

Martensite decomposition kinetics in additively manufactured Ti-6Al-4V alloy: in-situ characterisation and phase-field modelling

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Abstract

Additive manufacturing of Ti-6Al-4V alloy via laser powder-bed fusion leads to non-equilibrium α' martensitic microstructures, with high strength but poor ductility and toughness. These properties may be modified by heat treatments, whereby the α' phase decomposes into equilibrium $\alpha + \beta$ structures, while possibly conserving microstructural features and length scales of the α' lath structure. Here, we combine experimental and computational methods to explore the kinetics of martensite decomposition. Experiments rely on *in-situ* characterisation (electron microscopy and diffraction) during multi-step heat treatment from 400°C up to the alloy β -transus temperature (995°C). Computational simulations rely on an experimentally-informed computationally-efficient phase-field model. Experiments confirmed that as-built microstructures were fully composed of martensitic α' laths. During martensite decomposition, nucleation of the β phase occurs primarily along α' lath boundaries, with traces of β nucleation along crystalline defects. Phase-field results, using electron backscatter diffraction maps of

as-built microstructures as initial conditions, are compared directly with *in-situ* characterisation data. Experiments and simulations confirmed that, while full decomposition into stable $\alpha + \beta$ phases may be complete at 650°C provided sufficient annealing time, visible morphological evolution of the microstructure was only observed for $T \geq 700^\circ\text{C}$, without modification of the prior- β grain structure.

Keywords: Martensite decomposition; Ti-6Al-4V alloy; Additive manufacturing; Phase-field modelling; In-situ microstructure characterisation.

1 Introduction

Titanium (Ti) alloys, such as Ti-6Al-4V (weight %), play a central role in modern structural applications, in particular in aeronautics and biomedical applications [1, 2]. Additive manufacturing (AM) technologies, such as laser powder bed fusion (L-PBF) have demonstrated a great potential for the manufacture of high-performance Ti alloys, thanks to their ability to produce near-net shape components of complex geometry with minimal material waste [3, 4, 5]. L-PBF printed Ti-6Al-4V parts – with or without post-AM heat treatment – exhibit a broad range of microstructures, and a commensurate range of mechanical properties (Figure 1).

Equilibrium phases in Ti-6Al-4V consist of a hexagonal close-packed (hcp) α phase and a body-centred cubic (bcc) β phase, both of which are common in

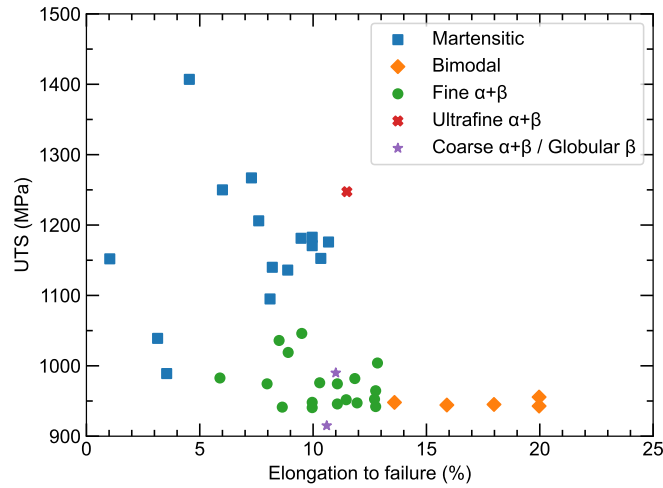


Figure 1: Ultimate tensile strength versus elongation to failure of Ti-6Al-4V samples built by L-PBF, with different types of microstructures, either martensitic (as built) or after heat treatment. Data compiled from Refs [6, 7, 8, 9, 10, 11, 12, 13, 14].

wrought or cast alloys (i.e. with low-to-moderate cooling rates) [15, 16]. Nonequilibrium phases include a hcp α' martensite obtained by rapid cooling [11, 12, 15] and an orthorhombic soft α'' martensite [17, 18, 19], which may form in localised regions with high vanadium concentrations (typically 9 to 13 wt%) [20].

While minor amounts of secondary phases have been reported [21, 22, 9, 23], as-printed L-PBF Ti-6Al-4V most often exhibits a fully acicular martensitic α' microstructure [9, 10, 11, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36]. The α' lath structure forms within prior- β grains, following Burgers crystallographic relationships, thus allowing the reconstruction of parent β grains [26, 27, 37, 38, 39, 40]. Primary β grains typically exhibit elongated shapes with strong $\langle 100 \rangle$ texture along their growth direction, but the resulting α' martensite has a weak texture due to the presence of many martensitic variants [27, 41, 42, 43].

