

Article

Analysis of Face-Centered Cubic Phase in Additively Manufactured Commercially Pure Ti

Claire L. Adams ^{1,2,*} and David P. Field ^{1,2} ¹ Institute of Materials Research, Washington State University, Pullman, WA 99164, USA; dfield@wsu.edu² School of Mechanical and Materials Engineering, Washington State University, Pullman, WA 99164, USA

* Correspondence: claire.l.adams@wsu.edu

Abstract: Metal additive manufacturing is a developing technique with numerous advantages and challenges to overcome. As with all manufacturing techniques, the specific raw materials and processing parameters used have a profound influence on microstructures and the resulting behavior of materials. It is important to understand the relationship between processing and microstructures of Ti to advance knowledge of Ti-alloys in the additive field. In this study, a face-centered cubic (FCC) phase was found in grade 2 commercially pure titanium specimens, additively manufactured with directed energy deposition in an argon atmosphere. Two scanning speeds (500 and 1000 mm/min) and three scanning patterns (cross-hatched and unidirectional patterns) were investigated. Electron backscatter diffraction and energy-dispersive X-ray spectroscopy were used for microstructural and compositional analysis. Inverse pole figure, phase, and kernel average misorientation (KAM) maps were analyzed in this work. Larger amounts of the FCC phase were found in the unidirectional scanning patterns for the slower scanning speed, while the cross-hatched pattern for both scanning speeds showed a lower amount of FCC. Higher KAM averages were present in the faster scanning speed specimens. According to EDS scans, small amounts of nitrogen were uniformly distributed throughout the specimens, leading to the possibility of interstitial content as a contributing factor for development of the observed FCC phase. However, there is no clear relationship between nitrogen and the FCC phase. The formation of this FCC phase could be connected to high densities of crystalline defects from processing, plastic deformation, or the distribution of interstitials in the AM structure. An unexpected Kurdjumov–Sachs-type orientation relationship between the parent beta phase and FCC phase was found, as $\{110\}_{\text{BCC}} \parallel \{111\}_{\text{FCC}}, \langle 111 \rangle_{\text{BCC}} \parallel \langle 110 \rangle_{\text{FCC}}$.

Keywords: FCC titanium; additive manufacturing; DED; EBSD; EDS; orientation relationship



Citation: Adams, C.L.; Field, D.P. Analysis of Face-Centered Cubic Phase in Additively Manufactured Commercially Pure Ti. *Metals* **2023**, *13*, 2005. <https://doi.org/10.3390/met13122005>

Academic Editor: Eric Hug

Received: 21 November 2023

Revised: 7 December 2023

Accepted: 11 December 2023

Published: 13 December 2023



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1. Introduction

Understanding the relationships between processing, structure, and properties in additive manufacturing (AM) is important to advancing the processing techniques to more commercial applications. The various AM techniques and myriad processing parameters allow for different processing strategies to be made, impacting material performance. AM is a relatively new manufacturing method, developed within the past 40 years [1], that involves layering melted material over itself in a specific pattern to create a three-dimensional part. Design freedom is one paramount characteristic of AM. Complex geometries such as lattices, overhangs, and passageways are possible, which are not easily accessible to conventional manufacturing methods. AM offers rapid prototyping, the possibility of tailoring mechanical properties, and the capability to integrate components in a single build that would traditionally be assembled from multiple parts. While conventional forms of manufacturing can still include large machines, tedious procedures, and considerable expense; the AM technique is on the road to improving production times and cost and reducing material waste. Over the years, metal AM has gained popularity in industry and academia; however, polymers are the most prevalent AM structures in application,

and even ceramics and natural materials are being manufactured additively. Aerospace, automotive, and biomedical industries are a few of the industries where metal AM is currently advancing to produce structural components [1–9].

Laser-directed energy deposition (DED) is one common type of metal AM, which deposits metal powder, or wire, through a nozzle onto a build plate. A laser source simultaneously melts this powder in an inert atmosphere, typically argon, by creating a melt pool on top of the substrate [1,10,11]. The bed moves while the laser and nozzle stay stationary, or, in some instances, the laser and nozzle move, and 3D construction can take place. The scanning path, or specific movement of the bed, is a parameter defined by the user. Multiple nozzles can be used, which allows the DED process to produce multi-material parts as needed [1,11]. DED has high deposition rates and can produce parts and clad or repair existing parts. Its ability to produce parts to exact dimensions specified in the CAD files (especially when additive and subtractive approaches are used in combination) is important in medical, aerospace, or military industries, for example, where exact dimensions are crucial for component performance [11]. Additive strategies also reduce material consumption and improve manufacturing sustainability.

Process parameters affect everything about the build (i.e., melt pool shape, cooling rate, local thermal gradients, incident energy) and the completed part (i.e., part geometry, microstructure, porosity, mechanical properties) [11]. Suppose one process parameter changes for a new build (i.e., laser power, scanning speed, scanning pattern, layer thickness, the temperature of the build plate, and time elapsed between layers); in that case, it may create a domino effect, changing something else about the final part. The combination of process parameters needed for a successful print depends on the specific AM technique used, component design, the material it is made from, and its geometry.

While AM provides new and advanced ways of processing, its continuous thermal cycles and plethora of process parameters also introduce challenges. An understanding of processing and material fundamentals is essential for the progress of AM. The microstructure of the part will depend on its thermal history from the print. Microstructure and grain size can vary throughout a printed part, where the top and bottom regions of a part may have different microstructures and consist of both tensile and compressive residual stresses [11]. Material properties, which are related to microstructure, are affected by AM whether advantageous or disadvantageous, so they must be understood and controlled [1,11,12]. Stresses are induced by thermal processing cycles and cooling rates, which may cause distortion or warping to a part [13] and may reduce the strength or lifespan of a part [11].

Significant AM research has been reported on titanium alloy Ti6Al4V (Ti-64) due to strength-to-weight ratio, corrosion resistance, and biocompatibility [14–16]. For this work, however, commercially pure titanium (CpTi) was chosen since it is crucial to understand the basics before the complex. Elements of this fundamental investigation will add to the foundation of AM research. This work found an unexpected face-centered cubic (FCC) phase in the manufactured specimens. No FCC phase is located on the titanium phase diagram because these diagrams only show equilibrium phases [17,18]. At high temperatures, there exists a body centered cubic (BCC) phase designated as Ti- β , while at lower temperatures, a stable hexagonal close packed phase (HCP) forms as Ti- α [19,20].

FCC phases have been reported in CpTi and Ti-alloys [18–24], and some reports on FCC forming in additive processed specimens [17,25]. It has been described that the FCC phase impacts mechanical performance [17,25]. Wang et al. considered Ti-64 and laser powder bed fusion (L-PBF) for their study, while Zhou et al. examined CpTi and pure aluminum with ultrasonic AM for thin film laminates. No reports were found on an FCC phase forming in CpTi from DED processing, but it could be expected that the issues leading to the so-called “C-phase” formation in Ti-64 would be similar for CpTi [17].

2. Materials and Methods

A powder-based DED Form alloy printer (Spring Valley, CA, USA) was used to create rectangular samples of grade 2 CpTi on a CpTi build plate in an argon atmosphere (<50 ppm of oxygen). Information on varied process parameters for six printed samples, labeled A through F, can be seen in Table 1 and Figure 1. Note that the 90° unidirectional pattern is parallel to the shorter edge of the rectangular specimen, while the 0° unidirectional pattern is parallel to the longer edge. All constant process parameters can be seen in Table 2. No support structures were used in the build, and the bed was not preheated.

Table 1. Varied process parameters for printed samples.

		Scanning Pattern		
		Cross Hatch	90° Unidirectional	0° Unidirectional
Scanning Speed (mm/min)	500	A	C	E
	1000	B	D	F

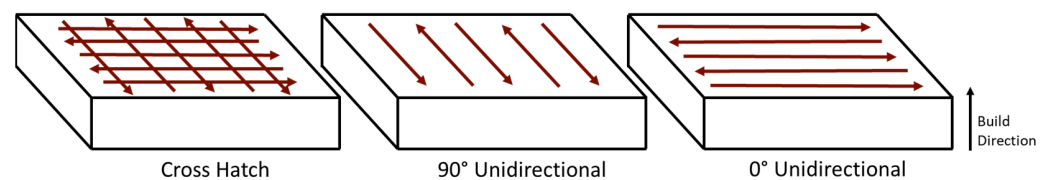


Figure 1. Illustration of scanning patterns used for printed rectangular samples A–F. Note the 90° pattern is parallel to the shorter (10 mm) edge while the 0° pattern is parallel to the longer (20 mm) edge.

