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# On the transformation temperatures of Ti-6Al-4V: effect of oxygen pick-up during Laser Powder Bed Fusion

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## Keywords:

Titanium, Ti-6Al-4V, additive manufacturing, L-PBF, heat treatments, transformation temperatures, X-Ray Diffraction, Differential Scanning Calorimetry

## Abstract

Ti-6Al-4V (Ti64) parts manufactured by Laser Powder Bed Fusion (L-PBF) exhibit a fine martensitic microstructure and significant residual stresses that are detrimental for their mechanical performance. Consequently, post-processing heat treatments are necessary to relieve these internal stresses and achieve a microstructure adequate for the mechanical requirements. Given the variations in powder compositions and processing parameters, there is a large scattering of physical properties of both as-built and heat-treated parts. In this context, this study quantifies the link between interstitial contents (specifically, oxygen, nitrogen) and the transition temperatures of as-built parts, using as-atomized pre-alloyed powders for reference. The martensite decomposition temperature and beta transus temperature are assessed using high-temperature X-Ray diffraction and differential scanning calorimetry for both the powder and as-built parts. It was found that the martensite that composes the as-built microstructure can be decomposed into a stable  $\alpha + \beta$  structure at temperatures exceeding 490 °C. Oxygen and nitrogen pick-up occurs during the L-PBF process, leading to an elevated beta transus temperature in as-built parts relative to the original powder. This insight provides a guide for optimizing post-processing heat treatments for Ti64 as-built components.

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# 1 Introduction

2 Research and development in additive manufacturing of metallic materials recently  
3 achieved a high degree of technological maturity. Laser powder bed fusion (L-PBF) in  
4 particular is now capable of producing dense and functional metallic parts of high geo-  
5 metrical complexity which are of great interest for many applications.

6 The two-phase Ti-6Al-4V (Ti64) titanium alloy is a widely used structural material in the  
7 aerospace industry due to its excellent specific strength and corrosion resistance. When  
8 elaborated with conventional processing techniques such as forging and annealing, Ti64  
9 shows a microstructure consisting of both the  $\alpha$  (hexagonal close-packed) and  $\beta$  (body-  
10 centered cubic) equilibrium phases at room temperature. When the thermo-mechanical  
11 manufacturing routine of the material is properly fixed, this stable microstructure im-  
12 plies a good combination of strength and ductility [1, 2]. In contrast, the high cooling  
13 rates involved during L-PBF processing of Ti64 create a microstructure consisting of  
14 very fine needles of an  $\alpha'$  martensitic phase [3, 4]. Significant thermal gradients are  
15 also generated during the building process and, as a consequence, large residual stresses  
16 develop in the parts as layers are consecutively built [5]. These characteristics result in  
17 typical tensile properties of L-PBF Ti64 parts that show a high yield stress and tensile  
18 strength but a low ductility compared to the wrought material taken as a reference [4,  
19 6].

20 To relieve the residual stresses of the as-built parts and achieve a microstructural evolu-  
21 tion that helps to balance the static properties of the material, the use of post-processing  
22 heat treatments is a topic of main interest for industrial applications. It has been shown  
23 in previous studies that post-processing heat treatments performed in the sub-transus  
24 range of the alloy (below beta transus temperature) lead to the transformation of the  
25 fine  $\alpha'$  needles to a coarser mixture of  $\alpha$  and  $\beta$  phases [4, 6–8]. It is therefore of great  
26 interest to determine the Martensitic Decomposition Temperature (MDT) above which  
27 this phase transformation occurs.

28 In addition, when designing heat-treatments of titanium alloys, a crucial technological  
29 parameter to consider is the Beta Transus Temperature (BTT) above which the  $\alpha + \beta$   
30 stability domain changes into 100 % of  $\beta$  phase. It is in fact known that exceeding the  
31 BTT during heat treatment of Ti64 alloy leads to a drastic  $\beta$  grains growth [9, 10] and  
32 possible microstructural heterogeneity due to the cooling rate dependence of the phase  
33 transformations from the  $\beta$  domain, followed by mechanical properties deterioration [7,  
34 8]. Based on information dispensed by manufacturers, the BTT for ASTM grade 5 Ti64  
35 ranges between 980 °C and 1 000 °C. As the BTT is dependent on the chemical com-  
36 position of the alloy [11], these values may vary. In particular, oxygen, nitrogen and  
37 carbon are  $\alpha$ -forming interstitial elements that increase the BTT significantly: Kahveci  
38 and Welsch found in fact that the BTT is raised by 243 °C by 1 wt% of oxygen equivalent  
39 [12]. This effect can be therefore drastic in Ti64 powders, where BTT can be as high as  
40 1 200 °C when oxygen is not properly controlled [13]. Regarding the L-PBF process, the

41 BTT is very likely to be underestimated with the use of powders chemical composition  
 42 as it is demonstrated that oxygen and nitrogen pick-up occur during samples fabrication  
 43 in the atmosphere-controlled chamber of the machine [14, 15].  
 44 Thus, the object of the present work is to propose an experimental estimation of the tran-  
 45 sition temperatures (MDT, BTT) of interest for designing post L-PBF process heat treat-  
 46 ments of Ti64. The investigations are conducted on as-built parts and on as-atomized  
 47 pre-alloyed powders as a reference. Then, the effects of oxygen and nitrogen pick-up  
 48 during the process are discussed.