Martensitic microstructures offer high strength but low ductility, due to the hcp nature and slightly distorted lattice of the supersaturated α' phase, making it undesirable for applications requiring a high elongation to failure [7, 8, 15, 44]. Since dual ($\alpha + \beta$) microstructures exhibit excellent mechanical properties (Fig. 1), post-printing heat treatment is often applied to improve mechanical properties (e.g. ductility) [10, 45, 46, 47, 48, 49]. Interestingly, beyond mechanical properties, post-printing heat treatment and the resulting microstructure evolution were also found to substantially improve corrosion resistance [50, 51, 52] and biocompatibility (e.g. hydrophilicity and surface roughness promoting early cell attachment, proliferation and osseointegration, as well as good cytocompatibility) [53].

Heat treatments below the β -transus temperature ($\approx 995^\circ\text{C}$) and above 400°C allow for the martensite decomposition ($\alpha' \rightarrow \alpha + \beta$), while conserving the lamellar features and length scales of the α' lath structure [8, 10, 29, 36, 54, 55, 56, 57, 58, 59]. Below 400°C , stress relaxation of the crystal lattice occurs without apparent phase transformation [45]. Above 400°C , martensite decomposition typically occurs with negligible influence of heating [45] or cooling [55, 60] rates. A broad range of experimental studies have confirmed that the kinetics of martensite decomposition is limited by the diffusion of excess vanadium from the α' martensite [13, 22, 31, 34, 61, 62, 63, 64, 65, 66]. While the enrichment in β -stabilisers at one- and two-dimensional lattice defects may promote β -phase nucleation along such defects [22, 59], the most common β phase nucleation sites were reported along V segregated grain boundaries between α' laths [31, 67, 68].

Traditional heat treatments utilised on L-PBF Ti-6Al-4V were designed for significantly different thermo-mechanical processes (and hence microstructures) [36, 58], and may thus be sub-optimal, or even not appropriate, for additively manufactured Ti-6Al-4V. As a result, new heat treatment processes need to be designed and tailored to L-PBF Ti-6Al-4V [59, 69]. Here, we argue that the exploration and optimisation of novel heat treatments suited to L-PBF Ti-6Al-4V

can be greatly accelerated by the development of state-of-the-art experimentally-informed simulations of microstructure evolution, supported by advanced *in-situ* characterisation techniques.

The rapid advance of *in-situ* characterisation of metals has provided key insight into microstructure formation and evolution [16, 59, 66, 70, 71]. Still, experimental techniques suffer limitations, in particular when multiple characteristics should ideally be tracked simultaneously. For instance, simultaneous monitoring of crystal structure/orientation jointly with chemical composition remains challenging. In that context, the use of computational models can provide a critical support to experimental-based interpretation, i.e. to “fill in the blanks” – e.g. complementing measurements limited by the finite response time and spatial accuracy of detectors, in particular at high temperatures – and reach a deeper understanding of microstructural evolution.

From the modelling perspective, martensite decomposition in Ti-6Al-4V has been studied using classical mean-field Avrami-based models [72, 73, 74, 75, 76, 77]. While mean-field models provide a fast and convenient tool to assess the evolution of phase fractions at different temperatures, they lack information on microstructure morphology and chemical composition, which have a significant effect on mechanical properties, even when phase fractions are equivalent (Figure 1). Microstructure-aware models, such as phase-field (PF) approaches, while more computationally expensive, offer a more detailed description of the evolution of microstructural features, and of their coupling with chemical composition fields [78, 79, 80, 81]. Phase-field models have been proposed to simulate the evolution of Ti-6Al-4V microstructures (phases and composition), for instance for the formation of β microstructure and subsequent precipitation and dissolution of precipitates during repeated thermal cycles [82], or for the evolution of an $\{\alpha + \beta\}$ microstructure subjected to annealing treatment [83, 84, 85]. Moreover, as mentioned in Ref. [80], the predictive capability of PF models depends strongly on the accuracy of the input materials data, in particular temperature-dependent thermodynamic and kinetic parameters, making direct comparison to experiments absolutely essential. Yet, to the best of our knowledge, PF models focused on the decomposition of α' martensite into α and β phases remain lacking.

Here, we propose an experimentally informed phase-field model for martensite decomposition in additively manufactured Ti-6Al-4V alloy. The underlying goal is to develop a digital tool to study the evolution of Ti-6Al-4V microstructure, so as to ultimately guide the design of novel heat treatments for optimal properties in additively manufactured Ti-6Al-4V. The proposed PF model goes beyond existing mean-field models for martensite decomposition by predicting the coupled spatial evolution of phase and solute in the heterogeneous microstructure. The model parameters are calibrated and validated using experimental data from orig-

inal *in-situ* annealing experiments on L-PBF manufactured Ti-6Al-4V. In order to address the computational cost of PF simulations, we solve PF equations by means of an original spectral Fourier-based method computationally parallelised on graphics processing units (GPUs), improving upon a method recently introduced in [86]. The resulting model is robust and efficient, it considers heterogeneous diffusivities in the different phases, and it allows for the use of initial α' martensite microstructures directly obtained from electron backscattered diffraction (EBSD) maps. We use the PF model to simulate the microstructure evolution under step-wise heating treatment and directly compare volume fractions and microstructural morphologies against our *in-situ* high-temperature EBSD data.