Table 2. Constant process parameters for printed samples.

Laser Power (W)	Layer Thickness (mm)	Layer Spacing (mm)	Powder Feeder Disk Rate (rpm)	Shield Gas Flow Rate (L/min)	Carrier Gas Flow Rate (L/min)
350	0.2	0.8	0.4	16	8

Each sample was programmed to be 20 mm × 10 mm × 10 mm; however, in reality, the heights varied slightly. This was due to variation in process parameters including laser power, scanning speed, layer height, and flow rate. Overbuilding occurred, meaning the experimental layer height was higher than the desired theoretical layer height. Overbuilding can occur from slower scanning speeds combined with higher powder flow rates, resulting in a higher power density. Current DED systems are unable to account for height variations for the deposited material [26]. Therefore, some scans were stopped before the theoretical 10 mm layer height was reached. These parameters must be optimized so the experimental parameters match the theoretical.

Samples were left attached to the build plate during sample preparation. Cross sections, as illustrated in Figure 2, were cut with a diamond slow saw, grinded (240, 320, 400, 600, 800, 1200 grit silicon carbide discs), and polished (5 µm, 3 µm, 1 µm, 0.3 µm alumina slurry, and 0.05 µm colloidal silica). The cross sections were then analyzed with a Thermo Scientific Apreo scanning electron microscope (SEM), with EDAX APEX V2.5.1000 Software for electron backscatter diffraction (EBSD), and energy dispersive spectroscopy (EDS) to characterize microstructure and composition. EBSD scans were completed with a beam voltage of 20 kV, current of 13 nA, a working distance of approximately 10 mm, and a step size of 0.1 µm. EDS was completed at the same working distance and voltage, but with a current of 0.80 nA. It should be noted that measurements taken with EBSD and EDS are surface measurements, and cutting and polishing the specimen will release some residual stresses in the material. In addition, as titanium has an affinity for oxygen, nitrogen, and

carbon, it is expected that these elements will be present on the newly prepared surfaces even if they do not exist in the bulk specimen.

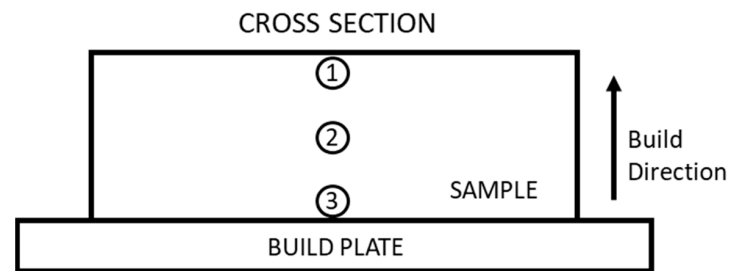


Figure 2. Schematic of the additive sample cross section. EBSD and EDS scans were taken at the top, middle, and bottom locations along the height of a built sample, labeled as 1, 2, and 3, respectively.

3. Results

Three EBSD scans were taken per additive sample as pictured in Figure 2, near the top, middle, and bottom of the specimen. Orientation maps, often referred to as inverse pole figure (IPF) maps, can be seen in Figures 3 and 4 for 500 mm/min and 1000 mm/min scanning speeds, respectively. The IPF color key refers to orientations that are aligned with the sample normal direction (transverse to the build direction of the AM specimens). IPF maps show a transformation structure, as expected. The EBSD data have been filtered so that all orientations shown have a confidence index of at least 0.1 ($CI > 0.100$). There was also a grain confidence index standardization cleanup, with a grain tolerance angle of 5 and minimum grain size of 5. No other data manipulation was performed.

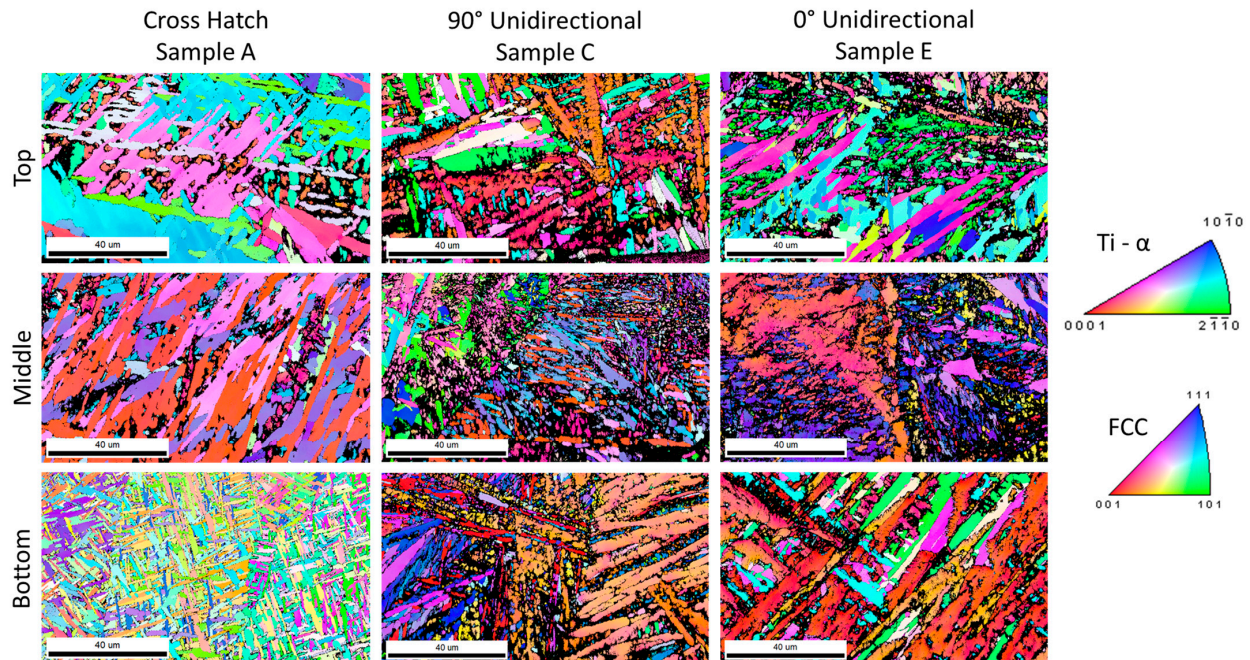


Figure 3. Inverse pole figure maps for 500 mm/min scanning speed samples, with 40 µm scale bars, and corresponding inverse pole figure color keys for each phase. Colors denote poles aligned with the sample normal direction (transverse to the build direction) The scan pattern and scan location are labeled.

Phase maps can be seen in Figures 5 and 6, showing both Ti- α and FCC phases, labeled as red and yellow, respectively. There is more FCC phase present in the unidirectional scanning patterns for the slower scanning speed samples. When comparing the IPF

maps with the phase maps, the FCC phase consists mainly of one orientation, while the Ti- α phase contains many orientations (all corresponding to the expected BCC to HCP orientation relationship).