## 49 2 Materials and methods

50 In the present work, a batch of plasma atomized pre-alloyed Ti64 powder manufactured  
 51 by Tekna Advanced Materials Inc., Canada, was used. The chemical composition is  
 52 detailed in Table 1.

Ti	Al	V	Fe	O	C	N	H
Base	6.22	3.87	0.18	0.14	0.009	0.02	0.004

Table 1: Chemical composition (wt%) of the batch of grade 5 Ti64 powder provided by the supplier.

53 Figure 1.a shows that most of the powder particles have a spherical shape and some of  
 54 them exhibit a few attached satellites whose size is below 5  $\mu\text{m}$ . Figure 1.b indicates  
 55 the particle size distribution of the powder batch measured by laser diffraction using a  
 56 Malvern Panalytical Mastersizer 3000 equipped with a dry dispersion unit. D(10), D(50)  
 57 and D(90) are 6.9  $\mu\text{m}$ , 13.8  $\mu\text{m}$  and 21.9  $\mu\text{m}$  respectively.

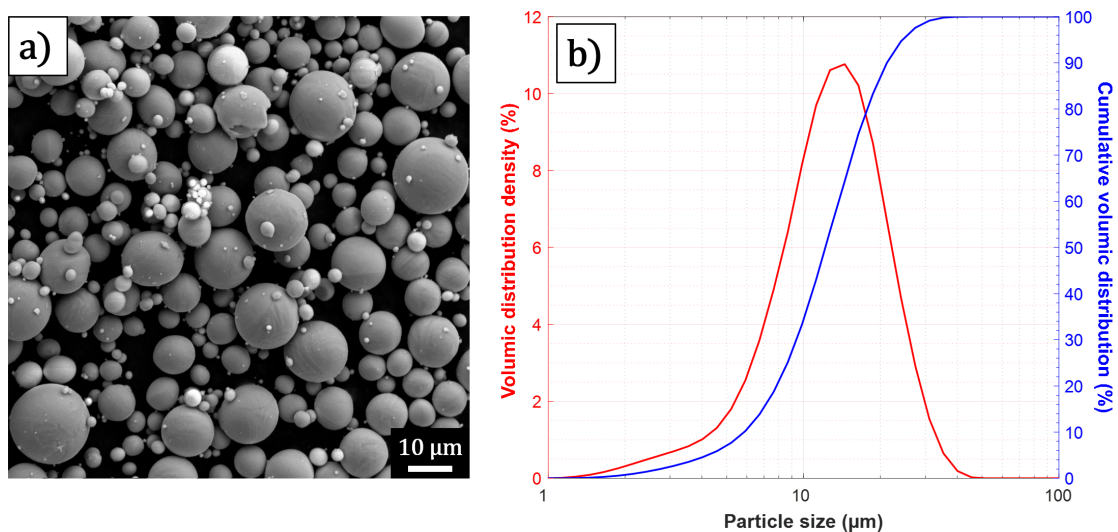


Figure 1: Secondary electron SEM image (a) and volumic particle size distribution (b) of the plasma atomized Ti64 powder batch used.

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58 Samples were built with the studied powder batch using a FormUp 350 L-PBF ma-  
59 chine provided by AddUp, France. The fabrication step was performed under an argon  
60 protective atmosphere with an oxygen concentration measured at the top of the chamber  
61 lower than 500 ppm. The orientations of the parts are described using the axis of the  
62 L-PBF machine with Z axis being the building direction.

63 Oxygen (O) and nitrogen (N) concentrations before (powder) and after (as-printed part)  
64 building was determined through an inert gas fusion method using a LECO device. To  
65 ensure the reproducibility of the technique, 5 measurements were made on 100 mg sam-  
66 ples. As-printed samples were extracted in the bulk of a *post mortem* Charpy impact  
67 V-notch specimen constructed near-net shape along the Z-axis. The impact properties  
68 of the as-printed material, as well as those after various sub-transus heat treatments,  
69 are detailed in Ref. [16]. Examinations of the microstructure by X-Ray Diffraction  
70 (XRD) and scanning electron microscopy (SEM) were made on 3 mm thick pieces cut  
71 from 15 mm<sup>3</sup> cubic samples. Sample preparation was conducted by grinding the pieces  
72 with SiC paper up to 320 grit size followed by 9 μm diamond solution and chemical-  
73 mechanical polishing with a mixture of colloidal silica, hydrogen peroxide and ammonia.  
74 A vibratory polishing step with colloidal silica was applied before taking the SEM pic-  
75 tures in backscattered electron mode. Micrographs were also taken on an Olympus GX51  
76 equipped with a motorized stage after etching of the samples for 90 s with Kroll reagent.  
77 To determine a first estimation of the MDT, high temperature XRD was performed on a  
78 Bruker D8 advance diffractometer equipped with a Ni K<sub>β</sub> filter, a Lynxeye XE detector  
79 and a Cu-K<sub>α</sub> ( $\lambda = 1.54 \text{ \AA}$ ) X-Ray tube source operating at 40 kV and 40 mA. Heating  
80 of the sample occurred in an Anton Paar HTK 1200N sample stage furnace capable of  
81 producing homogeneous temperature up to 1 200 °C by radiation. Secondary vacuum  
82 ( $10^{-3}$  mbar) was reached by use of a Pfeiffer Vacuum HiCube 80 pumping station.

