parts for aerospace and biomedical applications. In particular, the Ti-6Al-4V alloy is a popular biocompatible alloy commonly used in PBF-EB processes for its high strength-to-weight ratio and good corrosion resistance. However, AM Ti-6Al-4V alloys have yet to see widespread adoption for fatigue and fracture critical applications [1] due to an incomplete understanding of the processing-structure-properties-performance relationships in PBF-EB Ti-6Al-4V alloy with respect to the many process variables inherent to PBF-EB. From a practical standpoint, the feedstock powder used in PBF-EB must be reused in order to optimize the process cost, otherwise the technique would be too cost prohibitive to be sustainable. That said, powder reuse methodologies vary across industry and academia, as well as in other powder-bed fusion processes such as laser powder-bed fusion (PBF-L). A recent review by Derimow and Hrabe [2] summarized the existing literature to date with respect to powder reuse in PBF-EB and PBF-L Ti-6Al-4V alloy. The review postulates that due to the different powder reuse methods, heterogeneous oxidation in reused powder batches may play a role in resulting anisotropic mechanical properties of the material built from reused powder.

Studies by Tang et al. [3] and Popov et al. [4] investigated the effect of powder reuse on mechanical properties, which both demonstrated an increase in strength as a function of powder oxidation uptake in the reused powder batches. Nandwana et al. conclude that the number of reuse cycles for PBF-EB powder is governed by the oxygen pick up that occurs during and in-between the build cycles [5]. Ti-6Al-4V feedstock oxidation has been observed on the surface of the powder particles [6], as well as interstitially within the body-centered cubic (BCC) β-phase [7]. The review by Derimow and Hrabe [2] states that due to the high-background temperatures present in PBF-EB, there is a greater likelihood for oxidation based on the thermodynamics of TiO_2 production, which has also been observed to be more frequent in PBF-EB as opposed to PBF-L. Generally speaking, Ti is a common gettering material [8, 9] used to purify inert gas in metallurgical processing environments such as powder metallurgical sintering [10]. In order to act as a gettering media, Ti is typically heated to a range of temperatures between 600 °C to 800 °C, which coincidentally corresponds to the high-background processing temperature used in PBF-EB.

Although previous investigations have shown the likelihood of oxidation in PBF-EB Ti-6Al-4V, no studies have investigated whether oxidation is homogeneous within a single build. The present work investigates the potential for PBF-EB Ti-6Al-4V powder oxidation variation within a single build as a function of both build height and location on the build plate. This knowledge will enable further development of this highly industrially relevant material and process. It is a curiosity as to whether the beginning layers of the PBF-EB process contribute to a purification of the build chamber due to the gettering nature of Ti at high temperatures. This would therefore result in increased oxidation in the powder bed as a function of build height, as subsequent layers would be heated in a freshly Ti-gettered environment. In order to study these effects on the powder, thin-walled cylindrical powder capsules were utilized to achieve controlled powder sampling as a function of known build height.

2. Method and Materials

The AM process was carried out on an Arcam S12[1] machine with standard Ti-6Al-4V build theme and layer height of 50 µm (software version 3.2.132.14429). The feedstock powder consisted of plasma-atomized Grade 23 ELI spherical Ti-6Al-4V adhering to ASTM F3001-14 [11] from Advanced Powders & Coatings, with a powder size distribution (PSD) ranging from 45 µm to 106 µm. The portion of the particle diameters less than 10 %, 50 %, and 90 % (D10, D50, and D90) correspond to 50 µm, 67 µm, and 100 µm, respectively, and were measured by the manufacturer per ASTM B822-17 [12]. The schematic of the build is pictured in Fig. 1. The rectangular cuboids of 15 mm × 15 mm × 35 mm labeled I, II, III, IV, and V were used for a different study. The primary focus of this work employed the cylindrical powder capsules to investigate the chemistry of the sintered powder. The parts were recovered using an Arcam PRS, with special consideration taken towards the blasting of the open-top cylindrical powder capsules as not to remove layers of powder inside.