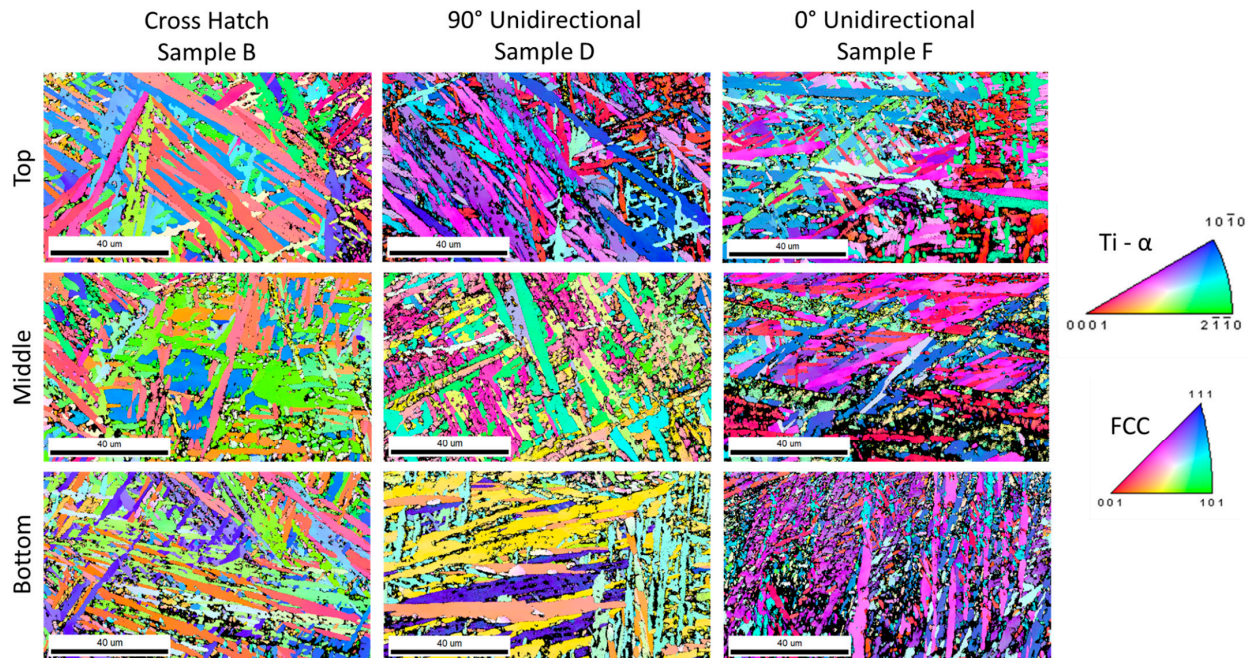


Figure 4. Inverse pole figure maps for 1000 mm/min scanning speed samples, with 40 μm scale bars, and corresponding inverse pole figures color keys for each phase. Colors denote poles aligned with the sample normal direction (transverse to the build direction) The scan pattern and scan location are labeled.

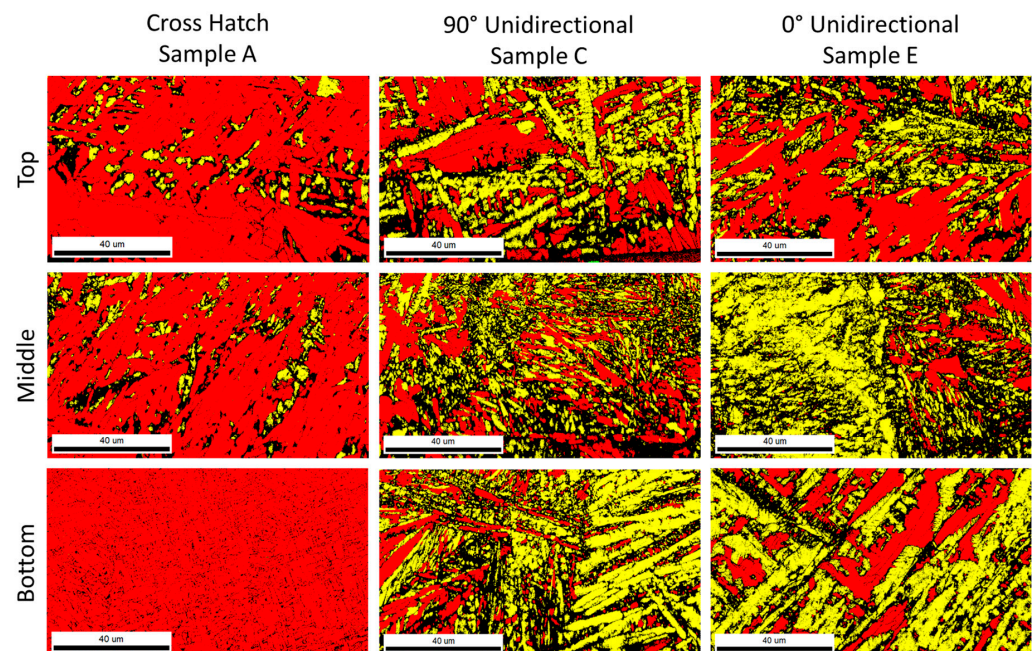


Figure 5. Phase maps of 500 mm/min scanning speed samples, with 40 μm scale bars. The scan pattern and scan location are labeled. Red-colored regions correspond to the titanium alpha phase, while yellow-colored regions correspond to the face-centered cubic phase.

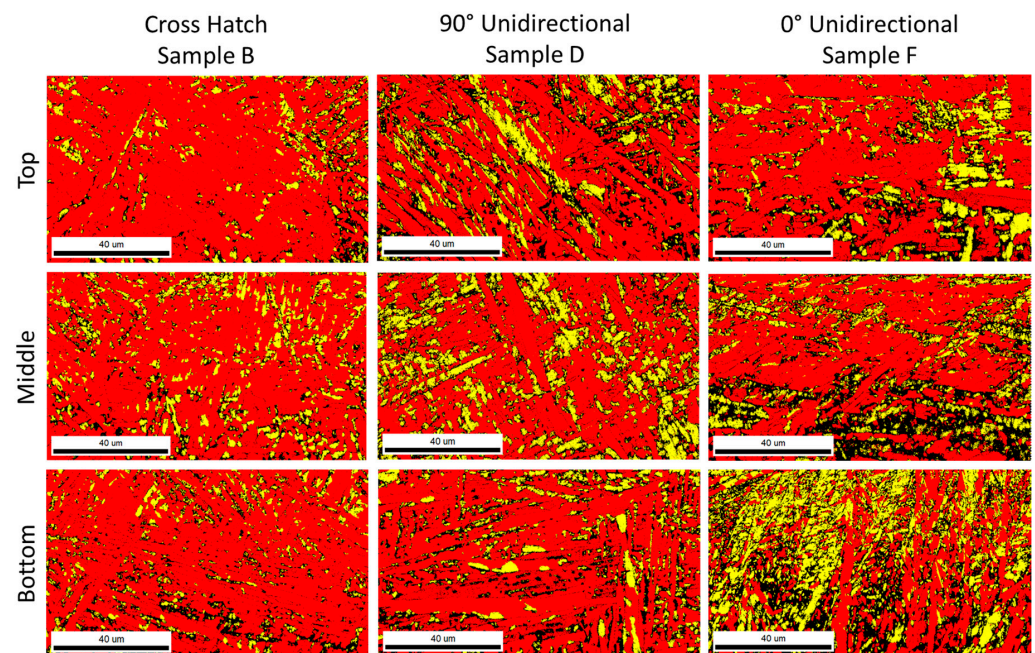


Figure 6. Phase maps of 1000 mm/min scanning speed samples, with 40 µm scale bars. The scan pattern and scan location are labeled. Red-colored regions correspond to the titanium alpha phase, while yellow-colored regions correspond to the face-centered cubic phase.

Third nearest neighbor kernel average misorientation (KAM) maps can be seen in Figures 7 and 8, where the maximum allowable misorientation in the kernel was set to 5 degrees. When comparing the KAM maps to the phase maps, it is seen that the higher KAM values are associated with the FCC phase. Furthermore, all black regions between grains observed in Figures 3–8 correspond to areas of low confidence EBSD data and are not considered in the analysis.