2 Materials and methods

2.1 Experiments

Samples used in this study were made of Ti-6Al-4V (grade 23) specimens produced by L-PBF on an EOSINT M290 printer using proprietary optimised process parameters [87]. Microstructural constituents of the as-built material were examined using X-ray Diffraction (XRD) with a Bruker D8 ADVANCE device in conjunction with the DAVINCI XRD system. The XRD pattern was scanned via a Cu-K α 1 X-ray source using a step size of 0.02° and a time step of 1.5 s.

In-situ microstructural observations were carried out on the frontal plane (xz -surface) of the specimens using a JEOL 7100F FEG-SEM equipped with a heating Scanning Electron Microscope (SEM) stage (Murano in-situ stages, Gatan), using a focus distance of 10 mm, emission energy of 15 kV, probe current of 8 μ A, and step size of 0.05 μ m. Flat specimen of 7 mm $\times$ 7 mm and 1.5 mm thick was mirror polished and then mounted on the heating stage via high-temperature carbon paste. The heating temperature was measured via a thermocouple attached to the bottom of the specimen. Such settings allow controlled heating of specimens up to 980°C, with simultaneous imaging and EBSD. Where needed, the area fraction of the β phase was quantified either using the EBSD data using HKL-Channel 5™, or using the SEM images using FIJI (ImageJ) via a Random Forest machine learning algorithm – as reported in detail elsewhere [88].

A multi-step thermal cycle, shown in Figure 2, was applied to the sample during the *in-situ* characterisation, in order to study the microstructure evolution at different annealing temperatures during the process.

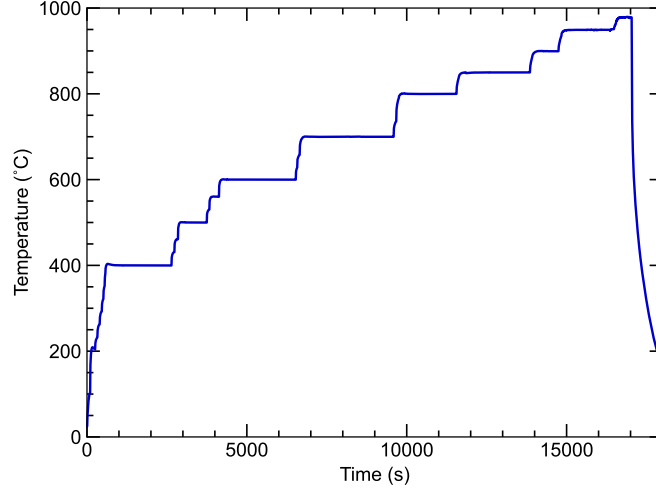


Figure 2: Temperature-time profile employed in the annealing process.

2.2 Modelling

2.2.1 Microstructure representation

In order to simulate the microstructure evolution during the multi-step annealing process, we used a numerical model based on the phase-field method. The model considers the bcc phase β , and hcp phases α (equilibrium) and α' (martensite). Since the martensite (α') phase may essentially be considered as a distorted equilibrium (α) phase supersaturated in solute, both α and α' phases are actually represented as the same phase, and they are differentiated from each other by their solute concentration. Hence, the phase field (order parameter), η , is equal to zero in the β phase and one in α and/or α' phases. Different orientations (variants) of the α' (or α) phase are represented by different phase fields η_i as commonly done in so-called multi-phase-field [89, 90, 91] or multi-order-parameter [92] approaches. Specifically, we consider p orientations of hcp phases. With $1 \leq i \leq p$, only one η_i reaches unity at a given point, corresponding to a hcp phase of orientation index i , while all η_i are equal to zero at β phase locations. Conceptually, the model could be extended to different to multiple β grains. However, here we consider only one β orientation, since we focus on the decomposition kinetics of a single prior- β grain, shown by experimental data (Section 4.1) to result in the same crystal orientation as the initial (prior) β grain.

It is recognised that the kinetics of martensite decomposition in Ti-6Al-4V alloy is limited by the diffusion of V solute [22, 31, 34, 62, 63, 64]. Therefore, for the sake of simplicity, solute diffusion and chemical free energies were calculated considering a pseudo-binary TiAl-V system, defined along the isopleth at $c_{Al} = 0.102$ (i.e.

10.2 at.%Al), as illustrated by the red line in Figure 3, and V is the sole considered solute element ($c \equiv c_V$) in the model. Note that, unless mentioned otherwise, all concentrations in the article are expressed in mole fraction.