The powder capsules in Fig. 1, labeled 1A, 1B, 1C, and 1D, were built to be 15 mm in diameter × 35 mm height, with wall thickness = 1 mm. These powder capsules were deliberately kept open-ended on both the top and bottom in order to scrape the powder out in a systematic fashion. Note that the powder within these capsules were sintered and stuck together, with no loose powder present inside. This build layout was repeated three times in order to increase the number of powder capsules for this study. Cylinders 1A, 1B, and 1C (belonging to Build 1) were analyzed by scraping powder in vertical increments of 3 mm throughout the entire length of the cylinder. Cylinder 1D, as well as eight cylindrical powder capsules from two additional builds were analyzed via scraping only the top 3 mm and bottom 3 mm of sintered powder. These additional nine powder capsules are referred to herein as 1D, 2A, 2B, 2C, 2D, 3A, 3B, 3C, and 3D, with the leading numbers referring to the specific build.

[1] Commercial names are identified in order to specify the experimental procedure adequately. Such identification is not intended to imply recommendation or endorsement by NIST nor does it imply that they are necessarily the best available for the purpose.

Powder morphology was characterized via secondary electron (SE) imaging using a thermionic emission SEM with an accelerating voltage of 20 kV. Chemistry determination of the built material was as follows: aluminum, vanadium, and iron were measured by optical emission spectroscopy (OES) per ASTM E2371-13 [13]. Oxygen and nitrogen were measured per ASTM E1409-13 [14], and hydrogen per ASTM E1447-09[15], all by inert gas fusion. Carbon was measured by the combustion method per ASTM E1941-10 [16]. Oxygen testing of the sintered powders collected from the powder capsules was also carried out by inert gas fusion [14]. The chemistry values can be found in Table 1.

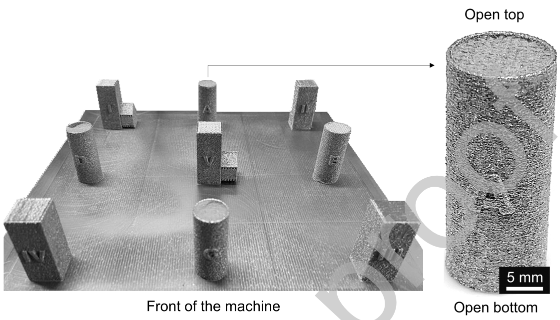

Figure 1: Build layout showing the 35 mm high pieces. Solid rectangular cuboids I – V were used for a different study. To the right is an enlarged picture showing powder capsule A.

3. Results and Discussion

The full chemistry data for the feedstock powder and the built Ti-6Al-4V material are presented with the ASTM F3001-14 limits in Table 1. Both powder and solid material conform to the pertinent material specification ASTM F3001-14.

The morphology of the Ti-6Al-4V powders was examined by SE imaging, as shown in Fig. 2. The image in Fig. 2a depicts a macroscopic view of the virgin powder batch, with higher magnification of an individual particle in Fig. 2b. The powder is generally spherical, with small satellites clinging to the larger powder particles, similar to what was observed in previous studies of virgin powder batches where many powder particles had small attached satellites [17]. The images in Fig. 2c–d and Fig. 2e–f correspond to powder capsule powder that was scraped from the top 3 mm and bottom 3 mm respectively. Generally speaking, there appears to be no morphological difference between any of the three powders examined in Fig. 2. That is, all three powders exhibit the same morphological characteristics with respect to size, sphericity, and presence of satellites. Like the virgin powders, the powder obtained from the top and bottom of the powder capsule show much similarity to the powder characteristics observed in Ref. [17]. This is not too surprising, as the powder is of the same Grade, similar PSD, and same manufacturer origin as the one examined in the work by Sun et al. [17]. Previous work by Sun et al. [7] revealed significant loss of sphericity of the particle exterior after 30 reuse cycles. Given that the powder obtained from the powder capsule had only been exposed to the PBF-EB process once, it did not have a chance to coarsen.

Table 1: Chemical composition in weight % of the ASTM F3001-14 [11] (Grade 23) limits, the feedstock, and the built material for this work. Feedstock chemistry is reported directly from the powder certification sheet from the manufacturer.