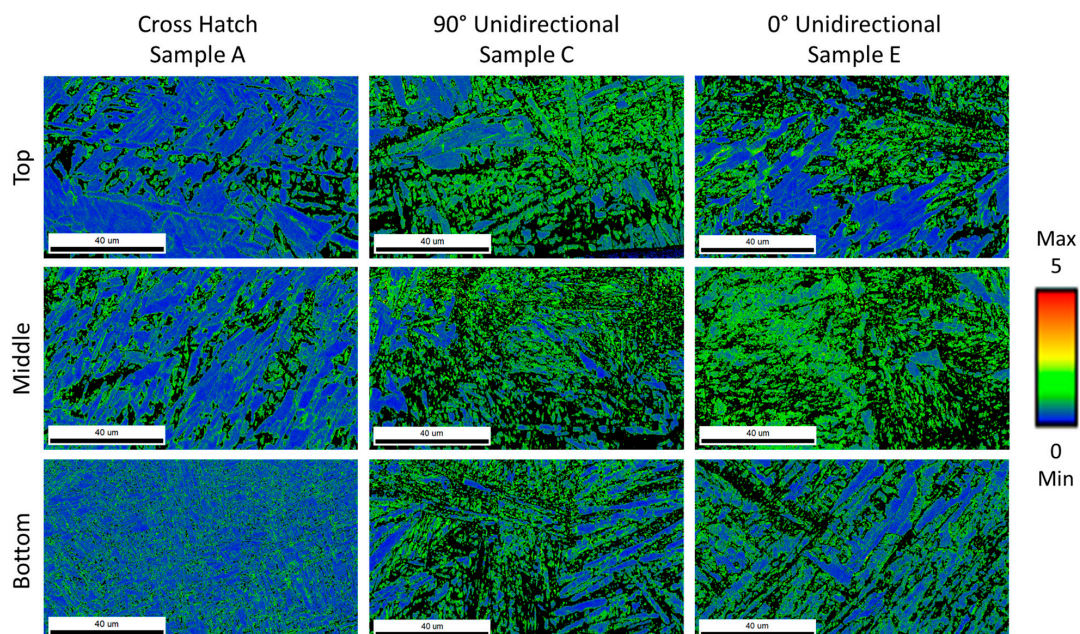


Figure 7. Kernel average misorientation maps of 500 mm/min scanning speed samples, with 40 µm scale bar. The scan pattern and scan location are labeled. The colored bar denotes degrees of misorientation.

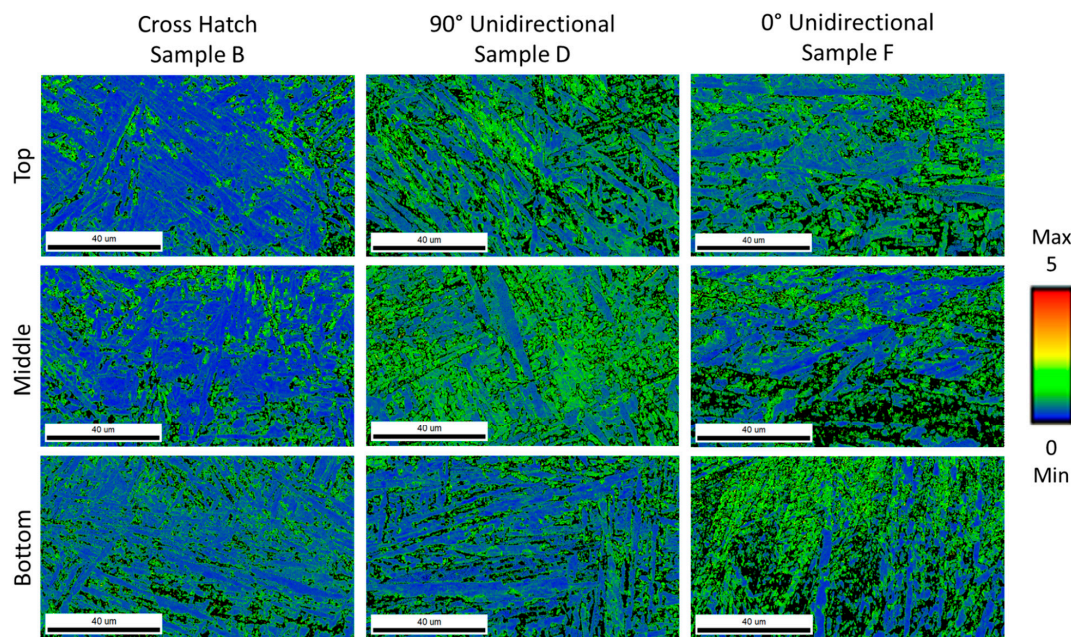


Figure 8. Kernel average misorientation maps of 1000 mm/min scanning speed samples, with 40 µm scale bar. The scan pattern and scan location are labeled. The colored bar denotes degrees of misorientation.

Figure 9 displays plotted KAM values for each specimen, organized by scanning speed and phase. These plots confirm that higher KAM values were generally found in FCC phases, with the highest being in the faster scanning speed. Three regions were analyzed for each measurement and the KAM averages for each area were found. Error bars were created from the standard deviation of these calculated KAM averages.

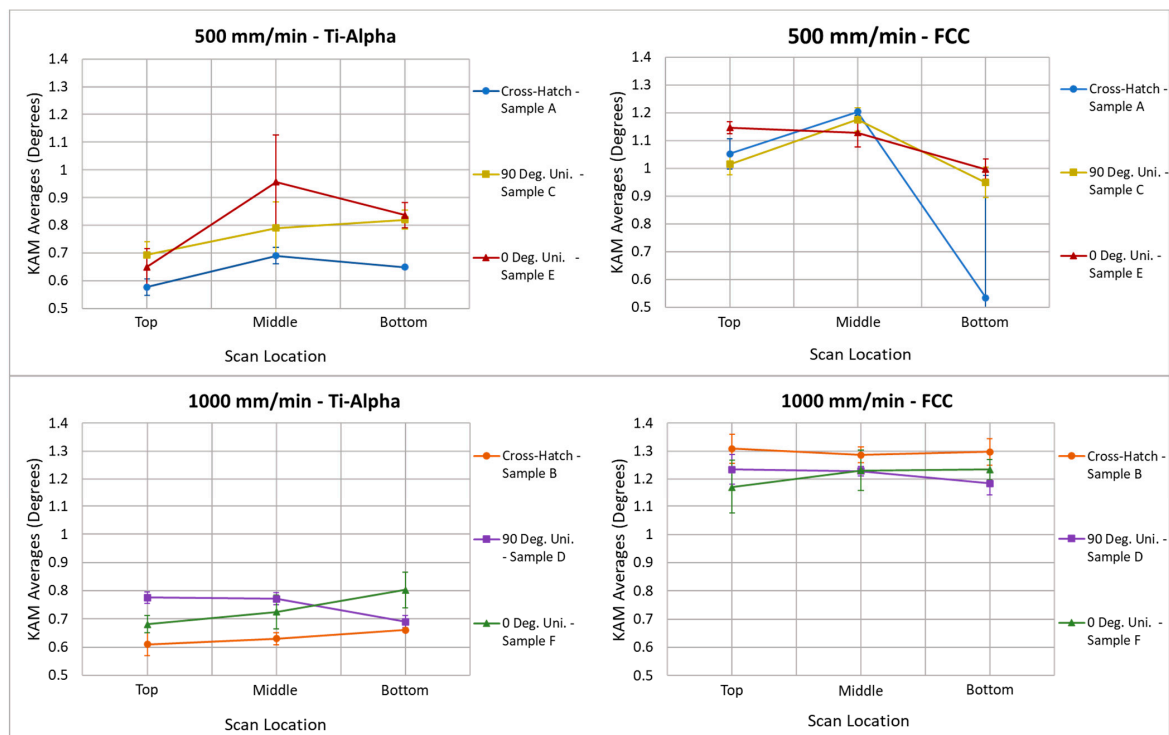


Figure 9. Comparison of KAM map averages for specific scanning speed and phase. The scan pattern and scan location are labeled.

In addition, Figure 10 displays an overall EDS spectrum. Only one sample is represented since all EDS data were similar. EDS element maps were also created from EDS data but are not shown here since there are no apparent defining features connecting nitrogen content to the FCC phase. An even distribution of nitrogen was displayed in all maps. This is not surprising since titanium has a standard $L\alpha$ energy of 0.452 keV and nitrogen has a $K\alpha$ energy of 0.392 keV [27], causing these peaks to overlap on the spectrum with sophisticated deconvolution techniques required to determine quantitative concentrations of these elements. Oxygen was not observed in the spectra above the noise threshold (about 0.05%), but the overall spectra generally indicated Ti and N peaks. The small peak seen at 2.77 keV is the escape peak from the Ti $K\alpha$ peak and is herein ignored.

