



HAL
open science

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

Quentin Gaillard, Xavier Boulmat, Sophie Cazottes, Sylvain Dancette,
Christophe Desrayaud

► To cite this version:

Quentin Gaillard, Xavier Boulmat, Sophie Cazottes, Sylvain Dancette, Christophe Desrayaud. On the transformation temperatures of Ti-6Al-4V: Effect of oxygen pick-up during Laser Powder Bed Fusion. *Materials Characterization*, 2023, 205, 10.1016/j.matchar.2023.113323 . hal-04292443

HAL Id: hal-04292443

<https://hal.science/hal-04292443v1>

Submitted on 18 Jan 2024

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

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

Quentin Gaillard ^{a,b,*}, Xavier Boulnat ^b, Sophie Cazottes ^b, Sylvain Dancette ^{b,c}, Christophe Desrayaud ^a

^a Mines Saint-Etienne, Univ Lyon, CNRS, UMR 5307 LGF, F-42023 Saint-Etienne, France

^b Université de Lyon, INSA Lyon, MATEIS, UMR CNRS 5510, F-69621 Villeurbanne, France

^c ElyTMax IRL3757, CNRS, Université de Lyon, INSA Lyon, Centrale Lyon, Université Claude Bernard Lyon 1, Tohoku University,

Sendai, 980-8577, Japan

* Corresponding author: quentin.gaillard@emse.fr

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.

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 α (hexagonal close-packed) and β (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 α' 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 α' needles to a coarser mixture of α and β 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 β phase. It is in fact known that exceeding the
31 BTT during heat treatment of Ti64 alloy leads to a drastic β grains growth [9, 10] and
32 possible microstructural heterogeneity due to the cooling rate dependence of the phase
33 transformations from the β 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 α -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 μm . 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 μm , 13.8 μm and 21.9 μm respectively.

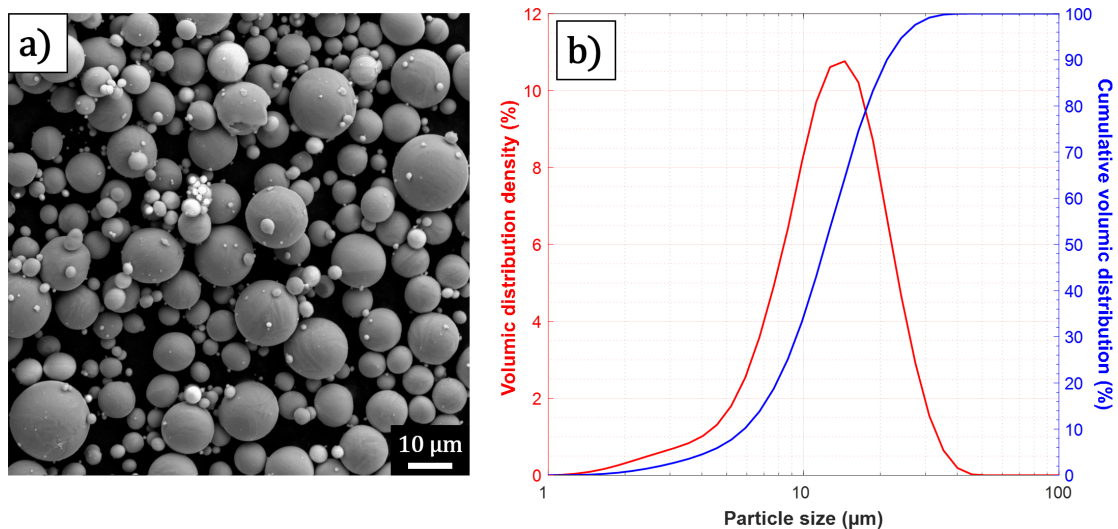


Figure 1: Secondary electron SEM image (a) and volumic particle size distribution (b) of the plasma atomized Ti64 powder batch used.

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 mm³ 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_β filter, a Lynxeye XE detector
79 and a Cu-K_α ($\lambda = 1.54 \text{ \AA}$) 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 Al₂O₃ crucibles with an empty crucible taken as a reference. The exper-
89 iments were conducted under an argon of commercial purity (Ar ≥ 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⁻¹). 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.