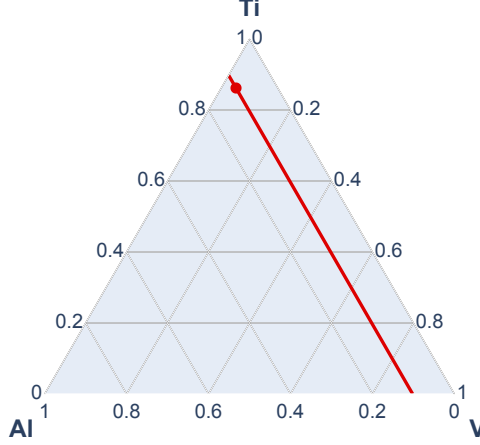


Figure 3: Pseudo-binary TiAl-V isopleth represented as a red line within the ternary Ti-Al-V system. For the sake of consistency with the model, units are in mole fraction. The nominal Ti-6Al-4V (wt%) alloy composition is marked by a circle at $c_{Al} = 0.102$ and $c = c_V = 0.036$.

As we specifically aim at modelling the martensite decomposition transformation ($\alpha' \rightarrow \alpha + \beta$) following L-PBF, the initial (as-built) microstructure is assumed to be fully martensitic (α') with grains of different crystal orientations, dictated by the orientation relations with prior- β grains. The nucleation of β grains was reported to occur along grain boundaries of the α' phase needles due to the local enrichment in vanadium [31, 67, 68]. Therefore, we chose to take advantage of the spontaneous nucleation of β at α' lath boundaries due to the multi-order-parameters interpenetration term (see Section 2.2.2), rather than explicitly (and arbitrarily) seeding β nuclei at defined spatiotemporal locations. During the $\alpha' \rightarrow \alpha + \beta$ transformation, V diffuses from α' martensite to the β phase. Martensite grains transform into α solely by the variation of their chemical composition.

2.2.2 Phase-field model

We use a standard formulation of the system free energy [93]:

$$F = \frac{1}{V_m} \int_V \left[f_c + \frac{\kappa_c}{2} |\nabla c|^2 + \sum_{i=1}^p \left(\frac{\kappa_\eta}{2} |\nabla \eta_i|^2 \right) \right] dV \quad (1)$$

where c is the V concentration, f_c is the chemical free energy density, η_i are the phase fields, $\kappa_\eta = 3\sqrt{2}\sigma\delta V_m$ is the gradient energy coefficient for η_i [94], with σ

the interface excess free energy, δ the diffuse interface thickness, and V_m is the molar volume of the alloy, κ_c is the gradient energy coefficient for c , and V is the volume of the simulation domain.

This formulation does not include the effect of elastic strain energies, which may lead to anisotropic interfacial behaviour. However, even though this may lead to morphological differences, since the kinetics of martensite decomposition in this alloy is limited by the diffusion of V [22, 31, 34, 62, 63, 64], we assume that this does not have a significant effect on the transformation kinetics per se. Also for the sake of simplicity, and since they are virtually identical in the model, both equilibrium (α) and martensitic (α') phases are simply referred to as phase α in the description of the model below.

The chemical free energy density is [95]:

$$f_c = f^\alpha h + f^\beta (1 - h) + wg \quad (2)$$

where f^α and f^β are the chemical free energy densities of α and β phases, respectively,

$$h = \sum_{i=1}^p \eta_i^3 (6\eta_i^2 - 15\eta_i + 10) \quad (3)$$

is an interpolation function, $w = 6\sigma V_m / (\sqrt{2}\delta)$ is a parameter that controls the height of the double well barrier [94], and the function

$$g = \sum_{i=1}^p \left[\eta_i^2 (1 - \eta_i)^2 \right] + \psi \sum_{i=1}^p \left[\sum_{j \neq i}^p (\eta_i^2 \eta_j^2) \right] \quad (4)$$

combines a standard double-well potential and a second term preventing the interpenetration of α grains of different orientations, with $\psi = \xi \delta \sqrt{w / (2\kappa_\eta)}$, where the coefficient ξ parametrises the free energy penalty associated with grain interpenetration (see, e.g. [92]).

The chemical free energy densities of phases α and β as a function of temperature and chemical composition were computed by considering them as a regular solution with:

$$\begin{aligned}
f^\varphi = & c_{Ti} \mu_{Ti}^\varphi + c \mu_V^\varphi + c_{Al} \mu_{Al}^\varphi + RT [c_{Ti} \ln(c_{Ti}) + c \ln(c) + c_{Al} \ln(c_{Al})] \\
& + c_{Ti} c \sum_{k=0}^n [L_{TiV_k}^\varphi (c_{Ti} - c)^k] + c_{Al} c_{Ti} \sum_{k=0}^n [L_{AlTi_k}^\varphi (c_{Al} - c_{Ti})^k] \\
& + c_{Al} c \sum_{k=0}^n [L_{AlV_k}^\varphi (c_{Al} - c)^k]
\end{aligned} \tag{5}$$