83 In this study, Differential Scanning Calorimetry (DSC) was chosen to determine the  
84 transition temperatures as this technique is characterized by high sensitivity to thermal  
85 effects induced by phase transformations [17, 18]. DSC investigations were carried out  
86 on a SETARAM Labsys Evo calorimeter equipped with a high sensitivity 3D-Cp sensor  
87 especially designed to detect low intensity thermal effects. All DSC experiments were  
88 performed in Al<sub>2</sub>O<sub>3</sub> crucibles with an empty crucible taken as a reference. The exper-  
89 iments were conducted under an argon of commercial purity (Ar  $\geq$  99.999 %). After  
90 pumping the working chamber three times to a vacuum level of 20 mbar, the argon  
91 flow is set to (50 mL min<sup>-1</sup>). The as-printed samples used for DSC were extracted in  
92 the bulk of the same Charpy impact V-notch specimen used for chemical composition  
93 analysis. When preparing the samples, attention was paid to fill at best the volume of  
94 the crucible with material in order to increase the magnitude of the DSC signal.

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### 95 3 Results and Discussion

96 The oxygen (O) and nitrogen (N) concentrations in the Ti64 powder and in as-built  
97 parts determined by inert gas fusion method are available in Table 2. From these results,  
98 it is found that Ti64 absorbs O during printing of the parts ( $\approx +200$  ppm). A little N  
99 pick-up also tends to occur even if it appeared to be less distinct than oxygen pick-up  
100 regarding the uncertainties of the concentrations measured in this study.  
101

Ti64 state	O mass content (ppm)	N mass content (ppm)
As-atomized powder	$1\,529 \pm 23$	$168 \pm 30$
As-built part	$1\,698 \pm 30$	$240 \pm 43$

Table 2: O/N chemical composition in the Ti64 powder and as-built parts.

102 Microstructural investigations reveal that both the powder and the as-built part con-  
103 sist of an acicular  $\alpha'$  microstructure with the presence of very thin and entangled nee-  
104 dles. These structures are inherited from the very fast cooling rates from the  $\beta$  domain  
105 occurring during both processes with an order of magnitude of  $10^3$  K s $^{-1}$  for plasma  
106 atomization [19] and  $10^4$  K s $^{-1}$  for laser melting of powders [20]. From Fig 2.a and 2.b,  
107 it can be observed that some martensitic needles contain a multitude of twins. The  
108 presence of twins inside the  $\alpha$  lamellae is typical from the  $\alpha'$  phase as they contribute  
109 to accommodate and release stresses of the martensitic transformation [3, 4]. According  
110 to these observations, it is expected that martensitic decomposition could take place in  
111 both the powder and the as-built parts leading to a possible estimation of the MDT.  
112

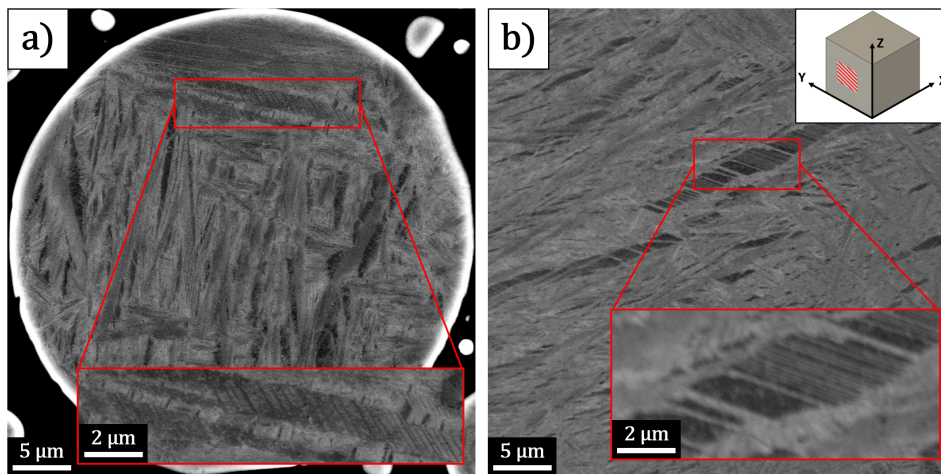


Figure 2: Backscattered electron SEM images showing the acicular microstructure of a powder particle (a) and of an as-built Ti64 cube (b). The high magnification inserts denote that some of the martensitic needles contain a multitude of twins.