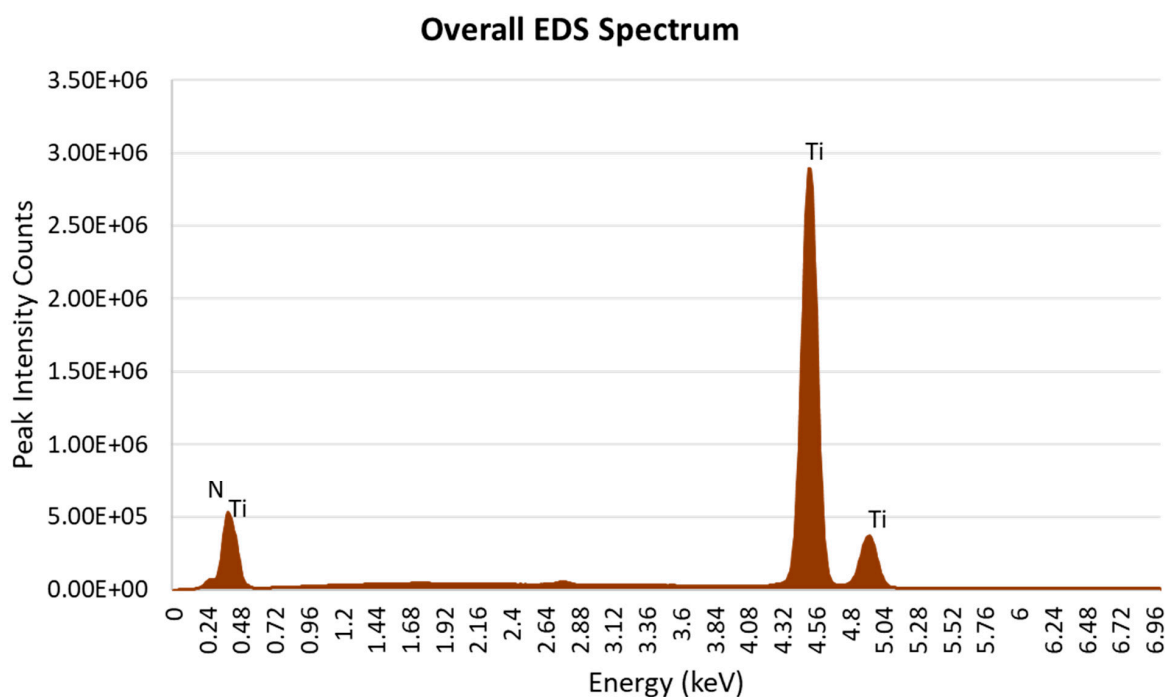


Figure 10. The overall energy dispersive X-ray spectroscopy spectrum, showing strong titanium peaks and perhaps the presence of nitrogen.

4. Discussion

IPF maps show a transformation or Widmanstätten structure, which is expected for rapidly cooled alpha titanium alloys. The maps shown are reconstructions of the grain structure, in which the grains are colored according to their crystallographic pole aligned with the surface normal direction. It can be noticed that FCC regions are mainly one crystallographic orientation, while Ti- α regions consist of many orientations. Beta parent grains were reconstructed from the alpha phase using OIM Analysis, assuming the standard orientation relationship between BCC and HCP titanium phases. Grain boundaries of the parent beta phase have not been superimposed on IPF maps since these observations were over small regions and generally within a single parent grain. When the FCC titanium phase was compared with the reconstructed beta titanium phase, the orientation relationship found is $\{110\}_{\text{BCC}} \parallel \{111\}_{\text{FCC}}$, $\langle 111 \rangle_{\text{BCC}} \parallel \langle 110 \rangle_{\text{FCC}}$. This resembles the Kurdjumov–Sachs (K–S) orientation relationship between the reconstructed BCC beta and FCC phases. The K–S relationship was observed in 1930 and was identified in mild steel when describing the martensitic transformation [28]. The K–S orientation relationship in this work offers evidence that the material consisted of a complete beta structure at high temperatures and then transitioned to FCC in some regions when cooled, while the remaining structure transformed to alpha titanium, as expected. If the FCC structure had formed after the transition to HCP, it would be less likely that the FCC grains

were all of the same orientation, and it would be highly unlikely that a known orientation relationship would be observed. This supports the argument that the FCC phase formed from prior beta grains.

Two complimentary studies [29,30] showcased the transformation of a BCC to FCC phase in $\text{Fe}_{17}\text{Mn}_5\text{Si}_{10}\text{Cr}_4\text{Ni}$ shape memory alloy manufactured through LPBF in an argon atmosphere. It was found that the amount of FCC increased with increasing laser power, and that the BCC and FCC phases showed a K–S orientation relationship [30]. The samples were heat treated after printing to try to dissolve any undesirable BCC phase, since shape memory effects in these alloys are due to transformations between HCP and FCC phases. However, BCC was suggested to be the primary solidification phase from LPBF, and that at high-volume energy densities and low cooling rates, FCC nucleated from BCC grain boundaries [29]. EBSD and XRD were used to identify these phases. While these complimentary studies consisted of a shape memory alloy rather than titanium, they demonstrate that an FCC phase can form from BCC not typical of the material, and that there exists a K–S orientation relationship between BCC and FCC phases.

In this current work, there is more FCC found in slower-scanning-speed specimens. Since it is assumed from the previously introduced complimentary studies that the BCC-to-FCC transformation is highly affected by the volume energy density, and that more FCC was found in higher laser powers, perhaps the combination of laser power and slow scanning speed in this study created the stress conditions conducive for FCC to form. The FCC phase specifically is more prominent in unidirectional scanning patterns for the slower scanning speed specimens, represented in Figure 11. The cross-hatched pattern has approximately the same amount of FCC for both scanning speeds. This shows that differences in scanning patterns may impact the formation of the FCC phase as well.

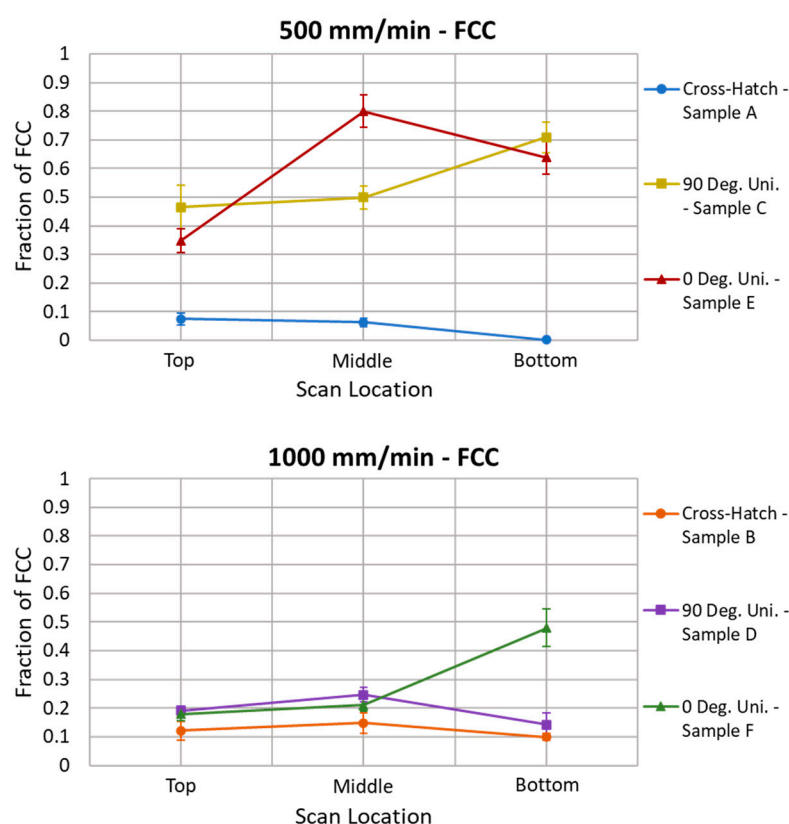


Figure 11. Fraction of FCC comparison between scanning speeds.

KAM maps measure the average misorientation of a given point with respect to its neighboring points [31–35]. The number of neighboring points is defined as the kernel which surrounds the point of interest [36]. In general, the maps provide a visual representa-

tion where regions of local misorientation is high [31]. KAM maps reflect changes in lattice orientation and local lattice curvature which can be related to and provide a qualitative measurement of geometrically necessary dislocation (GND) density distribution [32,36,37], which is an indirect indication of plastic strain and residual stresses [25,33,36].