Wt. %	Al	V	Fe	O	C	N	H	Ti
ASTM F3001	5.5<x<6.50	3.5<x<4.5	0.25	0.130	0.080	0.05	0.0120	bal.
Feedstock	6.39	3.93	0.20	0.080	0.010	0.02	0.0020	bal.
Built Part	6.00	3.99	0.19	0.081	0.014	0.03	0.0016	bal.

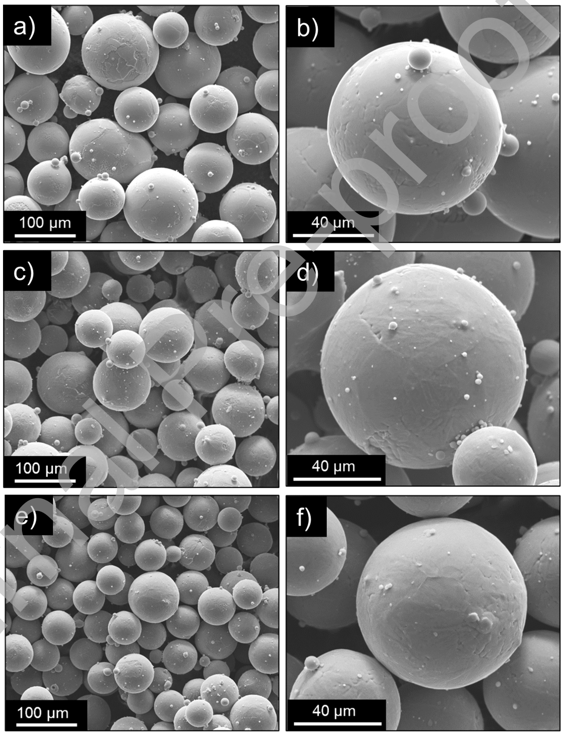

Figure 2: SEM secondary electron images of powder morphology of the a-b) Virgin powder, c-d) Top 3mm of the cylinder, and e-f) Bottom 3mm of the cylinder.

The bar chart in Fig. 3 is of cylinders 1A, 1B, and 1C, which show a general decrease in oxygen content as the powder is collected closer to the top of the cylinder. The error bars represent the 1 σ standard deviation of the mean for the average of three tests per each region. The dotted black line is a linear trendline for all three cylinders averaged together, which shows a general decrease in oxygen content with build height. This observation of oxygen decrease as a function of build height is consistent with the hypothesis that the first few millimeters of build height contribute to a Ti-gettering based purification of the build chamber and atmosphere. Whether the initial heated Ti-6Al-4V layers absorbed residual moisture from the build chamber and the powder, oxygen from leaks in the build chamber, or oxygen impurities in the cover gas/partial vacuum, remains to be investigated. However, the reduction in oxidation as a function of build height and the lack of oxidation at 35 mm build height (i.e. the sintered powder oxygen content after the build roughly matches that of the virgin powder before the build), suggests that the oxygen source for oxidation is transient instead of continuous throughout the build. Build chamber leaks and cover gas impurities would both be continuous sources of oxygen, compared to residual moisture which would exist at the beginning of the build but decrease during the build. This interpretation of likely oxygen sources will help focus future work to mitigate oxidation in PBF-EB Ti-6Al-4V.

Previous work on the oxidation kinetics of Ti in a pure H_2O environment at 850 °C revealed that oxidation at the surface is greater than when Ti is heated in a pure O_2 environment [18]. Previous work by Karlsson et al. [19] utilized time-of-flight secondary ion mass spectrometry (TOF-SIMS) and Auger electron spectroscopy (AES) to investigate the surface of PBF-EB Ti-6Al-4V with respect to oxidation. They found that for identical cubes built at different heights (using supports to vertically distance from the build plate) the oxide layer at the top surface of the cube becomes smaller with increased build height. Karlsson et al. conclude that the oxide species measured in Ref. [19] result from water molecules that are released from the powder and parts in the process chamber during preheating and melting. Possibly, a similar scenario existed in the current study with respect to residual moisture.