113 To determine a first estimation of the MDT, high temperature XRD was carried out  
 114 on a thin sample cut and polished in the XZ plane of an as-printed cube. For time saving  
 115 purposes, XRD acquisitions were only made in a low diffraction angles range. Before  
 116 high temperature measurements, a first scan was done at 30 °C to have a reference  
 117 before heating up to 500 °C. From 500 °C to 800 °C, heating with a step size of 5 °C  
 118 followed by a XRD scan was set. At each step, a timeout of 120 s was applied before  
 119 XRD measurements to reach equilibrium.  
 120 In the purpose to clarify the results, figure 3.a only shows the XRD spectra between  
 121 500 °C and 800 °C with a step size of 50 °C. As temperature rises, the peaks are shifted  
 122 to lower angular values, highlighting an increase of lattice parameters due to thermal  
 123 expansion [21, 22]. Peaks identification has been performed with MAUD software and  
 124 the corresponding crystal planes are indicated in figure 3.a. Zoom window (figure 3.b)  
 125 reveals a  $(110)_\beta$  peak starting from 600 °C which is not visible on the curves at lower  
 126 temperature. The detection of this peak indicates that  $\alpha'$  started to decompose into a  
 127 mixture of  $\alpha + \beta$  during the experiment. The  $(110)_\beta$  peak was distinctively seen starting  
 128 from the 565 °C XRD spectra. This gives a first estimation of the MDT using this  
 129 setup. It can be noticed on 3.b that the intensity of the  $(110)_\beta$  peak increases until  
 130 reaching a maximum around 650 °C, indicating an increase of the diffracting volume  
 131 of  $\beta$  phase. The intensity decreases at 700 °C and the peak is not anymore visible at  
 132 750 °C and 800 °C. This observation is likely due to the activation of oxygen diffusion  
 133 with temperature as the sample became very colored after the experiment (see figures  
 134 4.b and 4.c). Oxygen is indeed an  $\alpha$ -forming element so the more oxygen diffuses into the  
 135 metal, the less the stability of  $\beta$  phase. Estimated X-Ray penetration depth in titanium  
 136 with a copper source is about 5-6  $\mu\text{m}$  [23]. Thus, XRD measurements at temperatures  
 137 where oxygen is highly diffusive in titanium probably took place in the oxygen-enriched  
 138 layer, pointed out as alpha-case in several references [16, 24, 25] and visible in Fig. 4.d  
 139 after chemical attack with Weck's reagent ( $\text{NH}_4\text{HF}_2$  dissolved in ethanol and water).

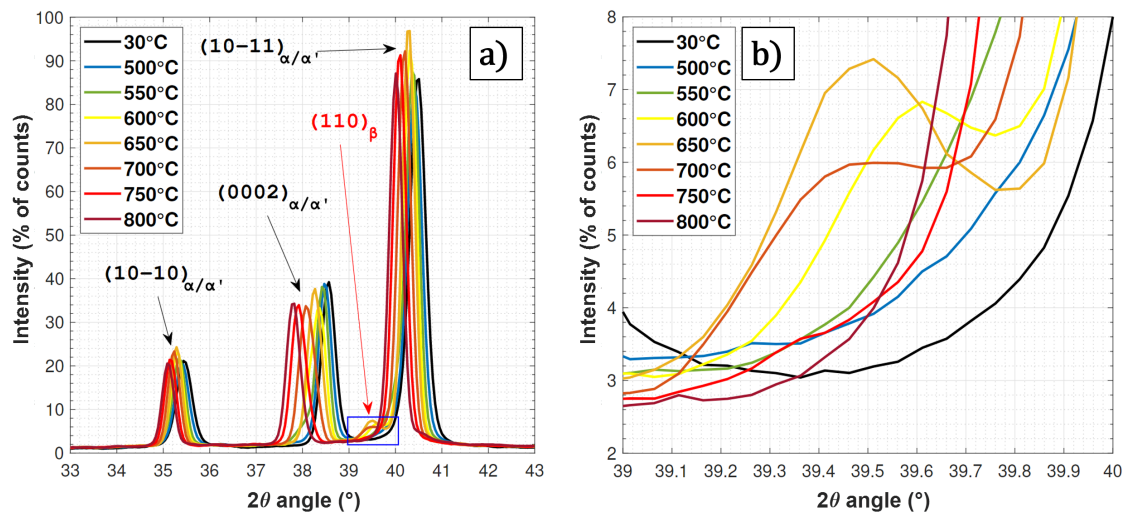


Figure 3: XRD spectra of Ti64 as-built part at various temperatures (a) and corresponding blue frame zoom on the  $\beta$  (100) peak (b).

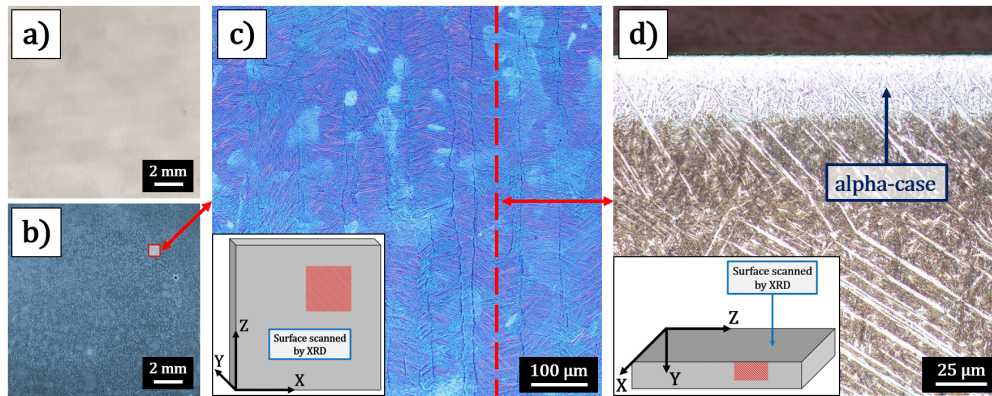


Figure 4: (a) Pictures of the sample's surface before and (b,c) after *in situ* XRD thermal cycle. (d) Transverse cross section of the post-XRD sample revealing an alpha-case layer below the probed surface.