Plotted KAM averages for each phase, scan speed, scan pattern, and sample location are seen in Figure 9. Three regions were analyzed for each measurement and the KAM averages for each area were found. The standard deviation was calculated from these averages, and error bars were created and shown on Figure 9. When only looking at the slower scanning speed (500 mm/min) results, the Ti- α phase has lower KAM values than the FCC phase. Additionally, the top scans for the Ti- α phase (higher in the build sequence) have the lowest KAM values for each individual sample of this scanning speed. This means there is more lattice curvature in FCC and less in Ti- α near the top of the specimen. It is likely that part of the reason that the FCC phase formed was from geometrical restrictions that impeded formation of the HCP phase. In this reasoning, it is reasonable that there may be more lattice curvature in the FCC phase, resulting from, and contributing to, the residual strains in the lattice at that point.

For the faster scanning speed (1000 mm/min), there is a larger difference in KAM values between Ti-alpha and FCC phases compared to the slower scanning speed samples. The FCC phase here shows the highest average KAM value of all scanning speeds; within those, the cross-hatched pattern holds the highest value for FCC. The cross-hatched pattern holds the lowest KAM values when looking at the Ti- α phase of this scanning speed. With a faster scanning speed, the material cools more rapidly in the additive process since the heat source quickly moves away from the deposited material. Faster cooling rates relate to more deformation in the material; thus, it makes sense that there are higher KAM averages in the faster scanning speed. Furthermore, the two unidirectional patterns behave similarly on the plots as far as the observed trends. In both cases, the 90°-pattern has higher KAM averages near the top of the specimen and lower KAM averages near the bottom, while it is vice-versa for the 0°-pattern. The curves intersect around the middle of the specimen.

When referring to only the cross-hatched pattern of the Ti- α phase, both scanning speeds have similar KAM values ranging from approximately 0.6 to 0.7°, which reflects the lowest KAM for Ti- α . However, the cross-hatched pattern for the FCC phase has the highest KAM averages for both scanning speeds, ignoring the possible outlier in Sample A where very little FCC phase was present.

EDS element maps were identical for all samples, showing a uniform distribution throughout the region. There is no difference or clear distribution of nitrogen between Ti- α and FCC phases. One EDS spectrum showing titanium and nitrogen peaks is presented since all spectra for all samples looked similar, with only small variations in the weight percent of nitrogen. EDS is not the most dependable characterization method because of its surface sensitivity confined to approximately 1 μm of depth [38]. Additionally, certain peaks within EDS spectra may overlap with one another, making it difficult to properly determine quantitative values. This is particularly the case with titanium and nitrogen peaks. It is also less effective at identifying trace elements, meaning elements of low concentrations. However, it provides detailed multielement detection, with a spatial resolution on the order of a micron [38].

Grade 2 CpTi has a maximum amount of 0.03 wt% nitrogen [39–42]. The measured nitrogen in this work exceeded that with values in the range of 3 wt% using standardless quantification, depending on the scanning pattern and location of scan. In one study using X-ray diffraction, the weight percent of nitrogen was found to be higher in CpTi when produced from laser powder bed fusion (LPBF) additive than the wrought CpTi [43]. In general, the nitrogen content exceeded the grade 2 specification. The material became closer to grade 3 than grade 2 according to the values obtained. The additive samples were created in an argon atmosphere, yet they assume that nitrogen impurities were picked up from the LPBF chamber. In addition, they claim higher temperatures lead to more nitrogen pick-up [43].

In this work, it may be possible that nitrogen was picked up from the DED chamber. It is important to note that EDS has its limitations and may not provide accurate quantitative results. While the exact content of nitrogen in these additive samples are not precisely ascertained from EDS, it can be assumed that a non-negligible amount of interstitial impurities are present. Middle and bottom scans consistently contained the most nitrogen in each sample, and their amounts were relatively equal, whereas there was less nitrogen in the top scans. There does not seem to be a clear relationship between KAM averages and the greater amount of nitrogen near the bottom of specimens. Figure 9 shows that some bottom scans have the greatest KAM value, but this is not true for all plots.

The EDS spectra in Figure 10 shows titanium and nitrogen peaks. Titanium and nitrogen peaks overlap around 0.4 keV due to their X-ray energies being similar. The small peak to the left of the overlapping peaks around 0.27 wt% belongs to carbon, which can commonly be detected in these spectra due to hydro-carbon contamination.

The solubilities of interstitials in HCP and FCC are significantly larger than solubilities in BCC [44]. HCP and FCC structures contain more accessible sites for interstitials than BCC with its limited interstitial sites. Nitrogen can dissolve in CpTi and Ti-alloys in the alpha phase [45], possesses a greater solubility in HCP forms of titanium than BCC forms [46], and may alter Ti microstructures [45]. Below the crystallographic transformation point, the solubility of nitrogen in titanium is higher than above this transformation point [46]. KAM results imply the existence of residual stresses, and EDS results suggest that impurities are present. Based on considerations of solubility, there should be less stress with higher solubility structures such as HCP and FCC since a high solubility means that interstitials have more locations to fill once mixed into the matrix. That is not necessarily the case here since KAM maps show regions of significant stresses in the FCC phase. However, the KAM values show the presence of significant local lattice rotations in some regions in spite of any residual stress advantage that would be gained from higher solubility of interstitials in the FCC and HCP phases.

The titanium phase diagram consists of BCC and HCP phases. These diagrams do not include an FCC phase because it is typically considered a metastable phase. However, an FCC phase can indeed occur in Ti-alloys and Ti multilayer structures, but it has been reported less in additively built Ti. FCC phases in Ti are sometimes considered hydrides, nitrides, or oxides, rather than allotropes [19]; sometimes, the FCC phase is considered phase segments that have been stabilized through defects [17]. In one study by Chang et al., an FCC phase was found in cold-rolled CpTi, which they report as a Ti-hydride. The hydrides may have occurred during specimen preparation, where hydrogen was introduced during electropolishing. They report two possible orientation relationships, either $\{1\bar{1}00\}_{\text{HCP}} \parallel \{1\bar{1}0\}_{\text{FCC}}$, $\langle 0001 \rangle_{\text{HCP}} \parallel \langle 001 \rangle_{\text{FCC}}$, or $\{0002\}_{\text{HCP}} \parallel \{111\}_{\text{FCC}}$, $\langle \bar{1}2\bar{1}0 \rangle_{\text{HCP}} \parallel \langle 1\bar{1}0 \rangle_{\text{FCC}}$ [19]. However, the additive specimens prepared for this current work were manually polished, so the FCC phase is presumed not to be a hydride in this case.

An FCC phase may also form in CpTi from attrition milling (ball milling), as reported by Manna et al. They claim that this FCC phase is unlikely to be a hydride, nitride, oxide, or carbide; it is not impurity driven. Attrition milling introduces crystal defects, such as dislocations and twins, that may be associated with this FCC phase due to their density influence. Attrition milling causes grain refinement, nanocrystallization, increasing lattice expansion, and plastic strain to occur, which could be responsible for this HCP to FCC transformation. Negative hydrostatic pressure arises from these features, causing structural instability [18].

An FCC phase in Al-Ti powder was also introduced from high-energy ball milling, as reported by Zhang et al. Thin layers of Ti formed in particles after eight hours of milling, and a small amount of an FCC phase was found. Powders were then heated, and it was discovered that 321 °C was the onset temperature for the transformation of HCP to FCC to occur. This phase is not assumed to be a hydride or an oxide. It is thought that the FCC

phase forms from an endothermic transformation from heating the particles. Therefore, longer milling times and the addition of heat activates the FCC phase [20].

AM subjects alloys to sudden thermal stress from the repeated heating cycles and has the potential to introduce interstitials. Wang et al. reported an FCC phase occurring in Ti-64, manufactured from laser powder bed fusion (L-PBF), due to oxygen interstitials. They reported that the FCC phase has different lattice parameters than a hydride or oxide, and conclude that the FCC phase forms from plastic deformation of the oxygen rich regions through the cyclic thermal loading of AM. The oxygen diffusion, enhanced through heating, from an oxide surface layer stabilizes the FCC phase. An orientation relationship was reported as $\{0001\}_{\text{HCP}} \parallel \{111\}_{\text{FCC}}, \langle 12\bar{1}0 \rangle_{\text{HCP}} \parallel \langle 110 \rangle_{\text{FCC}}$ [17], which is similar to the observations in this study.