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 ± 30
As-built part	$1\,698 \pm 30$	240 ± 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 α' microstructure with the presence of very thin and entangled nee-
104 dles. These structures are inherited from the very fast cooling rates from the β 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 α lamellae is typical from the α' 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

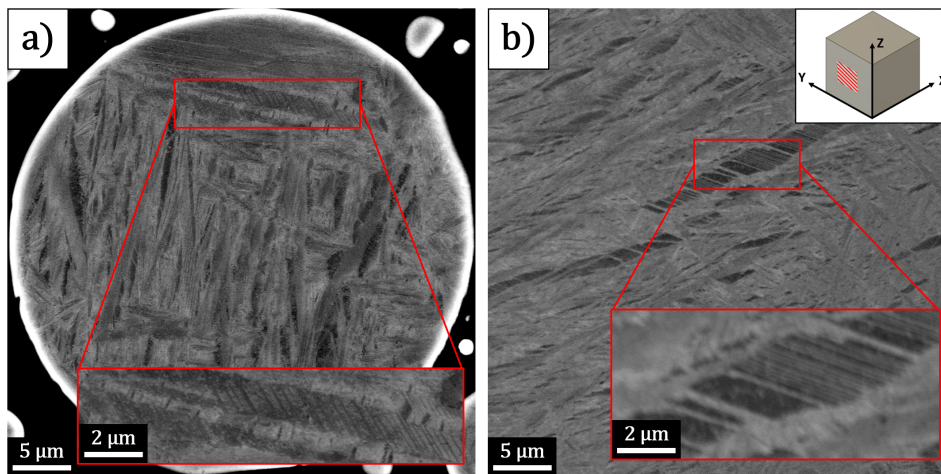


Figure 2: Backscattered electron SEM images showing the acicular microstructure of a powder particle (a) and of an as-built Ti64 cube (b). The high magnification inserts denote that some of the martensitic needles contain a multitude of twins.

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 α' 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 β 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 α -forming element so the more oxygen diffuses into the
 135 metal, the less the stability of β phase. Estimated X-Ray penetration depth in titanium
 136 with a copper source is about 5-6 μm [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 (NH_4HF_2 dissolved in ethanol and water).

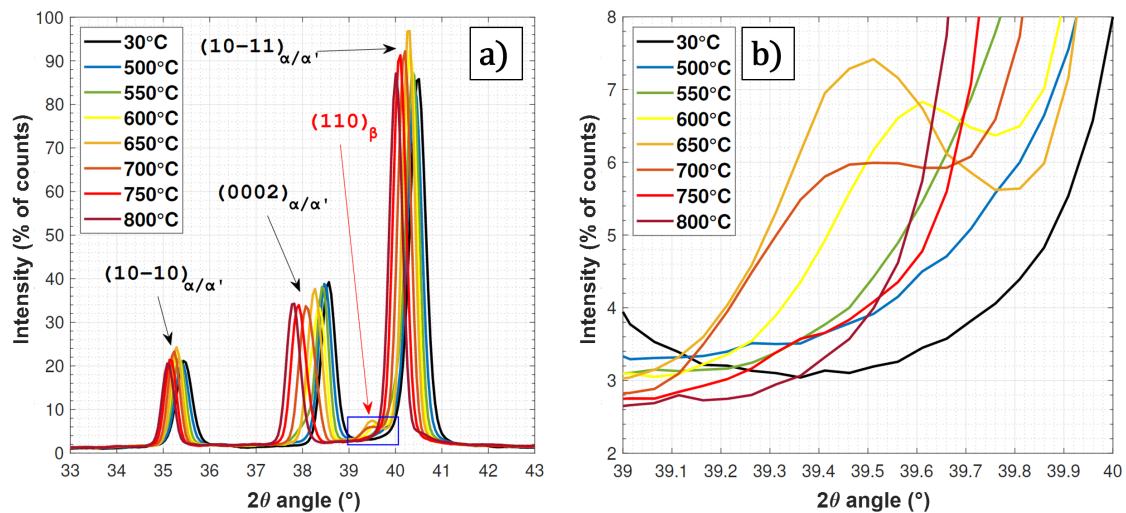


Figure 3: XRD spectra of Ti64 as-built part at various temperatures (a) and corresponding blue frame zoom on the β (100) peak (b).