140 For all the DSC analyses, the thermal cycle consisted in heating from 40 °C to 1 200 °C  
 141 followed by a 10 min isothermal exposure followed by cooling from 1 200 °C to 40 °C.  
 142 The cycle was applied twice consecutively on each sample. Heating and cooling rates are  
 143 crucial parameters to consider in thermal analysis: low heating rates lead to a consider-  
 144 able decrease of thermal peak intensity and high cooling rates result in inhomogeneity  
 145 between furnace temperature and sample temperature [17, 26]. For this research, heating  
 146 and cooling rates were fixed at 20 K min<sup>-1</sup>, as it appeared to be a good compromise with  
 147 this device. It is known that when an endothermic or an exothermic peak is detected  
 148 by use of thermal analysis during continuous heating, the corresponding phase transfor-  
 149 mation always begins and ends later than in equilibrium conditions (when heating rate  
 150 is nil). Hence, the extremum point does not correspond to the beginning or the end  
 151 of the phase transformation of interest. To avoid this, some authors use the extremum  
 152 of the first-time derivative of the heat flow versus temperature to determine a value  
 153 corresponding to the starting or the finishing temperature of a phase transformation  
 154 occurring during continuous heating [18, 27]. This approach was used to estimate the  
 155 MDT and BTT in this study. The DSC-curves (heat flow in W g<sup>-1</sup>) and D-DSC curves  
 156 (heat flow derivative in W g<sup>-1</sup> K<sup>-1</sup>) during continuous heating are presented in figure  
 157 5.a for powder and in figure 5.b for as-built part. It can be seen on both graphs that  
 158 an exothermic peak is visible around 500 °C during first heating while second heating  
 159 resulted in no exothermic peak. As shown in figures 6.a and 6.b, the microstructure  
 160 of the as-built part changed from acicular α' needles in columnar parent β grains to  
 161 equilibrium α + β with α-Widmanstätten colonies in equiaxial parent β grains. This  
 162 indicates that the exothermic peaks were associated to an irreversible metastable phase  
 163 transformation corresponding to the α' decomposition. The measured MDT are similar  
 164 for powder and as-built part, respectively 495 °C and 490 °C. It is therefore considered  
 165 that the stability of the α' phase is equivalent in both cases, leading to a comparable  
 166 martensitic decomposition kinetic upon heating. These MDT values are however lower  
 167 than the *in situ* XRD estimation. This result could be explained by the fact that when



168 the martensite decomposition started, the freshly transformed  $\beta$  phase fraction was too  
 169 low to give an intensity higher than the detection limit of the XRD device.

170

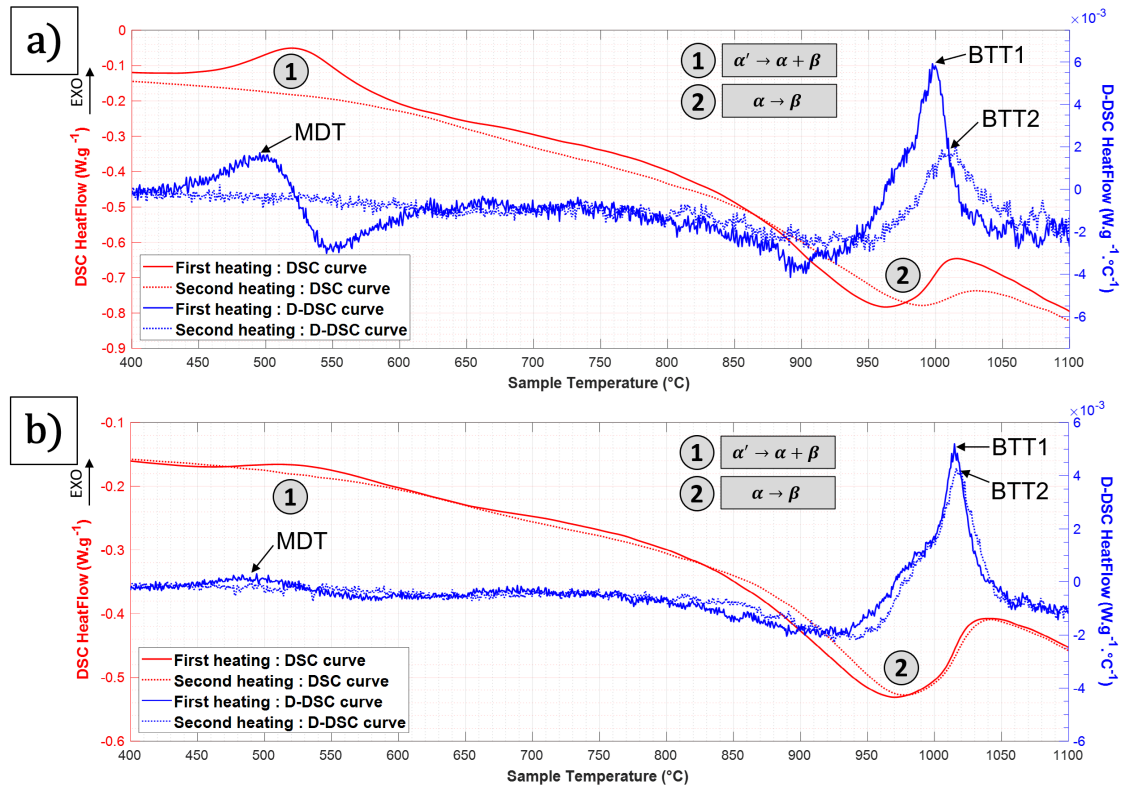


Figure 5: DSC curves of (a) powder and (b) as-built part during continuous heating.

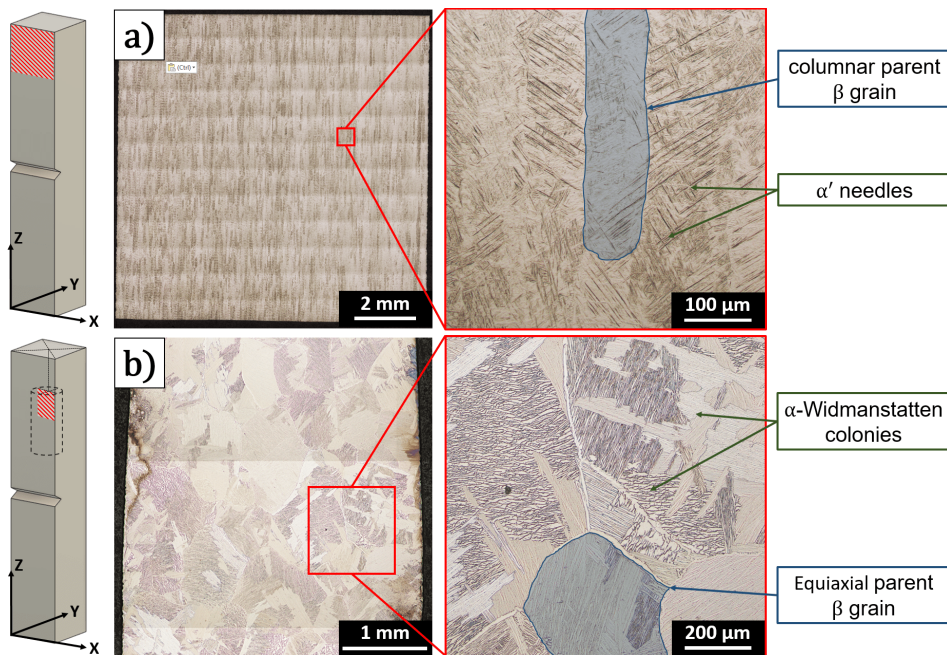


Figure 6: Optical micrographs showing the microstructure in the XZ plane of (a) an as-built part and (b) on the same part after cooling from 1 200 °C to 40 °C at 20 K min<sup>-1</sup> in the DSC device.

171 Figures 5.a and 5.b also show an endothermic peak around 1 000 °C that is present  
 172 in first and second heating of Ti64 powder and as-built part. These peaks correspond  
 173 to the beta transus of the alloy and are spread on a wide temperature range. In fact,  
 174 the kinetics of  $\alpha$  to  $\beta$  phase transformation is governed by a dissolution temperature  
 175 around 700 °C from which the  $\beta$  phase fraction grows exponentially with temperature  
 176 for slow heating [13, 21, 22]. For comparison with the experimental work, Thermo-Calc  
 177 calculations were performed with the TCTI4 database. The chemical composition of the  
 178 simulated alloy was taken from table 1 data, except for oxygen and nitrogen contents  
 179 that were taken from table 2 for both the powder and the as-built part. Figure 7 depicts  
 180 the evolution of the equilibrium mole fraction of  $\alpha$  and  $\beta$  phases as the function of tem-  
 181 perature. From these curves, simulated  $BTT_{TC}$  were determined as the temperatures  
 182 at which the equilibrium  $\alpha$  and  $\beta$  phase fractions reaches 0 % and 100 % respectively.  
 183

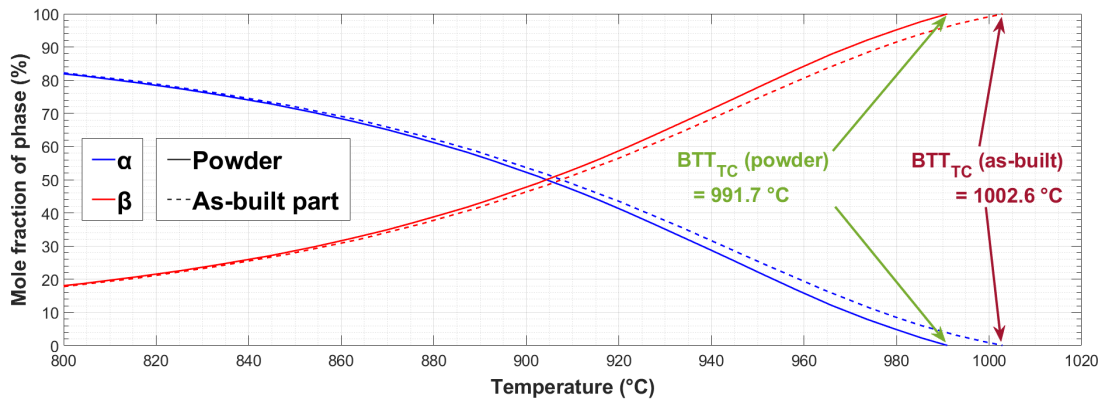


Figure 7: Equilibrium mole fraction of  $\alpha$  and  $\beta$  phases as the function of temperature calculated using the TCTI4 database of Thermo-Calc software. The chemical compositions of the powder and the as-built part were taken from tables 1 and 2.

184 The experimental BTT estimated with DSC for both first and second heating ( $BTT_1$   
 185 and  $BTT_2$  respectively) and the simulated  $BTT_{TC}$  are compared in figure 8.a. From  
 186 these results, it can be observed that the  $BTT_1$  and the  $BTT_{TC}$  are close for both the  
 187 powder and the as-built part. This illustrates the reliability of the BTT determination  
 188 by use of the extremum of the DSC heat flux first time derivative for Ti64 alloy. The gap  
 189 of +12 °C between the  $BTT_{TC}$  and the  $BTT_1$  for the as-built part may be explained by  
 190 the fact that the higher the heating rate, the lower the system is close to the equilibrium  
 191 conditions [22]. To measure the impact of the heating rate, two DSC cycles were made  
 192 with heating rates fixed at 10 K min<sup>-1</sup> and 40 K min<sup>-1</sup> on as-built samples similar to  
 193 the one performed at 20 K min<sup>-1</sup>. From figure 8.b, it is visible that the heating rate has  
 194 a strong influence on the BTT estimation and that the gap between the  $BTT_{TC}$  and the  
 195  $BTT_1$  measured at 10 K min<sup>-1</sup> is reduced to +4 °C only.  
 196 The  $BTT_1$  of the as-built part determined during first continuous heating is +17 °C  
 197 higher than the  $BTT_1$  of the powder. It is therefore noticeable that this increase is  
 198 correlated to the oxygen and nitrogen pick-up during the L-PBF process. Similar con-

199 clusions are dressed from the Thermo-Calc simulations with a lower deviation (+12 °C)  
 200 measured between powder and as-built part with different O/N concentrations. How-  
 201 ever, it should be noted that titanium alloys are also sensitive to carbon pick-up when  
 202 submitted to high temperature manufacturing routines [28, 29]. It was not possible to  
 203 characterize the carbon content in this study but by imposing an arbitrary [C] concentra-  
 204 tion of 0.02 wt% (+100 ppm compared to the powder) in the Thermo-Calc simulation,  
 205 the increase of  $BTT_{TC}$  between the powder and the as-built part raises to +16 °C.  
 206

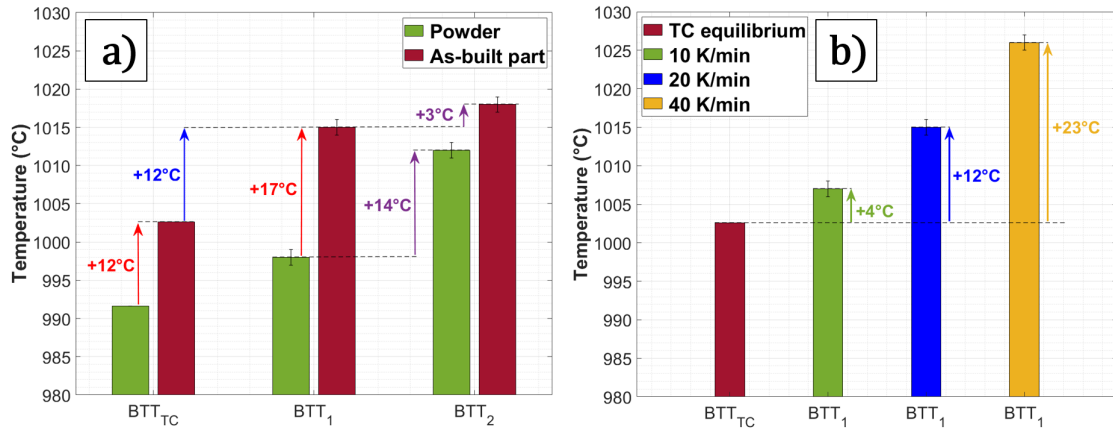


Figure 8: Beta transus temperatures estimated from the DSC scans performed at 20 K min<sup>-1</sup> on the powder and the as-built part (a).  $BTT_1$  and  $BTT_2$  correspond to first and second heating respectively.  $BTT_{TC}$  were taken from figure 7. Beta transus temperatures at first heating ( $BTT_1$ ) estimated from the DSC scans performed at 10 K min<sup>-1</sup>, 20 K min<sup>-1</sup> and 40 K min<sup>-1</sup> on as-built samples (b).

207 Finally, figure 9 show that the two DSC thermal cycles up to 1 200 °C performed  
 208 on the powder sample led to a partial sintering. The resulting powder aggregate was  
 209 cut in three identical sections and O/N inert gas fusion measurements were made. The  
 210 results displayed in figure 9 reveal an important increase of the oxygen content, with  
 211 a gradient from top to bottom that appears to be linked to the direction of the argon  
 212 flux. This result has to be compared with the difference between the first and the second  
 213 continuous heating in figure 8.a. Indeed, it can be observed that an important 14 °C  
 214 increase occurred for the powder while only a 3 °C increase occurred for the as-built  
 215 part. Specific surface area of the powder sample is very large compared to the as-built  
 216 fully dense sample used for DSC. Therefore, oxidation and oxygen pick-up in the powder  
 217 during first heating probably played an important role in increasing the BTT measured  
 218 during second heating [12]. The high affinity of Ti with interstitial elements makes very  
 219 difficult the complete protection of samples during DSC as-well-as during high tempera-  
 220 ture XRD. However, it should be borne in mind that  $\alpha$  phase morphology can also have  
 221 an effect on the shape of the endothermic peak related to the transformation [18, 27].  
 222

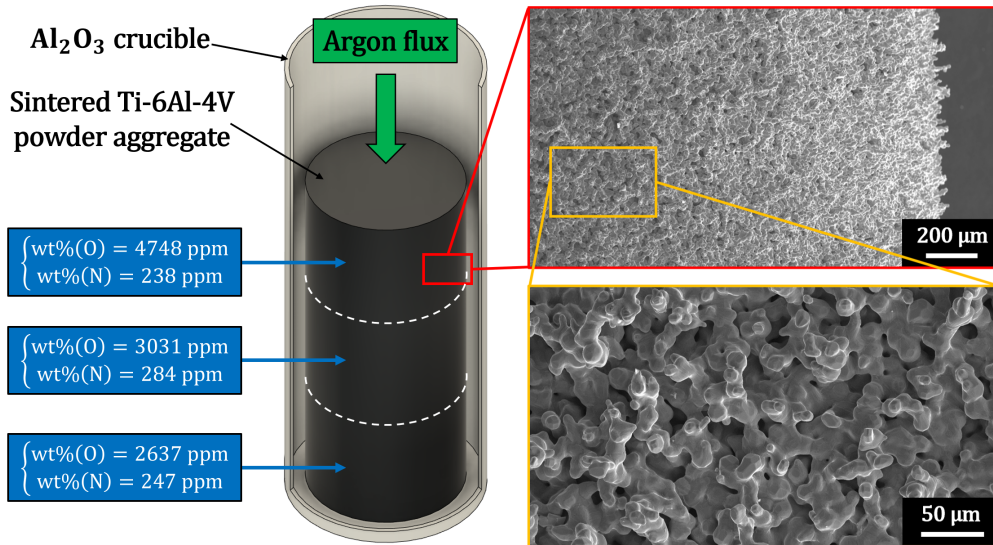


Figure 9: Secondary electron SEM images of the sintered Ti64 powder aggregate after DSC thermal cycle at  $20 \text{ K min}^{-1}$  and corresponding O/N chemical composition measured in three slices.

## 223 4 Conclusions

224 In this study, experimental measurements of the phase transformations that can occur  
 225 during the post-processing heat treatment of Ti64 parts, as printed by L-PBF,  
 226 were performed. These measurements were conducted for both as-printed material and  
 227 as-atomized pre-alloyed powders as a reference. Notably, DSC investigations were un-  
 228 dertaken to gauge the influence of oxygen content on the martensite decomposition tem-  
 229 perature (MDT) and the beta transus temperature (BTT). These findings offer insights  
 230 for devising post-processing heat treatments of Ti64 printed by L-PBF. The following  
 231 conclusions are drawn from this work:

- 232 • The oxygen concentration difference between the powder and the as-printed part  
 233 sees an average increase of 200 ppm, indicating that oxygen pick-up occurs during  
 234 the L-PBF process.
- 235 • Both the powder and the as-built part exhibit a martensitic microstructure. The  
 236 metastable  $\alpha'$  phase can be decomposed into a mixture of stable  $\alpha + \beta$  phases.  
 237 The MDT was estimated to be  $565 \text{ }^\circ\text{C}$  using the *in situ* high-temperature XRD  
 238 setup, and  $490 \text{ }^\circ\text{C}$  through DSC analysis. This underscores that martensite can  
 239 transition into equilibrium phases well below the dissolution temperature, typically  
 240 cited around  $700 \text{ }^\circ\text{C}$  for the Ti64 alloy.
- 241 • The variation in oxygen concentration between the powder and as-built parts re-  
 242 sults in an estimated increase of  $+17 \text{ }^\circ\text{C}$  in the alloy's BTT. In contrast, the  
 243 estimated MDT appears to remain unaffected by this shift in chemical compo-  
 244 sition.

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## Data availability

The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

## CRedit authorship contribution statement

**Quentin Gaillard**: Conceptualisation, Writing - Original Draft, Investigation, Visualisation. **Xavier Boulnat**: Conceptualisation, Supervision, Writing - Review & Editing. **Sophie Cazottes**: Conceptualisation, Supervision, Writing - Review & Editing. **Sylvain Dancette**: Conceptualisation, Writing - Review & Editing. **Christophe Desrayaud**: Supervision, Validation, Funding acquisition.

## 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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