for both phases $\varphi \in \{\alpha, \beta\}$, where μ_{Ti}^φ , μ_V^φ , and μ_{Al}^φ are the chemical potentials of Ti, V, and Al, respectively, $L_{TiV_k}^\varphi$, $L_{AlTi_k}^\varphi$, and $L_{AlV_k}^\varphi$ are Redlich-Kister coefficients, R is the perfect gas constant, and T is the temperature in Kelvin. Note that, given the chosen pseudo-binary description of the alloy (Fig. 3), c_{Al} is fixed, while c_{Ti} is constrained to be equal to $1 - c_{Al} - c$. Chemical free energy densities for α and α' were computed with the same equation but different local V concentrations. In the mixture term, the chemical potentials of the alloying elements, for the different phases, were benchmarked against ThermoCalc results (using database TCNI8). The excess term was computed by using standard Redlich-Kister polynomials with coefficients extracted from Ref. [96] (see Appendix A.1). For the β -phase free energy density, we re-assessed the value of $L_{AlTi_0}^\beta = -118500 + 33.5 T$, which corresponds to an increase by almost 5% from the original value suggested by Ansara *et al.* [96]. The modification of $L_{AlTi_0}^\beta$ was motivated by the resulting improved match between predicted β volume fraction, also compared with ThermoCalc computation accounting for Al addition in the Ti-V binary system.

Given the total free energy of the system, the evolution of V concentration and phase fields were computed using standard Cahn-Hilliard and Allen-Cahn equations, respectively:

$$\frac{1}{V_m^2} \frac{\partial c}{\partial t} = \nabla \cdot \left[\frac{M}{V_m} \nabla \left(\frac{\partial f_c}{\partial c} - \kappa_c \nabla^2 c \right) \right] \tag{6}$$

$$\frac{\partial \eta_i}{\partial t} = -\frac{L}{V_m} \left(\frac{\partial f_c}{\partial \eta_i} - \kappa_\eta \nabla^2 \eta_i \right) \tag{7}$$

where M and L correspond to solute and interface mobilities (see Section 2.2.4).

2.2.3 Numerical resolution

The simulation domain is spatially discretised in 2D and represents a point of the AM material, sufficiently small with respect to the macroscale to allow separation of scales and sufficiently large to contain a representative ensemble of grains. Even though the actual microstructures are not periodic, periodic boundary conditions

(BCs) produce a faster convergence with the size of the domain to the actual response, and therefore we apply periodic BCs on both directions. Thus, the system of partial differential equations (6)-(7) is solved in a monolithic way using Fourier spectral method with a first-order finite difference scheme for time discretisation.

Due to the complexity and stringent stability requirements of the fourth-order partial differential equation, the use of a non-implicit approach for Cahn-Hilliard equation resolution is not robust and eventually diverges. Therefore, the Cahn-Hilliard equation is solved by using a fully-implicit iterative method, described in Appendix B.1. The Allen-Cahn equation, on the other hand, can be solved by using a semi-implicit non-iterative algorithm, as described in Appendix B.2, as the second-order differential equation is inherently more stable. The resulting discretised system of equations form a system of two algebraical equations, as detailed in Appendix B.3. The resolution is accelerated by the use of a preconditioned conjugate gradient method (PCG) [97], following a procedure presented in [98], with a variable time step (see Appendix B.3).

A rectangular domain of size $l_x \times l_y$ is discretised into a regular grid containing p_x and p_y points in x and y directions, respectively. In order to reduce the aliasing effect in the presence of non-smooth functions, the discrete Fourier frequency vector and the square of the frequency gradient are computed by replacing the definition of the derivative in the Fourier space with a fourth-order finite difference computed through the use of Fourier transform. This procedure results in the redefinition of the frequencies [86]:

$$\boldsymbol{\xi} = \begin{bmatrix} \frac{8 \sin(2\pi n_x \Delta x / l_x) - \sin(4\pi n_x \Delta x / l_x)}{6\Delta x}, \\ \frac{8 \sin(2\pi n_y \Delta y / l_y) - \sin(4\pi n_y \Delta y / l_y)}{6\Delta y} \end{bmatrix} \quad (8)$$

$$\|\boldsymbol{\xi}\|^2 = \begin{bmatrix} \frac{\cos(4\pi n_x \Delta x / l_x) - 16 \cos(2\pi n_x \Delta x / l_x) + 15}{6\Delta x^2} + \\ \frac{\cos(4\pi n_y \Delta y / l_y) - 16 \cos(2\pi n_y \Delta y / l_y) + 15}{6\Delta y^2} \end{bmatrix} \quad (9)$$

where n_x and n_y are two-dimensional mesh grid matrices generated with two vectors of the form $[0, \dots, (p_x/2), -(p_x/2 - 1), \dots, -1]$ and $[0, \dots, (p_y/2), -(p_y/2 - 1), \dots, -1]$, and Δx and Δy are the distance between two consecutive points in the x and y directions, respectively. While, for the sake of generality, the equations above are presented for any $\Delta x \neq \Delta y$, here all application are with $\Delta x = \Delta y$.

The computational scheme, summarised in Algorithms 1 and 2 of Appendix B.4, is implemented using the Python programming language. For each time step, the computation of discrete Fourier transform ($\mathcal{F}$) and discrete inverse Fourier trans-

form ($\mathcal{F}^{-1}$) is performed on the GPU device using Scikit-CUDA [99]. To solve a system of algebraical equations on the GPU device, CUDA kernels are programmed through PyCUDA [100], where the arrays representing the field values in the domain are defined in double precision.

The simulations were performed using a single GPU on a computer with the following hardware features: Intel Xeon Gold 6130 microprocessor, 187 GB RAM, GeForce RTX 2080Ti GPU (4352 Cuda cores and 11 GB RAM), and software features: CentOS Linux 7.6.1810, Python 3.8, PyCUDA 2021.1, Scikit-CUDA 0.5.3, and CUDA 10.1 (Toolkit 10.1.243). The GPU block size was set to 16×16 , which was found to result in near-optimal performance.

2.2.4 Alloy and model parameters

The molar volume of the alloy was assumed to be independent of temperature and equal to that of pure Ti, i.e. $V_m = 1.064 \times 10^{-5} \text{ m}^3/\text{mol}$ [101]. The excess free energy of interfaces was taken as $\sigma = 0.1 \text{ J/m}^2$ [84] and the interpenetration of different α grains was prevented using a coefficient $\xi = 1000$. The chemical mobility is assumed isotropic, but phase/location-dependent, hence computed as $M = (1/V_m)[(1 - c)^2 c M_V + c^2 (c_{Al} M_{Al} + c_{Ti} M_{Ti})]$, where the individual atomic mobilities M_k (with $k \in \{V, Al, Ti\}$) depend upon the phase as $M_k = M_k^\alpha + M_k^\beta - M_k^{\alpha(1 - \sum_{i=1}^p \eta_i)} M_k^{\beta(\sum_{i=1}^p \eta_i)}$. The atomic mobilities M_k^α and M_k^β and their dependence upon temperature and V concentration, were modelled using Redlich-Kister polynomials with coefficients extracted from Ref. [102] (see Appendix A.2). Like in the computation of the chemical free energy, it was assumed that the atomic mobilities of α and α' could be computed with the same equation. The interfacial mobility, assumed isotropic and independent of grain orientations, was computed as $L = 0.00125 \exp\{-19500/T\} \text{ m}^3/(\text{Js})$ [84], which was adjusted to allow the simulated β volume fraction to reach the steady stable condition at the different plateau temperatures, in agreement with experiments and literature [73]. The phase field diffuse interface width was taken as $\delta = 10\Delta x$.

2.2.5 Model validations

Before comparing the PF results with our experiments, we validated the predictions in terms of thermodynamics (equilibrium) and transformation kinetics of the model. All validation simulations considered the initial microstructure of region 1 (see Section 2.2.6, Figure 4).

To validate the prediction of the equilibrium state, we simulated the isothermal annealing at several temperatures between 650°C and 980°C . The annealing time was large enough to reach equilibrium (i.e. full $\alpha' \rightarrow \alpha + \beta$ transformation when relevant). Then, we compared PF-predicted results (namely the volume fraction of

β phase at different temperatures) with theoretical equilibrium (lever rule), with our experiments, as well as with a polynomial fit to experimental data from the literature (however, for traditionally manufactured Ti-6Al-4V) [73]. The equilibrium concentrations of α and β phases used in the lever rule calculation were obtained by the common tangent construction from α and β free energy densities.

In order to validate the transformation kinetics with the identified parameters, we compared the results of the model to the martensite decomposition kinetics assessed experimentally by Gil Mur *et al.* [72]. Their results correspond to a wrought Ti-6Al-V alloy, annealed at 1050°C for 30 minutes and water quenched at room temperature in order to obtain a fully α' martensitic microstructure before the annealing experiment. The sample hardness, measured at different annealing times and temperatures, is used as a proxy for the fraction evolution in the assessment of Avrami exponents of the ($\alpha' \rightarrow \alpha + \beta$) transformation at different temperatures. Using the hardness as a stand-in for the phase fraction is a relatively strong assumption, since it neglects possible additional phenomena, such as a potential recovery process. While acknowledging this limitation and hence only using it as an order-of-magnitude estimate, we use this data because it is, to the best of our knowledge, the only available regarding the kinetics of the martensite decomposition at 700°C and 800°C. We discarded reported temperature of 400°C and 600°C to focus on cases with complete transformation by the end of annealing.

Because the thermal history is not clearly specified in [72], we consider a uniform temperature distribution with two different thermal paths: a) isothermal at the given temperature and b) with a heating ramp from room temperature up to the given temperatures. The nonlinear heating ramp was simulated with the thermal module of the finite element software Abaqus [103], considering a cylindrical sample of 3 mm in length and 5 mm in diameter, with a density 4430 kg/m³, specific heat capacity 526.3 J/(kg°C) and thermal conductivity 6.7 W/(m°C) [20]. The boundary condition imposed at the cylinder interface follows a Newton law, $q_c = -h_c(T - T_{env})$, where q_c is the normal heat flux, h_c is the heat transfer coefficient at interface, T is the temperature at the sample interface, and T_{env} is the environment/annealing temperature. The heat transfer coefficient $h_c = 70$ W/(m²K) corresponds to a regular furnace heating [104]. The temperature evolution of the cylinder, initially at room temperature, was extracted from the centre of the cylinder (but the temperature is almost uniform in all the sample) and imposed, as an input data of the PF model.

2.2.6 Simulations

Ultimately, we aim to simulate the microstructural evolution of the *in-situ* observed microstructures during the step-wise annealing process (Figure 2) and compare it with our *in-situ* experiments. Hence, we use experimentally characterised mi-

crostructures as initial conditions. In particular, two different regions of the fully martensitic as-built microstructure were separately used as the initial material microstructure. Both selected regions correspond to a single parent β grain, each hosting several α' variants (orientations).

Our model distinguishes regions of different orientations, but it does not attribute a specific given orientation to the grains. In other words, neighboring grains of different orientations result in grain boundaries (and subsequent grain boundary energies), but the behavior of the grain and grain boundaries is isotropic. We classified the different α' orientations into variants, for each prior- β grain. To sort the different α' variants, we used experimental EBSD maps to identify groups of hcp grains with respect to their c -axis orientation, using the following procedure, illustrated in Figure 4. For each pixel in the EBSD map, the tip of the unit vector oriented along the local crystalline c -axis and rooted at the origin of a Cartesian coordinated system (x, y, z) was orthogonally projected onto the (x, z) plane. The resulting clouds of points, visible on the right-hand-side of Figure 4 for both investigated regions, exhibit clusters of orientations, corresponding to a subset of the 12 possible variants [26, 27, 37, 38, 39, 40].

Here, we clearly found that 6 main clusters could be identified in each prior- β grain. For that reason, we considered that accounting for 6 variants in each prior- β grain was sufficient, assigning the same large cluster variant to the nearest small clusters. The resulting initial microstructures, composed of 6 α' lath orientations, are represented on the left-hand-side of Figure 4 – each colour corresponds to one of the identified orientations, and hence one of the phase fields η_i .

At the start of the simulations, the V concentration is assumed uniform in the entire domain, and equal to the nominal V concentration of the alloy. This is consistent with experimental observations showing that, under powder-bed fusion processing, only α' was formed at a chemical composition close to the nominal alloy concentration [64]. The experimental temperature-time profile (Figure 2) was used as input, considering a spatially homogeneous but time-dependent temperature.

Both considered regions are spatially discretised with a structured grid of 256×256 points, resulting in grid spacings $\Delta x = \Delta y$ of 41.0 nm for region 1 of size $(10.5 \mu\text{m})^2$, or 31.3 nm for region 2 of size $(8.0 \mu\text{m})^2$.

3 Results

3.1 Experiments

The microstructure in as-built L-PBF Ti-6Al-4V in the investigated area is shown in Figure 5. As discussed in previous works [105], LPBF leads to a fully acicular α' martensitic microstructure, (Figure 5(a) and (b)), with no detectable retained β

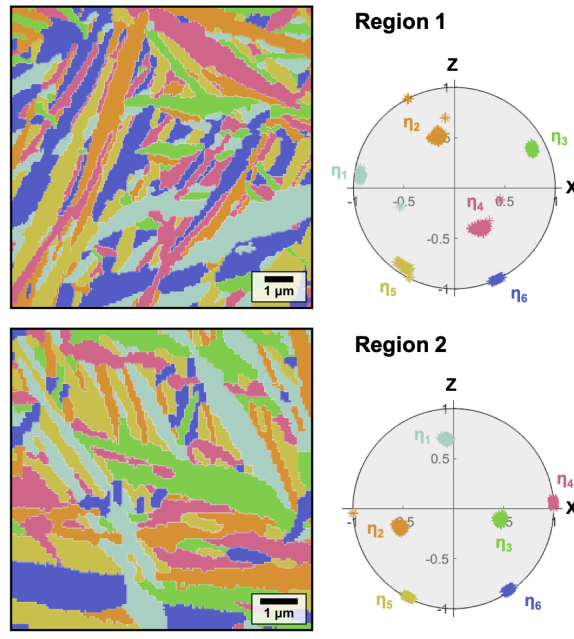


Figure 4: Initial conditions for the phase fields, based on EBSD maps in the as-printed material, showing region 1 and region 2. Colours represent the six different crystal orientations of α' considered in the simulation.

(Figure 5(c)). The XRD results in Figure 5(d) further confirm the absence of the β phase in the microstructure. The prior- β structure can also be identified from forescatter electron micrographs. A prior- β grain boundary is indicated by dotted lines in Figs 5(a)-(c). Multiple α' grains of distinct orientations were visible in the prior- β microstructure, and reveal a weak crystallographic texture.