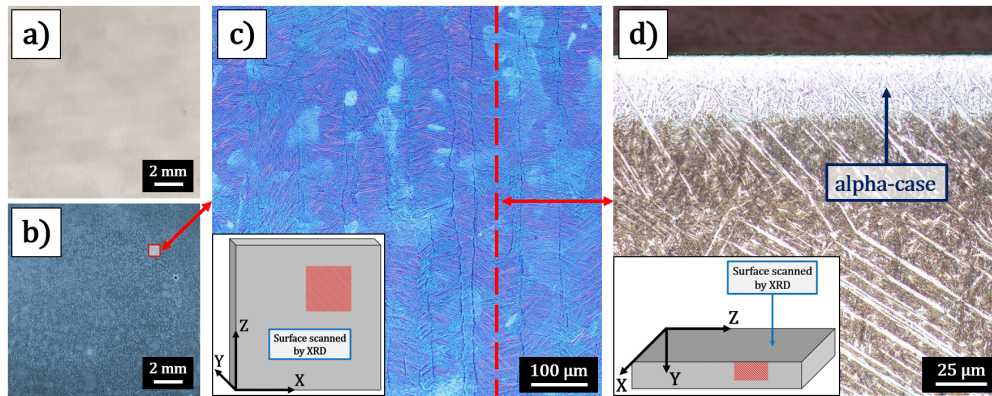


Figure 4: (a) Pictures of the sample's surface before and (b,c) after *in situ* XRD thermal cycle. (d) Transverse cross section of the post-XRD sample revealing an alpha-case layer below the probed surface.

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⁻¹, 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⁻¹) and D-DSC curves
 156 (heat flow derivative in W g⁻¹ K⁻¹) 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 β phase fraction was too
 169 low to give an intensity higher than the detection limit of the XRD device.

170

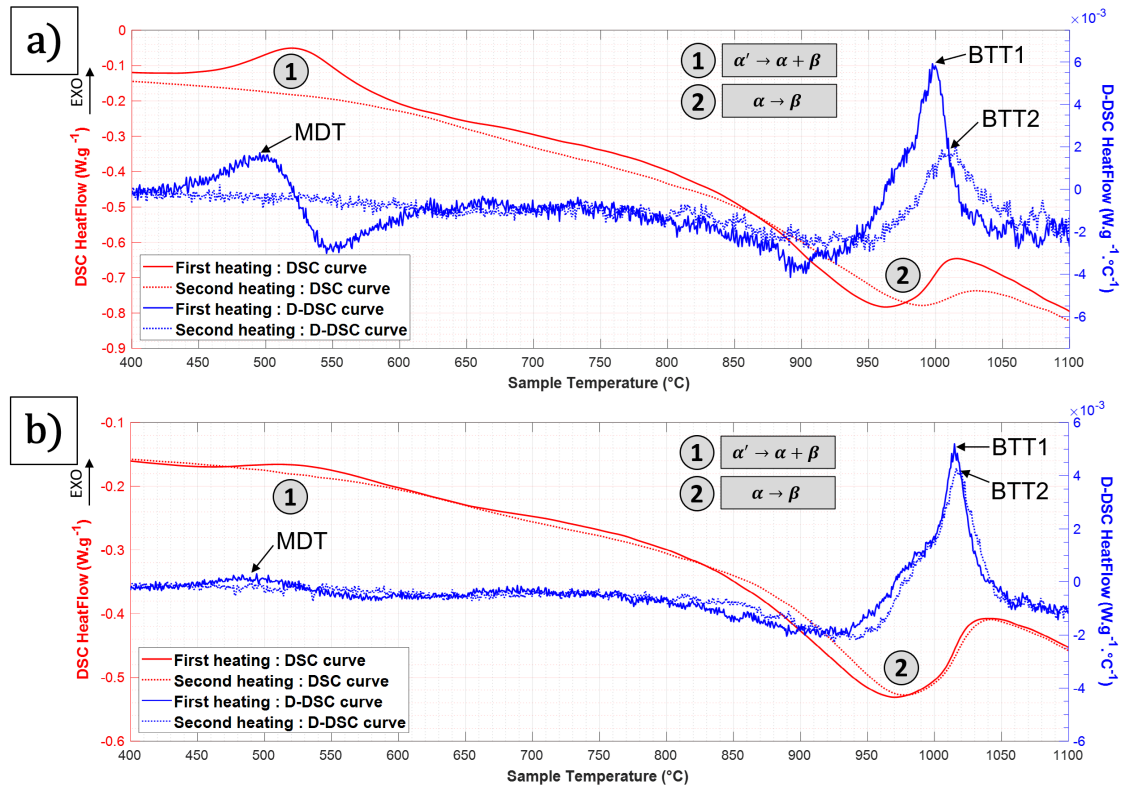


Figure 5: DSC curves of (a) powder and (b) as-built part during continuous heating.

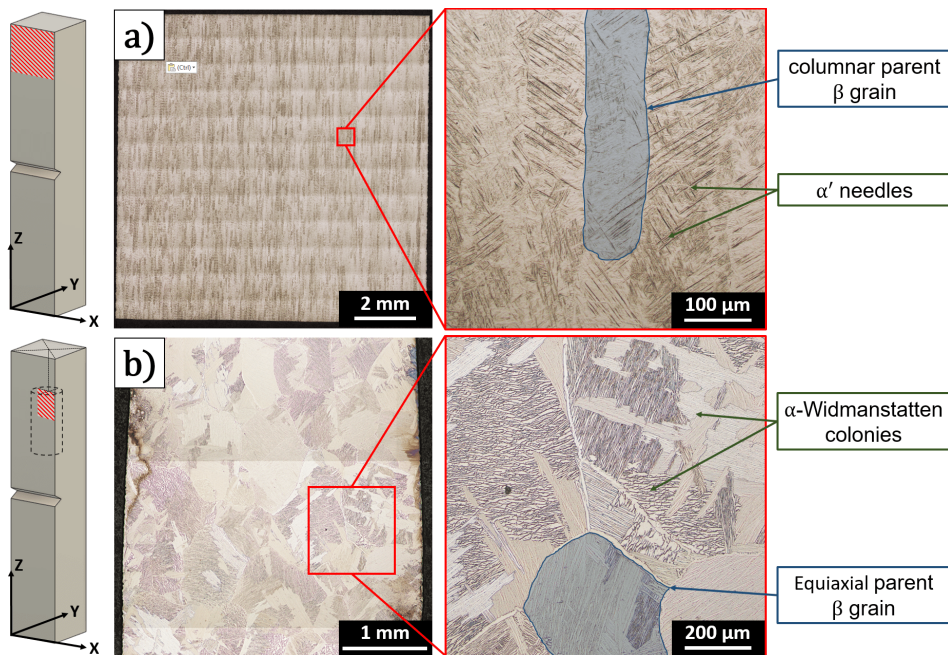


Figure 6: Optical micrographs showing the microstructure in the XZ plane of (a) an as-built part and (b) on the same part after cooling from 1 200 °C to 40 °C at 20 K min⁻¹ in the DSC device.

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 α to β phase transformation is governed by a dissolution temperature
 175 around 700 °C from which the β 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 α and β phases as the function of tem-
 181 perature. From these curves, simulated BTT_{TC} were determined as the temperatures
 182 at which the equilibrium α and β phase fractions reaches 0 % and 100 % respectively.
 183

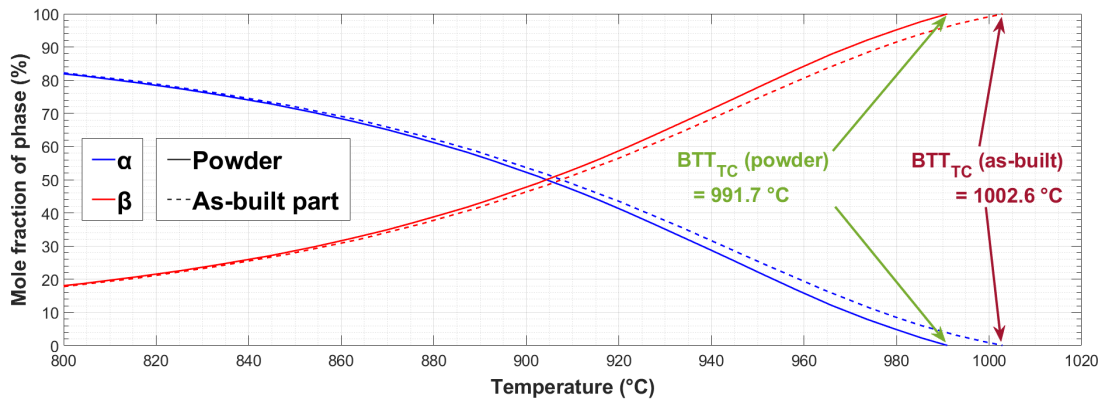


Figure 7: Equilibrium mole fraction of α and β phases as the function of temperature calculated using the TCTI4 database of Thermo-Calc software. The chemical compositions of the powder and the as-built part were taken from tables 1 and 2.

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⁻¹ and 40 K min⁻¹ on as-built samples similar to
 193 the one performed at 20 K min⁻¹. 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⁻¹ 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

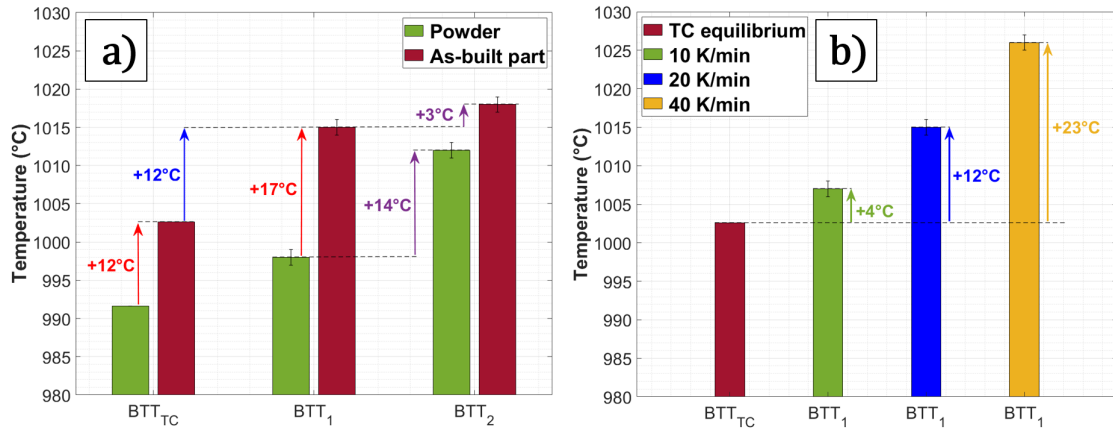


Figure 8: Beta transus temperatures estimated from the DSC scans performed at 20 K min⁻¹ on the powder and the as-built part (a). BTT_1 and BTT_2 correspond to first and second heating respectively. BTT_{TC} were taken from figure 7. Beta transus temperatures at first heating (BTT_1) estimated from the DSC scans performed at 10 K min⁻¹, 20 K min⁻¹ and 40 K min⁻¹ 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 α phase morphology can also have
 221 an effect on the shape of the endothermic peak related to the transformation [18, 27].
 222

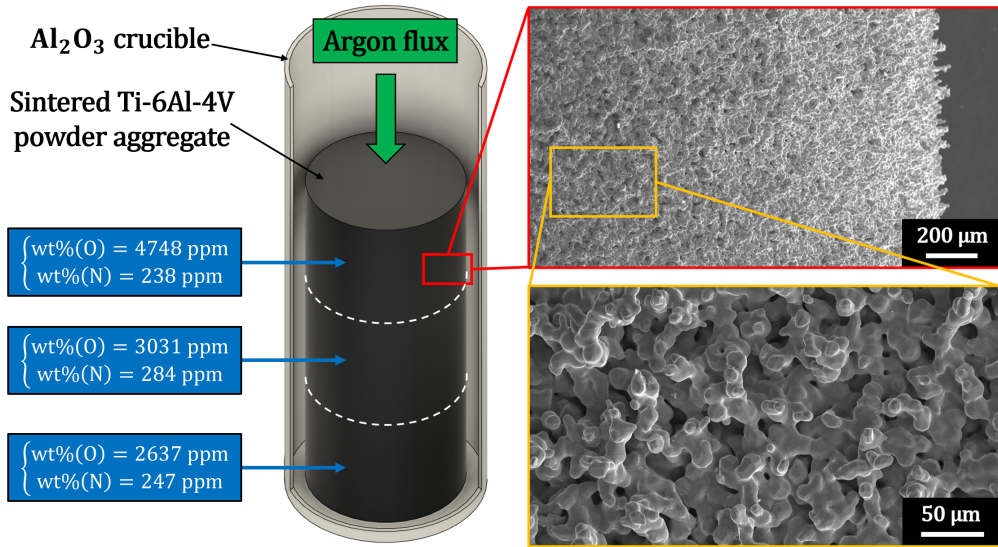


Figure 9: Secondary electron SEM images of the sintered Ti64 powder aggregate after DSC thermal cycle at 20 K min^{-1} and corresponding O/N chemical composition measured in three slices.

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 α' 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.

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.

Acknowledgments

This work performed at LGF and MATEIS laboratories falls within the framework of the AEROPRINT project supported by the French company Dassault Aviation and the Auvergne-Rhône-Alpes Region. The authors are grateful for their financial support and especially thank the project team of the Argonay production site for providing the powder and fabricating the samples studied in this work. The authors would like to acknowledge the help of Marie Janssonet for carrying out the oxygen and nitrogen analysis, Marie-Claude Bertholin for performing the particle size distribution measurements, Sandrine Cardinal for the XRD investigations and Michel Perez for helping with the DSC device.

References

- [1] G. Lütjering. “Property Optimization through Microstructural Control in Titanium and Aluminum Alloys”. In: *Materials Science and Engineering: A* 263.2 (1999), pp. 117–126. ISSN: 09215093. DOI: [10.1016/S0921-5093\(98\)01169-1](https://doi.org/10.1016/S0921-5093(98)01169-1).
- [2] S. Semiatin and T. Bieler. “The Effect of Alpha Platelet Thickness on Plastic Flow during Hot Working of Ti-6Al-4V with a Transformed Microstructure”. In: *Acta Materialia* 49.17 (2001), pp. 3565–3573. ISSN: 13596454. DOI: [10.1016/S1359-6454\(01\)00236-1](https://doi.org/10.1016/S1359-6454(01)00236-1).
- [3] J. Yang, H. Yu, J. Yin, M. Gao, Z. Wang, and X. Zeng. “Formation and Control of Martensite in Ti-6Al-4V Alloy Produced by Selective Laser Melting”. In: *Materials & Design* 108 (2016), pp. 308–318. ISSN: 02641275. DOI: [10.1016/j.matdes.2016.06.117](https://doi.org/10.1016/j.matdes.2016.06.117).
- [4] S. Cao, R. Chu, X. Zhou, K. Yang, Q. Jia, C. V. S. Lim, A. Huang, and X. Wu. “Role of Martensite Decomposition in Tensile Properties of Selective Laser Melted Ti-6Al-4V”. In: *Journal of Alloys and Compounds* 744 (2018), pp. 357–363. ISSN: 09258388. DOI: [10.1016/j.jallcom.2018.02.111](https://doi.org/10.1016/j.jallcom.2018.02.111).
- [5] P. Mercelis and J.-P. Kruth. “Residual Stresses in Selective Laser Sintering and Selective Laser Melting”. In: *Rapid Prototyping Journal* 12.5 (2006), pp. 254–265. ISSN: 1355-2546. DOI: [10.1108/13552540610707013](https://doi.org/10.1108/13552540610707013).
- [6] X. Yan, S. Yin, C. Chen, C. Huang, R. Bolot, R. Lupoi, M. Kuang, W. Ma, C. Coddet, H. Liao, and M. Liu. “Effect of Heat Treatment on the Phase Transformation and Mechanical Properties of Ti6Al4V Fabricated by Selective Laser Melting”. In: *Journal of Alloys and Compounds* 764 (2018), pp. 1056–1071. ISSN: 09258388. DOI: [10.1016/j.jallcom.2018.06.076](https://doi.org/10.1016/j.jallcom.2018.06.076).
- [7] B. Vrancken, L. Thijs, J.-P. Kruth, and J. Van Humbeeck. “Heat Treatment of Ti6Al4V Produced by Selective Laser Melting: Microstructure and Mechanical Properties”. In: *Journal of Alloys and Compounds* 541 (2012), pp. 177–185. ISSN: 09258388. DOI: [10.1016/j.jallcom.2012.07.022](https://doi.org/10.1016/j.jallcom.2012.07.022).
- [8] C. V. Funch, A. Palmas, K. Somlo, E. H. Valente, X. Cheng, K. Poullos, M. Villa, M. A. Somers, and T. L. Christiansen. “Targeted Heat Treatment of Additively Manufactured Ti-6Al-4V for Controlled Formation of Bi-lamellar Microstructures”. In: *Journal of Materials Science & Technology* 81 (2021), pp. 67–76. ISSN: 10050302. DOI: [10.1016/j.jmst.2021.01.004](https://doi.org/10.1016/j.jmst.2021.01.004).
- [9] O. Ivasishin, S. Shevchenko, and S. Semiatin. “Effect of Crystallographic Texture on the Isothermal Beta Grain-Growth Kinetics of Ti-6Al-4V”. In: *Materials Science and Engineering: A* 332.1-2 (2002), pp. 343–350. ISSN: 09215093. DOI: [10.1016/S0921-5093\(01\)01755-5](https://doi.org/10.1016/S0921-5093(01)01755-5).
- [10] S. Semiatin, P. Fagin, M. Glavicic, I. Sukonnik, and O. Ivasishin. “Influence on Texture on Beta Grain Growth during Continuous Annealing of Ti-6Al-4V”. In: *Materials Science and Engineering: A* 299.1-2 (2001), pp. 225–234. ISSN: 09215093. DOI: [10.1016/S0921-5093\(00\)01371-X](https://doi.org/10.1016/S0921-5093(00)01371-X).
- [11] Z. Guo, S. Malinov, and W. Sha. “Modelling Beta Transus Temperature of Titanium Alloys Using Artificial Neural Network”. In: *Computational Materials Science* 32.1 (2005), pp. 1–12. ISSN: 09270256. DOI: [10.1016/j.commatsci.2004.05.004](https://doi.org/10.1016/j.commatsci.2004.05.004).
- [12] A. Kahveci and G. Welsch. “Effect of Oxygen on the Hardness and Alpha/Beta Phase Ratio of Ti6Al4V Alloy”. In: *Scripta Metallurgica* 20.9 (1986), pp. 1287–1290. ISSN: 00369748. DOI: [10.1016/0036-9748\(86\)90050-5](https://doi.org/10.1016/0036-9748(86)90050-5).
- [13] M. Pontoreau, M. Coffigniez, V. Trillaud, C. L. Bourlot, J. Lachambre, L. Gremillard, M. Perez, E. Maire, J. Adrien, P. Steyer, T. Douillard, A. King, and X. Boulnat. “In Situ Synchrotron Study of Sintering of Gas-Atomized Ti-6Al-4 V Powders Using Concomitant Micro-Tomography and X-ray Diffraction: Effect of Particle Size and Interstitials on Densification and Phase Transformation Kinetics”. In: *Acta Materialia* 246 (2023), p. 118723. ISSN: 13596454. DOI: [10.1016/j.actamat.2023.118723](https://doi.org/10.1016/j.actamat.2023.118723).
- [14] B. Vrancken, S. Buls, J.-P. Kruth, and J. Van Humbeeck. “Influence of Preheating and Oxygen Content on Selective Laser Melting of Ti6Al4V”. In: *Annual International Conference on Rapid Product Development Association of South Africa*. Vol. 16. Pretoria, South Africa: Proceedings of the 16th RAPDASA Conference, 2015.
- [15] K. Dietrich, J. Diller, S. Dubiez-Le Goff, D. Bauer, P. Forêt, and G. Witt. “The Influence of Oxygen on the Chemical Composition and Mechanical Properties of Ti-6Al-4V during Laser Powder Bed

-
- Fusion (L-PBF)”. In: *Additive Manufacturing* 32 (2020), p. 100980. ISSN: 22148604. DOI: [10.1016/j.addma.2019.100980](https://doi.org/10.1016/j.addma.2019.100980).
- [16] Q. Gaillard, X. Boulmat, S. Cazottes, S. Dancette, and C. Desrayaud. “Strength/Ductility Trade-off of Laser Powder Bed Fusion Ti-6Al-4V: Synergetic Effect of Alpha-Case Formation and Microstructure Evolution upon Heat Treatments”. In: *Additive Manufacturing* (2023), p. 103772. ISSN: 22148604. DOI: [10.1016/j.addma.2023.103772](https://doi.org/10.1016/j.addma.2023.103772).
- [17] S. Vyazovkin, N. Koga, and C. Schick. *Handbook of Thermal Analysis and Calorimetry*. 2nd ed. Amsterdam: Elsevier. ISBN: 978-0-444-64062-8.
- [18] D. Gadeev and A. Illarionov. “Determination of Beta-Transus Temperature of Two-Phase Titanium Alloys Using Differential Scanning Calorimetry”. In: *Solid State Phenomena* 284 (2018), pp. 259–264. ISSN: 1662-9779. DOI: [10.4028/www.scientific.net/SSP.284.259](https://doi.org/10.4028/www.scientific.net/SSP.284.259).
- [19] A. Birt, V. Champagne, R. Sisson, and D. Apelian. “Microstructural Analysis of Ti-6Al-4V Powder for Cold Gas Dynamic Spray Applications”. In: *Advanced Powder Technology* 26.5 (2015), pp. 1335–1347. ISSN: 09218831. DOI: [10.1016/j.appt.2015.07.008](https://doi.org/10.1016/j.appt.2015.07.008).
- [20] T. Vilaro, C. Colin, and J. D. Bartout. “As-Fabricated and Heat-Treated Microstructures of the Ti-6Al-4V Alloy Processed by Selective Laser Melting”. In: *Metallurgical and Materials Transactions A* 42.10 (2011), pp. 3190–3199. ISSN: 1073-5623, 1543-1940. DOI: [10.1007/s11661-011-0731-y](https://doi.org/10.1007/s11661-011-0731-y).
- [21] J. Elmer, T. Palmer, S. Babu, and E. Specht. “In Situ Observations of Lattice Expansion and Transformation Rates of α and β Phases in Ti-6Al-4V”. In: *Materials Science and Engineering: A* 391.1-2 (2005), pp. 104–113. ISSN: 09215093. DOI: [10.1016/j.msea.2004.08.084](https://doi.org/10.1016/j.msea.2004.08.084).
- [22] Y. Lakroune, D. Connétable, J. Hugues, P. Hermantier, P. Barriobero-Vila, and M. Dehmas. “Microstructural Evolution during Post Heat Treatment of the Ti-6Al-4V Alloy Manufactured by Laser Powder Bed Fusion”. In: *Journal of Materials Research and Technology* 23 (2023), pp. 1980–1994. ISSN: 22387854. DOI: [10.1016/j.jmrt.2023.01.123](https://doi.org/10.1016/j.jmrt.2023.01.123).
- [23] V. Hauk and H. Behnken. *Structural and Residual Stress Analysis by Nondestructive Methods: Evaluation, Application, Assessment*. Amsterdam ; New York: Elsevier, 1997. ISBN: 978-0-444-82476-9.
- [24] R. Gaddam, B. Sefer, R. Pederson, and M.-L. Antti. “Study of Alpha-Case Depth in Ti-6Al-2Sn-4Zr-2Mo and Ti-6Al-4V”. In: *IOP Conference Series: Materials Science and Engineering* 48 (2013), p. 012002. ISSN: 1757-8981, 1757-899X. DOI: [10.1088/1757-899X/48/1/012002](https://doi.org/10.1088/1757-899X/48/1/012002).
- [25] P. Seth, J. S. Jha, A. Alankar, and S. K. Mishra. “Alpha-Case Formation in Ti-6Al-4V in a Different Oxidizing Environment and Its Effect on Tensile and Fatigue Crack Growth Behavior”. In: *Oxidation of Metals* 97.1-2 (2022), pp. 77–95. ISSN: 0030-770X, 1573-4889. DOI: [10.1007/s11085-021-10079-y](https://doi.org/10.1007/s11085-021-10079-y).
- [26] S. Malinov, Z. Guo, W. Sha, and A. Wilson. “Differential Scanning Calorimetry Study and Computer Modeling of $\beta \Rightarrow \alpha$ Phase Transformation in a Ti-6Al-4V Alloy”. In: *Metallurgical and Materials Transactions A* 32.4 (2001), pp. 879–887. ISSN: 1073-5623, 1543-1940. DOI: [10.1007/s11661-001-0345-x](https://doi.org/10.1007/s11661-001-0345-x).
- [27] Y. T. Zhu, J. H. Devletian, and A. Manthiram. “Application of Differential Thermal Analysis to Solid-Solid Transitions in Phase Diagram Determination”. In: *Journal of Phase Equilibria* 15.1 (1994), pp. 37–41. ISSN: 1054-9714. DOI: [10.1007/BF02667680](https://doi.org/10.1007/BF02667680).
- [28] H. Ogden and R. Jaffee. *The Effects of Carbon, Oxygen, and Nitrogen on the Mechanical Properties of Titanium and Titanium Alloys*. Tech. rep. TML-20, 4370612. 1955, TML-20, 4370612. DOI: [10.2172/4370612](https://doi.org/10.2172/4370612).
- [29] W. L. Finlay and J. A. Snyder. “Effects of Three Interstitial Solutes (Nitrogen, Oxygen, and Carbon) on the Mechanical Properties of High-Purity, Alpha Titanium”. In: *JOM* 2.2 (1950), pp. 277–286. ISSN: 1047-4838, 1543-1851. DOI: [10.1007/BF03399001](https://doi.org/10.1007/BF03399001).