Zhou et al. presented an FCC phase in a Ti/Al laminate made from ultrasonic AM. The material is subjected to severe plastic deformation, so the HCP to FCC transition may have formed to accommodate external strain. They claim the FCC phase is not a hydride but develops from interface shearing during their ultrasonic AM process. Partial dislocations were found in the proximity of the FCC phase, so it is expected that the gliding of Shockley partial dislocations is also a cause of this phase. The same orientation relationship was reported, namely, $\{0002\}_{\text{HCP}} \parallel \{111\}_{\text{FCC}}, \langle 2\bar{1}10 \rangle_{\text{HCP}} \parallel \langle 011 \rangle_{\text{FCC}}$ [25].

Considering the various studies briefly summarized above, the main causes of the formation of an FCC phase in this work could be thermal gradients from cyclic thermal loading, high densities of crystalline defects from processing, plastic deformation, the diffusion of interstitials, and the movement of dislocations. It was also mentioned that the FCC phase could be heat activated. When thinking about AM, it may make sense that the slower scanning speed specimens exhibited a larger amount of this FCC phase. The heat source travels across the surface more slowly, meaning it lingers in the recently deposited material longer than at a faster scanning speed. This deposited material cools more slowly, thus allowing more heat and time for the FCC phase to form compared with faster scanning speeds. Due to sample preparation, it is unlikely that hydrides cause this FCC phase. Since nitrogen was found in EDS scans, there may be some effect of the nitrogen interstitials in the additive specimens. However, there is no apparent connection with the amount of nitrogen found when considering the FCC phase since it encompasses a uniform distribution. Additionally, X-ray diffraction analysis, as well as physical mechanical property evaluation, would provide interesting complimentary information to this study but is beyond the scope of this present work.

5. Conclusions

An FCC phase has formed in additively manufactured commercially pure titanium, showing a Kurdjumov–Sachs orientation relationship between the parent beta phase and FCC phase as $\{110\}_{\text{BCC}} \parallel \{111\}_{\text{FCC}}, \langle 111 \rangle_{\text{BCC}} \parallel \langle 110 \rangle_{\text{FCC}}$. This suggests the material consisted of a complete beta structure at high temperatures and then transitioned to a combination of FCC and HCP. A larger amount of the FCC phase was found in unidirectional scanning patterns for the slower scanning speed specimens, while the cross-hatched pattern for both scanning speeds showed a lower amount of FCC, indicating that the scanning pattern could impact the formation of the FCC phase. Additionally, this FCC phase could be influenced or activated by the heating of the additive process, suggesting scanning speed could be a cause. The highest KAM averages belong to the FCC phase of the faster scanning speed specimens due to faster cooling in the additive process, causing more deformation in the material. There is a larger difference in KAM averages between Ti- α and FCC phases for the faster scanning speed. The cross-hatched pattern for the Ti- α phase shows the lowest KAM averages, while this pattern for the FCC phase shows the highest KAM averages, illustrating that there could be some inverse relationships between the Ti- α and FCC phases. The FCC phase must have more local lattice curvature and higher GND density, relating to higher local plastic strain. Additional EBSD scans are necessary to

identify clear relationships between EDS and KAM results and apparent trends throughout the height of the build.

Author Contributions: Conceptualization, C.L.A. and D.P.F.; Methodology, C.L.A.; Validation, C.L.A. and D.P.F.; Formal Analysis, C.L.A. and D.P.F.; Investigation, C.L.A.; Data Curation, C.L.A.; Writing—Original Draft Preparation, C.L.A.; Writing—Review and Editing, C.L.A. and D.P.F.; Supervision, D.P.F. All authors have read and agreed to the published version of the manuscript.

Funding: The equipment for this research was funded, in part, by the Joint Center for Deployment and Research in Earth Abundant Materials (JCDREAM). This work was supported by the U.S. Department of Energy through the Los Alamos National Laboratory. Los Alamos National Laboratory is operated by Triad National Security, LLC, for the National Nuclear Security Administration of the U.S. Department of Energy under Contract 89233218CNA000001. This work was funded through Los Alamos National Laboratory Directed Research and Development (LDRD) Project DR20230128.

Data Availability Statement: The authors declare that all data supporting the findings of this study are available within the paper.

Acknowledgments: The authors would like to acknowledge Amit Bandyopadhyay for the use of additive equipment and Cory Groden for equipment operation.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Bandyopadhyay, A.; Bose, S. *Additive Manufacturing*, 2nd ed.; CRC Press: Boca Raton, FL, USA, 2019.
2. Pasang, T.; Budiman, A.S.; Wang, J.C.; Jiang, C.P.; Boyer, R.; Williams, J.; Misiolek, W.Z. Additive manufacturing of titanium alloys—Enabling re-manufacturing of aerospace and biomedical components. *Microelectron. Eng.* **2023**, *270*, 111935. [\[CrossRef\]](#)
3. Zhao, N.; Parthasarathy, M.; Patil, S.; Coates, D.; Myers, K.; Zhu, H.; Li, W. Direct additive manufacturing of metal parts for automotive applications. *J. Manuf. Syst.* **2023**, *68*, 368–375. [\[CrossRef\]](#)
4. Alami, A.H.; Olabi, A.G.; Alashkar, A.; Alasad, S.; Aljaghoub, H.; Rezk, H.; Abdelkareem, M.A. Additive manufacturing in the aerospace and automotive industries: Recent trends and role in achieving sustainable development goals. *Ain Shams Eng. J.* **2023**, *14*, 102516. [\[CrossRef\]](#)
5. Omiyale, B.O.; Olugbade, T.O.; Abioye, T.E.; Farayibi, P.K. Wire arc additive manufacturing of aluminium alloys for aerospace and automotive applications: A review. *Mater. Sci. Technol.* **2022**, *38*, 391–408. [\[CrossRef\]](#)
6. İyibilgin, O.; Gepek, E. Additive Manufacturing Technologies and its Future in Industrial Applications. *Int. J. Integr. Eng.* **2021**, *13*, 245–257.
7. Pant, M.; Pidge, P.; Kumar, H.; Nagdeve, L.; Moona, G.C. Additive manufacturing: The significant role in biomedical and aerospace applications. *Indian J. Eng. Mater. Sci.* **2021**, *28*, 330–342.
8. Top, N.; Şahin, İ.; Gökçe, H.; Gökçe, H. Computer-aided design and additive manufacturing of bone scaffolds for tissue engineering: State of the art. *J. Mater. Res.* **2021**, *36*, 3725–3745. [\[CrossRef\]](#)
9. Shah, R.; Pai, N.; Rosenkranz, A.; Shirvani, K.; Marian, M. Tribological Behavior of Additively Manufactured Metal Components. *J. Manuf. Mater. Proc.* **2022**, *6*, 138. [\[CrossRef\]](#)
10. Wang, Z.; Palmer, T.A.; Beese, A.M. Effect of processing parameters on microstructure and tensile properties of austenitic stainless steel 304L made by directed energy deposition additive manufacturing. *Acta Mater.* **2016**, *110*, 226–235. [\[CrossRef\]](#)
11. Shamsaei, N.; Yadollahi, A.; Bian, L.; Thompson, S.M. An overview of Direct Laser Deposition for additive manufacturing; Part II: Mechanical behavior, process parameter optimization and control. *Addit. Manuf.* **2015**, *8*, 12–35. [\[CrossRef\]](#)
12. Carpenter, K.; Tabei, A. On Residual Stress Development, Prevention, and Compensation in Metal Additive Manufacturing. *Materials* **2020**, *13*, 255. [\[CrossRef\]](#)
13. Bartlett, J.L.; Li, X. An overview of residual stresses in metal powder bed fusion. *Addit. Manuf.* **2019**, *27*, 131–149. [\[CrossRef\]](#)
14. Liu, S.; Shin, Y. Additive manufacturing of Ti6Al4V alloy: A review. *Mater. Des.* **2019**, *164*, 107552. [\[CrossRef\]](#)
15. Shipley, H.; McDonnell, D.; Culleton, M.; Coull, R.; Lupoi, R.; O'Donnell, G.; Trimble, D. Optimisation of process parameters to address fundamental challenges during selective laser melting of Ti-6Al-4V: A review. *Int. J. Mach. Tools Manuf.* **2018**, *128*, 1–20. [\[CrossRef\]](#)
16. Nguyen, H.D.; Pramanik, A.; Basak, A.K.; Dong, Y.; Prakash, C.; Debnath, S.; Shankar, S.; Jawahir, I.S.; Dixit, S.; Buddhi, D. A critical review on additive manufacturing of Ti-6Al-4V alloy: Microstructure and mechanical properties. *J. Mater. Res. Technol.* **2022**, *18*, 4641–4661. [\[CrossRef\]](#)
17. Wang, H.; Chao, Q.; Cui, X.Y.; Chen, Z.B.; Breen, A.J.; Cabral, M.; Haghdadi, N.; Huang, Q.W.; Niu, R.M.; Chen, H.S.; et al. Introducing C phase in additively manufactured Ti-6Al-4V: A new oxygen stabilized face-centered cubic solid solution with improved mechanical properties. *Mater. Today* **2022**, *61*, 11–21. [\[CrossRef\]](#)
18. Manna, I.; Chattopadhyay, P.P.; Nandi, P.; Banhart, F.; Fecht, H.J. Formation of face-centered-cubic titanium by mechanical attrition. *J. Appl. Phys.* **2003**, *93*, 1520–1524. [\[CrossRef\]](#)