The bar chart in Fig. 4 displays the oxygen content as measured via inert gas fusion for the top 3 mm and bottom 3 mm of powder scraped from capsules 1D, 2A, 2B, 2C, 2D, 3A, 3B, 3C, and 3D. All nine powder capsules reveal the same height dependence for the oxygen content differences between the top 3 mm and bottom 3 mm of the cylinders. It is important to note that these cylinders represent three separate builds, suggesting the observed behavior is not an anomaly. The error bars represent 1σ standard deviation of the mean of three measurements each for the top and bottom of each cylinder. The average oxygen content for all nine cylinders are calculated to be: Top = 0.0763 ± 0.0054 wt.% O and Bottom = 0.0919 ± 0.0054 wt.% O. This is consistent with the gettering hypothesis that the bottom of the powder capsules reduce the atmosphere present at high temperatures and therefore lead to greater oxygen contents than the top of the powder capsules. This presents a problem with respect to tracking oxidation of entire powder batches when there is a differential oxidation rate of the powder bed within individual builds.

The results of both Fig. 3 and Fig. 4 suggest there is no location dependence of the observed oxidation gradient, and the dominant oxidation variation occurs in the build direction. The average bottom 3 mm oxidation (0.016 wt.% increase over virgin powder) observed after a single build is significant when considering that material specification (ASTM F3001-14) is 0.13 wt.%. Also, based on previous literature [3], a change in oxygen content from 0.08 wt.% to 0.096 wt.% would be expected to cause an approximately 50 MPa increase in tensile yield strength. This observed oxidation gradient as a function of build height has implications for powder handling and mixing, possibly exacerbating undesirable variations in mechanical properties within a single build over the life of a powder batch.

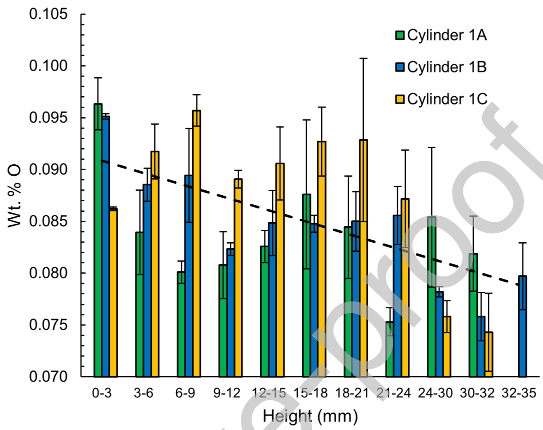

Figure 3: Bar chart representing the oxygen wt.% content in 3 mm increments for cylindrical powder capsules 1A, 1B, and 1C. Error bars represent 1σ standard deviation of three measurements for each bar.

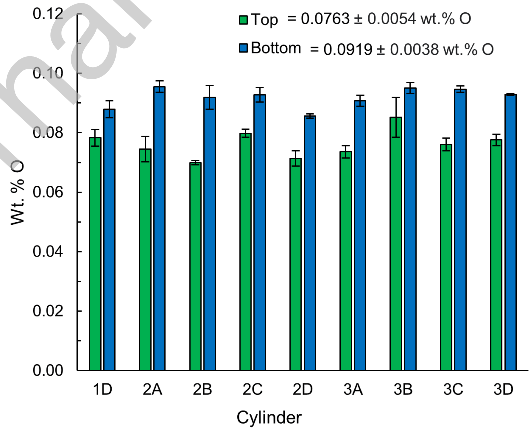

Figure 4: Bar chart representing the oxygen wt.% content from the bottom 3 mm to the top 3 mm of collected powder in the 35 mm height powder capsule. Error bars represent 1 σ standard deviation of three measurements for each of the bottom and top 3 mm of the powder capsule cylinder.

4. Conclusions

It has been shown that there is a heterogeneous oxygen concentration in the powder bed for PBF-EB Ti-6Al-4V builds. The results indicate that a Ti-gettering effect occurs during the initial stages of the PBF-EB process due to the high-background processing temperature paired with titanium's natural affinity to create a reducing environment at elevated temperatures. As the powder layers increase in height, the oxidation of the powder decreases towards nominal levels. In the case of the current work, virgin powder (0.08 wt.% O) was shown to increase on average by 0.016 wt.% O during the first 3 mm of build height, followed by a general decrease in oxidation as a function of build height. This may present issues in solid parts, as the feedstock layers that are being used for melting may have different oxygen contents as a function of height, which may lead to uncontrolled changes in mechanical properties.

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Declaration of interests

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

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: