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Original Article

Microstructural evolution during post heat treatment of the Ti–6Al–4V alloy manufactured by laser powder bed fusion



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ABSTRACT

The purpose of the present study is to investigate the effect of post heat treatment as well as the manufacturing strategy on the microstructure evolution during martensite decomposition of Ti-6Al-4V manufactured by laser powder bed fusion (LPBF). The microstructural evolution was tracked using in situ high-energy synchrotron X-ray diffraction and differential thermal analysis. The phase fraction, the mean lattice parameters, d-spacing and the Full Width at Half Maximum (FWHM) variations were determined by Rietveld refinement from XRD patterns during continuous heating up to the single β phase domain with different heating rates and manufacturing strategies. The complementarity of characterization tools clearly evidences a shift of the $\alpha/\alpha' \rightarrow \beta$ transformation kinetics toward higher temperatures as the heating rate increases. The variations in transformation kinetics are discussed with regard to the predicted values at thermodynamic equilibrium. In addition, the combined analysis of d-spacing and FWHM shows the deviations from linearity at intermediate and high temperatures that are related to the heating and manufacturing strategy. These variations were analyzed in regard of internal stress relaxation or changes of chemical composition. Moreover, the anisotropic elastic distortions in martensite α' caused by the manufacturing strategy were examined. © 2023 The Author(s). Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

1. Introduction

In recent years, an increased interest in additive manufacturing (AM) emerged due to the design freedom

ensuing from the novel technologies [1,2]. It is an approach that differs from traditional manufacturing methods, such as machining, forging or molding requiring a tool or mold. AM techniques manufacture parts layer-by-layer leading to manufacturing of complex geometries with potential reduced

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cost and manufacturing time [3,4]. Many metals are being used in additive manufacturing, such as aluminum alloys [5], nickel-base superalloys [6], steels [7], copper [8], Co-Cr [9] and titanium alloys [10,11]. Ti-6Al-4V is a widely used alloy in the AM production due to its applications in various fields such as aerospace, automobile, medical and energy. This is related to its desirable properties such as high corrosion resistance, fracture toughness, biocompatibility, high specific strength and good combination of mechanical properties [12-14]. The feedstock material used is usually in the form of powders [15] or wire [16]. There are different energy sources, such as electron beam [17], laser beam [18] and arc [19]. In the laser powder bed fusion (LPBF) process given in Ref. [20], melted layers undergo extremely fast heating ($\sim 10^5$ - 10^7 K. s⁻¹) and cooling (~ 10^3 - 10^8 K. s⁻¹) [21]. Otherwise, many studies are interested on solid-state welding process like ultrasonic spot welding, friction stir welding to join Ti–6Al–4V with NiTi alloy [22–24]. Joining these alloys constitutes a major challenge and allow to achieve a component with interesting features. However, process conditions lead to the formation of a brittle intermetallic phase which resulted in the crack initiation due to an accumulation of residual stress in the welding. These various factors are responsible for the degradation of mechanical properties. In addition, this brittle phase causes an effect similar to the martensite α' generated by the LPBF process. In addition, the LPBF as-built microstructure consists of acicular martensitic phase within columnar β grains with strong < $100 >_{\beta}$ orientation along the building direction [25]. The martensitic needles are generally observed to be inclined about 45° with respect to the manufacturing direction [21]. Unfortunately, there are always significant microstructural and mechanical anisotropies in LPBF components to restrict their applications [26]. Especially, the anisotropies of tensile properties [27,28] and fatigue performance are frequently reported [29]. The formation of the α' martensitic phase, which have a distorted hexagonal close-packed (hcp) structure will cause a decrease in ductility [30]. Additionally, due to the large thermal gradients, which are inherently present in the process, residual stresses will also appear progressively during the process as a result of the expansion/contraction interactions between the layers [31]. This can vary across the thickness of the built part [32], thus contributing to the reduction in ductility and the failure of the parts [33]. Therefore, post-fabrication heat treatments could be a choice to transform of the acicular α' martensite into $\alpha + \beta$ microstructures to reduce defects and to lower residual stresses at the same time [28,34]. These heat treatments commonly applied to the as-built components in order to achieve desirable mechanical properties like ductility, include α/β , β treatments or Hot Isostatic Pressing (HIP) [28,35]. Currently, the conventional solution for reducing residual stresses and decomposing the a' martensite is to perform a stress relieving heat treatment whose conditions are inspired by the conventional heat treatments applied to wrought parts. In addition, other studies tend to modify the AM process parameters. Thus, the improved properties are achieved by inducing microstructural changes during post heat treatment.

Recently, several studies have been caried out in order to optimize the as-built components to lower or/and eliminate residual stresses. For example, Zhang et al. and Ali et al. demonstrated that the residual stresses can be also reduced by optimizing LPBF parameters such as laser power, scan speed and scan pattern, whereby the cooling rate is lowered [36,37]. Furthermore, recent research study of Ti-6Al-4V manufactured by LPBF have focused on the effect of stress relieving heat treatment parameters [38]. The holding time required and the temperature reached must be carefully selected in order to achieve an excellent reduction in the residual stresses. In this regard, two heat treatments 1043-1113 K (770-840 °C) for 7200 s (2 h) have been performed on LPBF samples with a heating rate of 1.66 K s⁻¹ (100 °C. min^{-1}) and they were tracked by in situ High-Energy X-ray Diffraction (HEXRD). The authors reported that the dislocation density and the internal stresses decrease simultaneously at a temperature of 770 K (497 °C). In this temperature range between 913 and 1281 K (640-1008 °C), the same authors, reported a solute distribution and diffusion of vanadium from α $\rightarrow \beta$, which was evaluated by changes in the mean lattice parameters and d-spacing for both phases α and β [38]. Moreover, Combres et al. [39] observed a complete relaxation after annealing at 1003 K (730 °C) for 7200 s (2 h). In the same manner, Zhang et al. [40] seek to establish a relation between the microstructure evolution and heat treatment applied to Ti-6Al-4V between 1003 and 1173 K (730-900 °C) for 7200 s (2 h) followed by furnace cooling. They examined the effect of post heat treatment on the microstructure. As a result, it reveals that the post-LPBF treatment as an effective method to relieve internal stresses and improve the mechanical properties.

On the other hand, most investigations focus on understanding the link between post heat treatment, mechanical properties and the retained microstructure. From a microstructure change point of view, many studies have been carried out on microstructures quenched rapidly at room temperature, followed by the decomposition of the α' martensite [41,42]. Zhang et al. [36], for example, reported an enhancement in ductility after annealing at a temperature range of 1123–1173 K (850–900 °C) for 7200 s (4 h) followed by furnace cooling. Additionally, Liang et al. [43] investigated the phase transformation of Ti-6Al-4V based on the understanding of microstructure evolution occurring during post-LPBF heat treatment. The resultant mechanical properties of the alloy after heat treatments at a temperature range between 873 K (600 °C) and 1173 K (900 °C) for 14,400 s (4 h) followed by air cooling were assessed, though the heating rate was not reported, their results showed that the samples heated at 1073 K (800 °C) and 1123 K (850 °C) for 14,400 s (4 h) contain the finest lamellar α and a remarkable volume fraction of β phase, displaying the improved ductility and suitable ultimate tensile stress. Moreover, Brown et al. [38] used in situ high-energy X-ray diffraction to study the phase transformation kinetics of Ti-6Al-4V manufactured by LPBF during heat treatment at 1.66 K s⁻¹ (100 $^{\circ}$ C. min⁻¹) between 1043 K (770 °C) and 1281 K (1008 °C). Through an EBSD analysis, they showed an increase in size of the α lath width in sample heat treated at 1281 K (1008 °C) for 7200 s (2 h), than in the sample heat treated at 1043 K (770 °C) for 7200 s (2 h). Additionally, Yan et al. [44] introduce a series of heat treatments ranging between 1073 K (800 °C) and 1353 K (1080 °C), with a heating rate of 0,33 K s⁻¹ (20 °C. min⁻¹) and an isothermal holding of 7200 s

(2 h), followed by furnace cooling. They revealed that heat treatment can change the microstructure allowing thus improving the mechanical properties. Nevertheless, in some cases, it should be noted that the increased ductility of the material may cause a decrease in yielding strength ($\sigma_{0.2}$) and ultimate tensile strength (σ_{UTS}) [45].

Otherwise, to optimize post-LPBF heat treatment, the understanding of the decomposition mechanism of martensite α' is considered essential. The effect of conventional and alternative heat treatments on the mechanical behavior was studied by several authors. As an example, it was observed that the decomposition of martensite α' reached by annealing at 1123 K (850 °C) for 7200 s (2 h), followed by air cooling, induced an increase in hardness [28,34]. In addition, Wu et al. [46] carried out post-LPBF heat treatment between 573 K (300 °C) to 1293 K (1020 °C), followed by water quenching to understand its effect on microstructure and hardness. The results demonstrated that the acicular martensite α' partially decomposes close to 873 K (600 °C), and then decomposes into platelet α and β phases between 1023 K (750 °C) and 1173 K (900 °C). In the same manner, Brown et al. [38] showed that the α' martensite fully decomposes into α platelets and generates the formation of β phase in the temperature range between 1023 and 1173 K (750-900 °C). Furthermore, Xu et al. [45] revealed that a near-complete martensite α' decomposition into a mixture of α and β phases can be achieved at temperatures near to 673 K (400 °C).

However, due to the lack of understanding about the decomposition kinetics of α' martensite, it is difficult to optimize the post-LPBF heat treatment and consequently the achievement of acceptable mechanical properties. Nevertheless, most of the prior investigations are based on post-mortem analyses completed with existing analytical tools that allow characterization on a grain scale (few micrometers) or on an atomic scale (few hundredths of a nanometer). Therefore, these experimental conditions lead to difficult interpretations due to microstructure modification during the quenching process. Moreover, they are confronted with obvious limitations when the heating rate is high. These considerations are the motivation of the present work about providing a keen understanding of the decomposition kinetics of α ' martensite during heating of Ti-6Al-4V manufactured by LPBF with particular focus on the effect of the heating rate and the manufacturing strategy. In situ high-energy X-ray diffraction is used to monitor the phase transformation in real time during heating by extracting mass fraction, mean lattice parameters and FWHM (Full Width at Half Maximum) from Rietveld refinement. This time-resolved information is complemented by microstructural characterizations and Differential Thermal Analysis (DTA).

2. Material and methods

2.1. Material

Specimens were additively manufactured by LPBF using an EOS M280 machine equipped with a fiber laser under argon atmosphere. The atomized plasma Ti–6Al–4V (grade 23) powders with a particle size of 15–45 µm were used. Its

chemical composition (in wt.%) is 6.41Al, 3.94 V, 0.21Fe, 0.090 and balance Ti. Fabrication was made using standard EOS parameters for Ti–6Al–4V alloys to obtain fully dense part. Two manufacturing orientations of the LPBF samples were considered as illustrated in Fig. 1 (a-b): the first has its axis of the revolution parallel to the z axis (referred as "vertical 0°") and the second normal to the z axis (referred as "vertical 0°") and the second normal to the z axis (referred as "horizontal 90°") (Fig. 1c). The manufacturing direction is unchanged, only the manufacturing angle which changes. Cylindrical samples (10 mm length, 6 mm diameter) (Fig. 1d) with 0° and 90° angles to the substrate were cut from the middle area along the height of the built samples (50 mm length, 6 mm diameter). All samples for the characterizations were taken at the center of each cylinder.

2.2. In situ synchrotron X-ray diffraction

In situ synchrotron High-Energy X-Ray Diffraction (HEXRD) experiments were performed at the beamline P07 of the Petra III storage ring (Deutsches Elektronen-synchrotron, Hamburg, Germany). Thanks to the high-energy beam, complete Debye-Scherrer rings were collected in transmission geometry up to $2\theta \approx 8^{\circ}$ on a 2D PerkinElmer XRD1621 detector with an image size of 2048 \times 2048 (pixels) and 200 μ m pixel size. The estimated acquisition time of each pattern is 3.5 s. The experimental parameters are given in Table 1.

A Bähr DIL805 A/D dilatometer (induction heating) was used to perform the continuous heating. The samples were kept fixed and placed horizontally in the dilatometer during heat treatment. The temperature was controlled by a spotwelded thermocouple Pt/Pt-Rh on the surface close to the analyzed volume by HEXRD. Heat treatments were carried out in a controlled atmosphere under secondary vacuum to limit the oxygen contamination of the samples. Two heating rates were considered from room temperature up to 1323 K (1050 °C): the first is 1 K s⁻¹ (60 °C. min⁻¹) (considered to be close to furnace loading) and the second is 0.16 K s^{-1} (10 $^\circ\text{C}.$ min^{-1}) (considered to be close to thermodynamic equilibrium condition). Complete azimuthal integration of the intensity along the Debye-Scherrer rings at each temperature for a 2Θ range between 2.0° and 8.0° was carried out using the software Fit2D to obtain standard 1D diffractograms (Intensity vs. diffraction angle 20) [47]. Fig. 2 displays the schematic illustration of the experimental setup. Sample was mounted inside a dilatometer.

Quantitative phase analysis of the I/2 Θ diffraction patterns was carried out by the Rietveld method as implemented in the Fullprof software [48]. Thus, the evolutions of mass fraction, mean lattice parameters and Full Width at Half Maximum of each phase involved during heating were determined. To highlight possible anisotropic behavior, partial integration of Debye-Scherrer rings was considered. In this regard, an angular integration interval of 40° was considered in 20° steps for a domain of 180° The inset figure in Fig. 11-a illustrates the principle of partial integration on the semi-circle. To better understand the principle, for example angle θ_1 represents the first integration angle between 0° and 40°. Angle θ_2 represents the second one between 20° and 60°. Angle θ_3 represents the third one between 40° and 80°. The last integration angle θ_8 is between 140° and 180°. It corresponds to a number of 8



Fig. 1 – A schematic layout of the samples fabricated by LPBF in the powder bed on a substrate: (a) manufactured "vertical 0°", (b) manufactured "horizontal 90°", (c) The two manufacturing angles (vertical 0° and horizontal 90°) adopted vs. build direction, (d) geometry of sample for in situ high energy X-ray diffraction.

integrations. The d-spacing were determined from the individual refinement of the diffraction peaks by considering a Pseudo-Voight function.

2.3. Differential thermal analysis (DTA)

In order to support the HEXRD experiments, DTA analyses were carried out on a SETSYS EVO apparatus. Recall, that the DTA analyses and HEXRD experiments were carried out independently at different times. Alumina crucibles with a volume of 80 µL were used, and an alumina powder was considered as a reference. The samples weighed 142 mg. In order to prevent the sample from oxidation, the experiments were performed under an argon atmosphere, with a gas flow of 0.33 ml. s^{-1} (20 ml. min^{-1}). The as-built sample was heated from room temperature up to 1373 K (1100 $^{\circ}$ C) at 0.16 K s⁻¹ (10 °C. min⁻¹), isothermally held at 1373 K (1100 °C) for 1800 s (30 min) and cooled up to room temperature at 0.33 K $\rm s^{-1}$ (20 $^{\circ}$ C. min⁻¹). At the end of this cycle, the microstructure consists in coarse α lamellar precipitates embedded in the β matrix [49]. The solution treatment was repeated from the heat-treated sample in order to compare the heat flow evolution from the martensitic α' and $\alpha+\beta$ microstructures. Moreover, the methodology used to calculate the onsets/end

temperatures of the transformation is to consider the inflection points of the derivative curve.

2.4. Microstructure characterization

A FEG JEOL JSM-7800 F Prime microscope operated at 10 kV was employed to obtain the Back-Scattered Electron (BSE) images. Before the observations, the samples were first embedded using a carbon-rich epoxy resin with a Mecapress 3 hot mounting press. Then, they were abraded using SiC paper until P2400 grade, and mirror-polished by a mixture of oxide polishing suspension (OP–S) and hydrogen peroxide. In addition, Electron Probe MicroAnalysis EPMA observation was carried out (CAMECA SX Five FE). An accelerating voltage of 20 kV and a beam current of 100 nA were applied for the element mapping.

3. Results

3.1. As-built microstructure

Fig. 3(a–b) show typical SEM micrographs of the as-built sample cross-section manufactured vertically (0°) and

Table 1 – Experimental parameters of the high-energy X-ray diffraction experiments.						
Energy (keV)	Wavelength (nm)	Slit-aperture size (mm²)	Sample-detector distance (mm)	Acquisition time (s)	Image size (pixels)	Analysis volume (mm³)
100	0.012394	1×1	1511	3.5	2048×2048	~6



Fig. 2 - Schematic illustration of the experimental setup at the beamline P07 at DESY.

horizontally (90°). Samples present similar microstructure at this observation scale. In both cases, the microstructure consisted of a fine tempered martensite α' with acicular morphology and with a strong disparity in size. This phase α' has a hexagonal close-packed (hcp) crystal structure. It can be noticed that no residual β phase was observed at this observation scale. This phase β has a body-centered cubic (bcc) crystal structure.

From a chemical distribution point of view, a large EPMA mapping including several deposited layers in the case of the "vertical 0°" sample was made and is displayed in Fig. 4. The spatial distribution of titanium and solute elements is clearly homogeneous despite the fact that the material was subject to cyclic heating and cooling. The average chemical composition resulting from the EPMA mapping was found to be close to the nominal chemical composition, thus supporting the analysis procedure.

3.2. Effect of heating rate

Fig. 5-a displays some of the HEXRD diffractograms obtained during heating with a rate of 0.16 K s⁻¹ (10 °C. min⁻¹) for the "vertical 0°" sample. These data are the result of a complete integration of the Debye-Scherrer rings. At this observation scale, all intense peaks at room temperature were indexed on the basis of a compact hexagonal structure. Due to the absence of partitioning of solute elements in the as-built state, it can be considered that these are the characteristic peaks of α' martensite. On the other hand, the X-ray diffractograms

reveal the presence of β phase as shown in Fig. 5-b. Fig. 5-b depicts an enlargement of a restricted angular domain (4.25°–4.50°) showing the evolution of $\{200\}_{\beta}$ peak. It is expected that volume fraction of this phase is small given the intensity of the peaks. In addition, the size of the apparent β domains is probably extremely fine since it is difficult to locate by electron microscopy. As heating is applied from as-built state, it can be observed a shift towards lower angles for all peaks mainly due to thermal expansion. Between 823 and 1273 K (550–1000 °C), the α/α' peaks gradually disappear and the β peaks narrow and gain intensity when the temperature increases, indicating more β phase presence, until all the α/α' phase transforms into β phase.

a. Mass fraction of the β phase

Fig. 6 shows the mass fraction evolution of the β phase determined by Rietveld refinement from *in situ* HEXRD patterns during heating for the rates 0.16 K s⁻¹ (10 °C. min⁻¹) and 1 K s⁻¹ (60 °C. min⁻¹), and between the temperature range 873–1273 K (600–1000 °C). Nevertheless, between room temperature and 873 K (600 °C), the intensity of β phase peak is too low to perform Rietvield refinement, as seen in Fig. 5-b. For this purpose, the mass fraction of β phase was performed for temperatures above 873 K (600 °C). Regardless of the heating rates, the trend is roughly similar. At 873 K (600 °C), the mass fraction of β phase approximately 4,77 wt%/4.64 wt% respectively for 0.16 K s⁻¹ (10 °C. min⁻¹) and 1 K s⁻¹ (60 °C. min⁻¹). Up to 973 K (700 °C), the mass fraction of β phase exhibits a



Fig. 3 – Typical SEM micrographs of the as-built LPBF samples showing a mixture of martensitic needles α' : (a) "vertical 0°" sample, (b) "horizontal 90°" sample.



Fig. 4 – EPMA maps of titanium and main solute elements of the "vertical 0° " sample.

slightly increase, and is equal to 5.83 wt%/5.81 wt% respectively for 0.16 K s⁻¹ (10 °C. min⁻¹) and 1 K s⁻¹ (60 °C. min⁻¹). From above 973 K (700 °C), a gradual increase of β phase amount is observed until the complete disappearance of the α/α' phase at temperatures close to 1273 K (1000 °C). On the other hand, focusing on the heating rate, significant differences in the kinetics can be noticed. The onset temperature of $\alpha/\alpha' \rightarrow \beta$ transformation thus changes from 973 K (700 °C) to 1002 K (729 °C) for heating rates of 0.16 K s⁻¹ and 1 K s⁻¹ (60 °C. min⁻¹), respectively. Above 1223 K (950 °C), this difference gradually reduces with increasing temperature and becomes negligible.

b. Mean lattice parameters

The relative variation of the mean lattice parameters of β phase during heating by applying two heating rates 1 K s⁻¹ (60 °C. min⁻¹) and 0.16 K s⁻¹ (10 °C. min⁻¹) for "vertical 0°" sample is displayed in Fig. 7-a. Three temperature ranges can be clearly distinguished for both heating rates. The first temperature range is between room temperature and around (623 K, 671 K) (350 °C, 398 °C) for 0.16 K s⁻¹ (10 °C. min⁻¹) and 1 K s⁻¹ (60 °C. min⁻¹), respectively. For this temperature range, the linear evolution is observed with a thermal expansion



Fig. 5 – (a) HEXRD diffractograms of the Ti–6Al–4V as-built "vertical 0°" sample at various temperatures during heating at the rate of 0.16 K s⁻¹ (10 °C. min⁻¹), (b) an enlargement of a restricted angular domain showing the evolution of $\{200\}_{\beta}$ peak at various temperatures during heating.



Fig. 6 – Evolution of the mass fraction of β phase in the "vertical 0°" sample determined by in situ HEXRD during heating using two different rates.

coefficient equal to 11.50 x 10^{-6} K⁻¹ for both heating rates. As heating continues above (623 K, 671 K) (350 °C, 398 °C), $\frac{\Delta a_{g}}{a_{00}}$ strongly decreases with different slopes. In the temperature range (623–823 K) (350–550 °C) and (671–797 K) (398–524 °C), respectively, it can be seen that the amplitude depends on the heating rate, suggesting that a kinetic effect is operating.

In the third temperature range, above (823 K, 797 K) (550 °C, 524 °C), $\frac{\Delta a_{\beta}}{\alpha \alpha}$ increases considerably, when the α phase dissolution takes place. Fig. 7(b–c) compares the variations of $\frac{\Delta a_{\alpha}}{a_{\alpha}}$ and $\frac{\Delta c_{\alpha}}{c_{\infty}}$ for the "vertical 0°" sample for two heating rates 1 K s⁻¹ (60 °C. min⁻¹) and 0.16 K s⁻¹ (10 °C. min⁻¹), respectively. The relative evolutions of the two mean lattice parameters are very different from those of the β phase. An almost linear behavior with temperature is observed for the a_{α} lattice parameter with a slight deviation from 853 K (580 °C) for the two heating rates. In the case of the c_{α} lattice parameter, the deviation from linearity occurs at 723 K (450 °C) with a slight deviation, but with a stronger slope at 853 K (580 °C). In the linear domain between room temperature and 723 K (450 °C), the thermal expansion coefficient in the two directions is quite similar with a value of 9.97 x 10^{-6} K⁻¹. c. Full Width at half Maximum

Fig. 8(a–b) show the evolution of the FWHM of the $\{200\}_{\beta}$ and $\{10\overline{1}0\}_{\alpha/\alpha'}$ diffraction peaks as a function of temperature for two heating rates 1 K s⁻¹ (60 °C. min⁻¹) and 0.16 K s⁻¹ (10 °C. min⁻¹), respectively. These peaks were chosen because they do not overlap with any other peak. Pseudo-Voigt curve fitting and a simplified Caglioti's formula (FWHM = $\sqrt{U.\tan(\theta)^2 + V.\tan(\theta) + W}$) were considered for the calculation of FWHM, with U, V and W the fitted parameters by the Rietveld method. The FWHM is an indicator of the



Fig. 7 – Relative variations of the mean lattice parameters on heating for the "vertical 0°" sample: (a) β phase for two heating rates, (b) α phase at 1 K s⁻¹ (60 °C. min⁻¹), (c) α phase at 0.16 K s⁻¹ (10 °C. min⁻¹).

phase state in terms chemical heterogeneity, latticedistortion and domain size. In the case of the $\{200\}_{\beta}$ diffraction peak, the FWHM remains relatively constant within the temperature range 297–623 K (24–350 °C). From 623 K (350 °C),



Fig. 8 – FWHM evolution during heating for two different heating rates for the "vertical 0°" sample: (a) $\{200\}_{\beta}$, (b) $\{10\overline{1}0\}_{\alpha/\alpha'}$

the FWHM decreases down to the T_{β} . The rate of change from 973 K (700 °C) is slow. In the case of $\{10\overline{1}0\}_{\alpha/\alpha'}$ diffraction peaks, it is observed that the FWHM remains relatively constant between room temperature and 723 K (450 °C). Above 723 K (450 °C), the FWHM decreases down to 973 K (700 °C) and the T_{β} with high and low rate of change, respectively. Above this temperature, the FWHM is again constant with temperature. As for the mean lattice parameters, an increase in the heating rate leads to a shift towards high temperatures because of a diffusion-driven kinetics effect.

d. Differential Thermal Analysis (DTA)

Fig. 9 shows the evolution of the heat flow as a function of temperature during the first heating for the "vertical 0°" sample. An exothermic reaction during heating occurring in the temperature range of 708–865 K (435–592 °C) is first observed. Then, an endothermic reaction take place between



Fig. 9 – DTA heat flow evolution during the first heating with a rate of 0.16 K s⁻¹ (10 °C. min⁻¹) for the "vertical 0°" sample.

993 and 1268 K (720–995 °C). These evolutions support the temperature transformation domain established by HEXRD. Fig. 10 displays the heat flow evolution during heating from the sample that underwent the first heat-treatment cycle. Unlike the as-built state, the microstructure is composed of acicular α phase embedded in a β matrix. The change in the initial microstructure leads to the absence of the exothermic peak in the intermediate temperature range of 708–865 K (435–592 °C). On the other hand, the endothermic peak is preserved, which can be attributed to the dissolution of the α phase. Also, these evolutions have been experimentally observed in previous investigations of the Ti–6Al–4V manufactured by LPBF [50]. The sample was heated from room



Fig. 10 – DTA heat flow evolution during the second heating with a rate of 0.16 K s⁻¹ (10 °C. min⁻¹) from the "vertical 0°" sample that underwent the first heat-treatment cycle.

temperature up to 1473 K (1200 °C) at 0.083 K s⁻¹ (5 °C. min⁻¹) followed by furnace cooling. The results indicate the presence of an exothermic peak at 823 K (550 °C) during the first cycle. Therefore, this peak is not observed during the second cycle. Thus, the presence of an endothermic peak is preserved for both cycles.

3.3. Effect of manufacturing strategy

Initially, the effect of manufacturing strategy on phase decomposition/dissolution kinetics of the α/α' phases was studied. Fig. 11 shows the evolution of the mass fraction of β phase in the "vertical 0°" and "horizontal 90°" samples during heating at 1 K s⁻¹ (60 °C. min⁻¹). Regardless of the manufacturing strategy, the evolution of the mass fraction of β phase (Fig. 11) in the vertical 0° and horizontal 90° samples during heating at 1°C.s⁻¹ is similar and suggests that the decomposition/dissolution kinetics of the α/α' phases is independent to the manufacturing strategy. However, to highlight possible strain anisotropy of the lattice depending on the manufacturing strategy, the partial integration of Debye-Scherrer rings was preferred.

Fig. 12(a–b) show the evolution of the $d_{\{10\overline{1}2\}_{\alpha/\sigma'}}$ spacing during heating for various angular integrations in the case of the samples manufactured vertically (0°) and horizontally (90°). An angular integration interval of 40° in 20 steps for an angular domain of 180° was considered, which corresponds to a number of 8 integrations. At room temperature, for the "vertical 0°" sample, significant differences can be observed in the d-spacing depending on the orientation of the grains. A difference of 0.0074 Å was observed between the 80° and 160° orientation. The disparities decrease progressively as a function of temperature. Above 973 K (700 °C), the small differences are contained within the uncertainty of the measurement. These differences are similar for "horizontal



Fig. 11 – Evolution of the mass fraction of β phase in the "vertical 0°" and "horizontal 90°" samples determined by in situ HEXRD during heating at 1 K s⁻¹.



Fig. 12 – Evolution of the $d_{\{10\overline{1}2\}_{a/a'}}$ d-spacing at heating 1 K s⁻¹ (60 °C. min⁻¹) for several angular integrations, (a) "vertical 0°" sample, (b) "horizontal 90°" sample.

90°" sample. However, the disparities at low temperatures are clearly less compared to the "vertical 0°" sample. Nevertheless, the difference between the 80° and 160° orientation is 0.0018 Å at room temperature. As for the "horizontal 90°" sample, the disparities tend to decrease with the temperature. Furthermore, above 1223 K (950 °C) for both manufacturing directions, the d-spacing is identical.

4. Discussion

4.1. As-built microstructure

The microstructure of Ti–6Al–4V manufactured by LPBF is related to the drastic conditions incur by the material during the process. For LPBF, the cooling rate produced is close to ($\sim 10^3$ -10⁸ K. s⁻¹) [21]. However, for traditional strategies

such as water quenching, the cooling rate produced is in the order of 1500 K s⁻¹. Moreover, a difference was reported in the length of the acicular martensite α' . The sample manufactured by LPBF has smaller needles with a higher amount compared to the water-quenched sample [51]. In addition, during LPBF process, residual stresses can result from a variety of mechanisms mainly the large thermal gradient which drives localized plasticity. Also, the magnitude of cooling rate undergone during the process is presumably to influence the level of residual stresses developed during evolution of martensite α ' [31,52]. If we refer to the literature, the materials used in layer-by-layer manufacturing are subjected to cyclic heating and cooling leading to martensite α' with hcp (hexagonal close packed) lattice [53]. During the process, the first layer is spread over the build platform, then a laser fuses it. At this moment, the temperature of the first layer added is above the melting point. A second layer of powder is spread across the previous layer, then a laser fuses it. The first layer remains above the melting point at the time when the second layer is added. Additionally, further layers are added and fused. Therefore, the temperature of the first layers drops but remains above the T_{β} temperature until the addition of four at five layers. In addition, an increase in temperature above T_{β} associated with high heating rates leads to the complete transformation of α' martensite into the β phase. This occurs in the areas adjacent to the molten pool, where previously solidified layer is partially remelted to insure metallurgical bonding between layers. This cycle is repeated until the final height of the part is reached [52]. From a chemical composition point of view, the geometry of the part as well as the complex thermal path undergone by each layer during the process can lead to differences in the nature of the phases and affect the resulting microstructure. Depending on the duration of exposure to high temperature, the distribution and the content of solute elements in the β phase can be different, which affects the mean lattice parameter of the phase. Previous studies have shown that the vanadium content in the β phase at different build heights may vary due to the different thermal cycles undergone by each deposited layer [54,55]. In our case, the EPMA analysis carried out on a sample manufactured vertically (0°) showed a chemical homogeneity of main solute elements.

4.2. Microstructure evolution during heating

In the as-built LPBF state, characteristic peak of β phase is detected. The reasons of its presence and its location in the microstructure are not in the scope of the present study. It can be noted that Brown et al. [38] did not detect the presence of β phase in the case of Ti–6Al–4V manufactured by LPBF despite of the use of high energy X-ray diffraction.

Based on the qualitative analysis of diffractograms during heating, it was shown that the intensity of α' peaks decreases continuously in favor of those of the β phase. Moreover, the analysis carried out in the present work did not reveal additional characteristic peak during heating suggesting that the decomposition of supersaturated α' martensite does not occur via pathways involving metastable phases. From a quantitative phase fraction point of view, the examination of



Fig. 13 – Evolution of the mass concentrations of the elements Al and V as a function of temperature at equilibrium in the α and β phases determined by the ThermoCalc[®] software using Saunders database TTTI₃: (a) aluminum, (b) vanadium.

diffractogram has clearly showed a beginning of transformation comparable to the forged material [56]. Thus, it can be assumed that the α' martensite decomposition takes place by a gradual decrease in the supersaturation tending towards the chemical composition of α phase. During the transformation, the β phase fraction increases. Consequently, it is necessary to estimate the temperature at which the phase can be considered close to thermodynamic equilibrium.

Several authors have determined the decomposition temperature range of α' martensite during post-heating. Significant differences were found in the starting and ending temperatures of the decomposition of this metastable phase. Xu et al. [45] reported that near complete decomposition of α' martensite can be achieved at a temperature of 673 K (400 °C). This observation suggests that the microstructural evolution is dependent on the rate of decomposition of the α' martensite, as well as being controlled by the content and diffusion of vanadium and aluminum to form the α and β

phases. In contrast, Formanoir et al. [57] observed that complete decomposition of α' occurs at 973 K (700 °C). Xu et al. [55] observed complete decomposition of α' at 1023 K (800 °C). Kashel et al. [58] reported that the complete decomposition of martensite α' occurred at 1023 K (750 °C), showing that increasing temperature leads to a higher rate of martensite dissolution, as well as crystal lattice expansion. On the other hand, Brown et al. [38] reported that the range temperature between 1023 and 1173 K (750–900 °C) leads to the complete decomposition of the α' martensite into α platelets and generates the formation of the β phase. Thus, they report that the β phase initially appears approximately at 913 K (640 °C), after recovery had happened.

Quantitative analysis of diffractograms gives additional information. Thus, in terms of mean lattice parameters, it was found that the lattice parameters a_{α} and c_{α} obtained during heating in both heating rates (1 K s⁻¹ and 0.16 K s⁻¹) (60 °C. min^{-1} and 10 °C. min^{-1}) show similar evolutions up to 723 K (450 °C). The coefficient of thermal expansion between 297 K (24 °C) and 723 K (450 °C) is 9.97 x 10^{-6} K⁻¹ and is close to the literature values for α phase [38,59]. The evolution of the lattice parameter c_{α} shows a deviation from linearity at 723 K (450 °C). Nevertheless, the lattice parameter a_{α} remains substantially linear during heating. According to the literature, this elastic anisotropy can be caused by differences in the coefficient of thermal expansion along the a and c directions [60] or by an increase in the interstitial (O, N) content [61], leading to a lattice distortion. In our case, the post heat treatment was carried out under secondary vacuum and the diameter of the sample is 6 mm, which means that the volume affected by oxygen and nitrogen contamination is negligible. Consequently, it is highly unlikely that the main contribution comes from differences in the coefficient of thermal expansion.

Furthermore, considering a gradual decrease in the supersaturation of α' martensite, a non-linear monotonic evolution should have been observed from the intermediate temperatures. The chemical composition of α phase predicted at thermodynamic equilibrium using the ThermoCalc© software and TTTI₃ Saunders database is displayed in Fig. 13(a-b). It can be seen that the variations in aluminum and vanadium compared to the nominal chemical composition are low, which would explain why the non-linear monotonic evolution is absent. In the case of the a_β lattice parameter, as seen in Fig. 7-a, the variations are more complex with three distinct domains. In the first temperature range between room temperature and (623 K, 673 K) (350 °C, 400 °C), the relative evolution is near to linearity with a thermal expansion coefficient of 8.45 x 10^{-6} K⁻¹. This value is also comparable to those in the literature for β phase which are between 9 x 10⁻⁶ K⁻¹ and 10 x 10⁻⁶ K⁻¹ [38,59].

Subsequently, negative slope of the $\frac{\Delta a_{\theta}}{a_{00}}$ is observed between 673 and 803 K (400–530 °C) for 1 K s⁻¹ (60 °C. min⁻¹) and 623–823 K (350–550 °C) for 0.16 K s⁻¹ (10 °C. min⁻¹). This trend was also reported in the literature for the two alloys Ti–6Al–4V [56,62] and Ti–6Al–6V–2Sn heated at 0.083 K s⁻¹ (2 °C. s⁻¹) and 0.083 K s⁻¹ (0.33 °C. s⁻¹) [63]. However, the variation amplitudes are less significant. Two hypotheses were suggested to explain this effect: relaxation of thermal stresses, elastic distortion generated during the process and element partitioning between α and β phases, mainly diffusion of V into β . Compared to α , β phase is more susceptible to the compositional changes occurring during element partitioning which leads to a decrease in a_{β} . Moreover, this effect is also observed in previous works not processed by AM, *i.e.*, Ti–6Al–4V conventionally processed (ingot) and may be related to diffusion-driven element partition [64]. Additionally, the most probable contribution in this domain would be that of the relaxation of internal stresses because of the large variation amplitudes and the severe cooling conditions. Thus, the absence of the exothermic peak in the temperature range between 723 and 823 K (450–550 °C) recorded by DTA supports this hypothesis.

In the third temperature range of 773 K (500 $^\circ\text{C})$ and a temperature above T_{β} , $\frac{\Delta a_{\beta}}{a_{0\beta}}$ increases highly when the α phase dissolution takes place. Boyer et al. [65] and Castro et al. [66] showed that when the $\alpha/\alpha' \rightarrow \beta$ transformation occurs, the vanadium content in the β phase decreases, causing a increase in the mean lattice parameter. A similar evolution of the β lattice parameter was reported by Elmer et al. [64], Dobromyslov et al. [67] and Andi et al. [56]. This trend has been observed by Brown et al. [38] in the temperature range between 913 and 1281 K (640–1008 $^{\circ}$ C), the authors showed that the transformation from $\alpha \rightarrow \beta$ is accompanied by solute distribution and diffusion of vanadium which is evidenced by a constant increase in the lattice parameters and d-spacing for both phases α and β . In our case, the significant increase can be mainly attributed to the change in solute content of the β phase considering that the elastic strain is negligible. This assumption is supported by plotting the relative variation of a_{β} (after removing of thermal contribution) as a function of the phase transformation progress $\frac{f_a}{1-f_a}$ as shown in Fig. 14. This calculation is provided in details as supplementary material (Appendix A). The relative variation of a_{β} decreases continuously with the rate of transformation progress. A quasi-linear relationship between the relative variation of a_{β} and the



Fig. 14 – Relative variations of the mean lattice parameters a_{β} on heating vs. phase transformation progress from the "vertical 0°" sample.

transformation progress is highlighted, which assumes that the decomposition mechanism of the α' martensite takes place by diffusion of solute elements. Thus, the slight deviation from linearity can be explained by the contribution of elastic strain.

The last parameter extracted from the Rietveld refinement is FWHM of X-ray diffraction profiles. The FWHM parameter is sensitive to the domain size and microstrains generated by crystal defect and by local fluctuation in chemical composition. For both phases, FWHM drops significantly before the phase transformation starts. This drop is mainly attributed to an internal stress relaxation and progressively to an alteration in the size of α/α' and β phases when the phase transformation progresses. With regard to the literature, Brown et al. [38] observed the same trends, which they attributed to the decrease in dislocation density and internal stresses from 770 K (497 °C). Additionally, in situ conventional XRD experiments recently published by Kaschel et al. [58] carried out on Ti-6Al-4V manufactured by LPBF assumed the same hypothesis. The assumption of chemical contribution cannot be ruled out. However, following the considered temperature range, the decomposition of α^\prime martensite should lead to a progressive partitioning of solute elements with short-range diffusion. Consequently, chemical heterogeneities in the β phase resulting from the decomposition of the martensite α' should exist and lead to a broadening of diffraction peaks of the β phase.

4.3. Effect of heating rate

As expected considering kinetics effect, an increase in the heating rate leads to a shift of the transformation domains towards high temperatures. However, the shift remains small considering the difference in heating rate. This suggests that the fine martensite α' needles and the presence of internal stresses are linked to rapid phase transformation kinetics. To support this assumption, the volume fraction of β phase at



Fig. 15 – Comparison of f_{β} phase amount obtained experimentally by Rietveld refinement during heating for two heating rates from the "vertical 0°" sample and predicted at thermodynamic equilibrium (ThermoCalc©).

thermodynamic equilibrium as a function of the temperature was calculated with ThermoCalc[®] software, using TTTI₃ Saunders database. The comparison with experimental values is reported in Fig. 15. Despite a rapid heating rate of 1 K s⁻¹ (60 °C. min⁻¹), the phase transformation kinetics is very close to the predicted values at thermodynamic equilibrium, which proves that the phase transformation kinetics is very rapid on heating. Moreover, the fact that the kinetics is close to the equilibrium values suggests a partitioning of solute elements in the two phases at intermediate temperatures.

4.4. Effect of samples orientations

The sample manufactured vertically (0°) reflects a significant accumulation of residual stress (Fig. 12-a) compared to the one manufactured horizontally (90°) (Fig. 12-b). For a heating rate of 1 K s⁻¹ (60 °C. min⁻¹) the results of the two samples manufactured vertically (0°) and horizontally (90°), showed that the mass fraction of the β phase remains constant up to 1013 K (740 °C) and gradually increases for higher temperatures. This result means that the differences in size of the martensite α' needles and the presence of residual stresses are not sufficient to impact the dissolution kinetics of the α/α' phases. However, significant differences have been observed in the d-spacing up to 973 K (700 °C) depending on the sample orientation and the orientation of the grains. In the case of "vertical 0°" sample, it has been shown that the disparities are more pronounced. At this stage of the study, it is difficult to understand and explain why large disparities were found at low temperatures in the case of the sample manufactured vertically at an angle of 0°. However, the texture combined with the interaction between variants may contribute to introduce anisotropic lattice distortions. Brown et al. [38] also observed the same trends for samples characterized in the radial and longitudinal direction by high energy X-ray diffraction. They suggest that these behaviors are related to intergranular residual stresses that evolve through the large thermal gradient during cooling which drives localized plasticity and that depend on crystallographic direction.

5. Conclusions

In this contribution, in situ high-energy X-ray diffraction (HEXRD) is employed to study the phase transformations of Ti-6Al-4V manufactured by LPBF technology during heating. An analysis of successive diffraction patterns allowed characterizing and providing real time observations of the transformation kinetics. The following conclusions were drawn from this work.

- The as-fabricated LPBF sample consisted of acicular α' martensite. The presence of β phase was detected by HEXRD.
- A kinetic effect has been observed with a shift of the onset temperatures of α/α' decomposition/dissolution toward high temperatures when the heating rate increases.
- The combined analysis of different features obtained from HEXRD diffractograms suggests a continuous evolution of α' martensite towards the characteristics of the α phase

with an internal stress relaxation at intermediate temperatures and with a gradual decrease in the supersaturation to achieve the chemical composition of α phase when the phase transformation progresses.

- The behavior of different features between the temperatures (673-803 K) (400-530 $^{\circ}$ C) is related to an internal stress relaxation. This result is supported by Differential thermal analysis (DTA).
- The decomposition/dissolution kinetics of the α/α' phases was found independent to the manufacturing strategy.
- The anisotropic lattice distortions have been observed and their amplitude depends on the manufacturing strategy.

Declaration of competing interest

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

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jmrt.2023.01.123.

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