19. Chang, T.; Zhang, S.; Liebscher, C.; Dye, D. Could face-centered cubic titanium in cold-rolled commercially-pure titanium only be a Ti-hydride? *Scr. Mater.* **2020**, *178*, 39–43. [\[CrossRef\]](#)
20. Zhang, D.L.; Ying, D.Y. Formation of fcc titanium during heating high energy ball milled Al-Ti powders. *Mater. Lett.* **2002**, *52*, 329–333. [\[CrossRef\]](#)
21. Banerjee, R.; Dregia, S.; Fraser, H.L. Stability of f.c.c titanium in titanium/aluminum multilayers. *Acta Mater.* **1999**, *47*, 4225–4231. [\[CrossRef\]](#)
22. Sugawara, Y.; Shibata, N.; Hara, S.; Ikuhara, Y. Interface structure of face-centered-cubic-Ti thin film grown on 6H-SiC substrate. *J. Mater. Res.* **2000**, *15*, 2121–2124. [\[CrossRef\]](#)
23. Sarkar, R.; Ghosal, P.; Prasad, K.S.; Nandy, T.K. An FCC phase in a metastable β -titanium alloy. *Philos. Mag. Lett.* **2014**, *94*, 311–318. [\[CrossRef\]](#)
24. Jankowski, A.F.; Wall, M.A. Formation of face-centered cubic titanium on a Ni single crystal and in Ni-Ti multilayers. *J. Mater. Res.* **1994**, *9*, 31–38. [\[CrossRef\]](#)
25. Zhou, Y.; Wang, Z.; Jiang, F. Microstructure change of titanium layer in titanium/aluminium laminate metal composites during ultrasonic additive manufacturing. *Sci. Technol. Weld. Join.* **2023**, *28*, 894–904. [\[CrossRef\]](#)
26. Craig, O.; Bois-Brochu, A.; Plucknett, K. Geometry and surface characteristics of H13 hot-work tool steel manufactured using laser-directed energy deposition. *Int. J. Adv. Manuf. Technol.* **2021**, *116*, 699–718. [\[CrossRef\]](#)
27. Bearden, J.A. X-ray Wavelengths. *Rev. Mod. Phys.* **1967**, *39*, 78–124. [\[CrossRef\]](#)
28. Kurdjumow, G.; Sachs, G. Über der Mechanismus der Stahlhärtung. *Z. Phys.* **1930**, *64*, 325–343. [\[CrossRef\]](#)
29. Ferretto, I.; Kim, D.; Della-Ventura, N.M.; Shahverdi, M.; Lee, W.; Leinenbach, C. Laser powder bed fusion of a Fe-Mn-Si shape memory alloy. *Addit. Manuf.* **2021**, *46*, 102071. [\[CrossRef\]](#)
30. Kim, D.; Ferretto, I.; Jeon, J.B.; Leinenbach, C.; Lee, W. Formation of metastable bcc- δ phase and its transformation to fcc- γ in laser powder bed fusion of Fe-Mn-Si shape memory alloy. *J. Mater. Res. Technol.* **2021**, *14*, 2782–2788. [\[CrossRef\]](#)
31. Schwartz, A.J.; Kumar, M.; Adams, B.L.; Field, D.P. *Electron Backscatter Diffraction in Materials Science*, 2nd ed.; Springer: New York, NY, USA, 2009.
32. Rui, S.S.; Niu, L.S.; Shi, H.J.; Wei, S. Diffraction-based misorientation mapping: A continuum mechanics description. *J. Mech. Phys. Solids* **2019**, *133*, 103709. [\[CrossRef\]](#)
33. Gussev, M.N.; Leonard, K.J. In situ SEM-EBSD analysis of plastic deformation mechanisms in neutron-irradiated austenitic steel. *J. Nucl. Mater.* **2019**, *517*, 45–56. [\[CrossRef\]](#)
34. Allain-Bonasso, N.; Wagner, F.; Berbeni, S.; Field, D.P. A study of the heterogeneity of plastic deformation in IF steel by EBSD. *Mater. Sci. Eng. A* **2012**, *548*, 56–63. [\[CrossRef\]](#)
35. Shen, R.R.; Efsing, P. Overcoming the drawbacks of plastic strain estimation based on KAM. *Ultramicroscopy* **2018**, *184*, 156–163. [\[CrossRef\]](#) [\[PubMed\]](#)
36. Wright, S.I.; Nowell, M.M.; Field, D.P. A review of strain analysis using electron backscatter diffraction. *Microsc. Anal.* **2011**, *17*, 316–329. [\[CrossRef\]](#)
37. Rui, S.S.; Han, Q.N.; Wang, X.; Li, S.; Ma, X.; Su, Y.; Cai, Z.; Du, D.; Shi, H.J. Correlations between two EBSD-based metrics Kernel Average Misorientation and Image Quality on indicating dislocations of near-failure low alloy steels induced by tensile and cyclic deformations. *Mater. Today Commun.* **2021**, *27*, 102445. [\[CrossRef\]](#)
38. Czichos, H.; Saito, T.; Smith, L. *Springer Handbook of Materials Measurement Methods*; Springer Science + Business Media, Inc.: Würzburg, Germany, 2006.
39. Pohler, O.E.M. Unalloyed titanium for implants in bone surgery. *Inj. Int. J. Care Injured.* **2000**, *31*, D7–D13. [\[CrossRef\]](#) [\[PubMed\]](#)
40. Gariboldi, E.; Previtali, B. High tolerance plasma arc cutting of commercially pure titanium. *J. Mater. Process. Technol.* **2005**, *160*, 77–89. [\[CrossRef\]](#)
41. Ellis, D.L. *Effects of Long-Term Thermal Exposure on Commercially Pure Titanium Grade 2 Elevated-Temperature Tensile Properties*; National Aeronautics and Space Administration, Glenn Research Center: Cleveland, OH, USA, 2012.
42. Deepak, J.R.; Joy, N.; Krishnamoorthy, A.; Jaswanth, C.P.; Harish, G. Gas nitriding of CP grade—2 commercially pure titanium and Ti6Al4V grade—5 titanium alloy. *Mater. Today Proc.* **2021**, *44*, 3744–3750. [\[CrossRef\]](#)
43. Hasib, T.M.; Ostergaard, H.E.; Liu, Q.; Li, X.; Kruzic, J.J. Tensile and fatigue crack growth behavior of commercially pure titanium produced by laser powder bed fusion additive manufacturing. *Addit. Manuf.* **2021**, *45*, 102027. [\[CrossRef\]](#)
44. Uebing, C. On the ordering of interstitials in BCC metals and BCT martensites: A lattice gas approach. *Scr. Metall. Mater.* **1994**, *30*, 1183–1188. [\[CrossRef\]](#)
45. Texier, D.; Sirvin, Q.; Velay, V.; Salem, M.; Monceau, D.; Mazères, B.; Andrieu, E.; Roumiguier, R.; Dod, B. Oxygen/nitrogen-assisted embrittlement of titanium alloys exposed at elevated temperature. In Proceedings of the MATEC Web of Conferences, the 14th World Conference on Titanium, Nantes, France, 10–14 June 2019.
46. Fast, J.D. *Interaction of Metals and Gases*; Macmillan Press Ltd.: London, UK, 1971; Volume 2.

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