Figure 6 shows *in-situ* micrographs captured during the stepwise thermal treatment (Figure 2). Up to 600°C, Figure 6(a)-(c) display forescatter electron images. At 700°C and above (Figure 6(d)-(g)), the forescatter detectors were completely saturated, and the microstructure image was then captured by secondary electron detectors. The last two panels highlight the crystallographic texture at 850°C, via the α (h) and β (i) orientation map in Z-IPF overlaid with band contrast image. The two distinct prior- β grains also appear clearly in Figure 6(f) to (i), corresponding to high temperatures, yet not high enough to lead to substantial evolution of the prior- β grain structure within the considered time. Moreover, while we only present here the EBSD maps in the as-built state (Fig. 5) and at 850°C (Fig. 6) after the stepwise heat treatment, further experimental characterization can be found in previous publications (e.g. [59]).

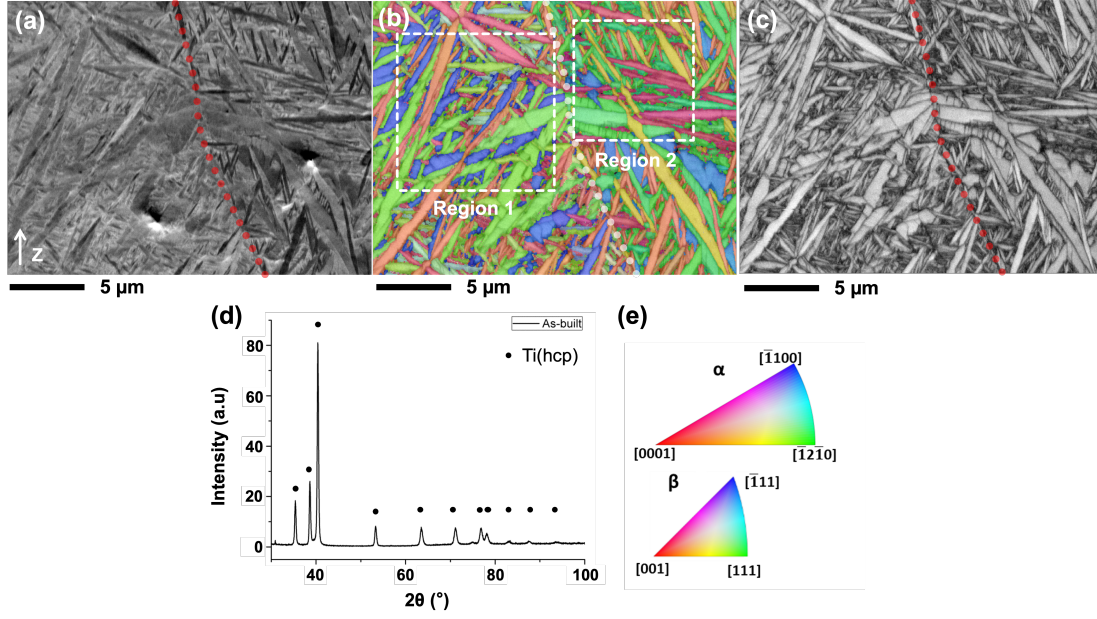


Figure 5: Electron micrographs of as-printed microstructure of L-PBF Ti-6Al-4V: (a) microstructure image captured by forescatter detectors; (b) measured α orientation map in Z-IPF overlaid on band contrast image; (c) measured β orientation map in Z-IPF overlaid on band contrast image (here, highlighting the absence of β phase); (d) XRD results of the crystal lattices; (e) colour scheme used to map the orientation data. Semi-transparent dotted lines in (a)-(c) mark the location of the prior- β grain boundary.

3.2 Model & parameters validations

Figure 7 (top) shows the simulated evolution of the β volume fraction during isothermal annealing of region 1 at different temperatures (green crosses) compared with our experimental data (purple circles), the lever rule (solid blue line), and the experimental fit for traditionally manufactured Ti-6Al-4V (red dashed line) [73]. As expected for a nominal Ti-6Al-4V across this temperature range [106, 107], the β volume fraction increases with temperature. Figure 7 (bottom) also includes the evolution of β volume fraction, computed with the PF model, normalised with respect to the final β volume fraction at each temperature.

Figure 8 presents the evolution of the temperature (top) and the transformation kinetics (bottom) at 700°C and 800°C for the two considered thermal paths, namely fully isothermal or accounting for the heating up of the sample (see Section 2.2.5). The transformed β fraction is compared to the (hardness-based) experimental data (symbols) from the literature [72]. In order to compare the different data sets (namely, hardness from experiments [72] and β fraction from our PF simulations), at each temperature we compute the normalised β fraction $\bar{f}_\beta = f_\beta / f_\beta^{end}$ and normalised hardness $\bar{H} = (H - H^{min}) / (H^{max} - H^{min})$, where

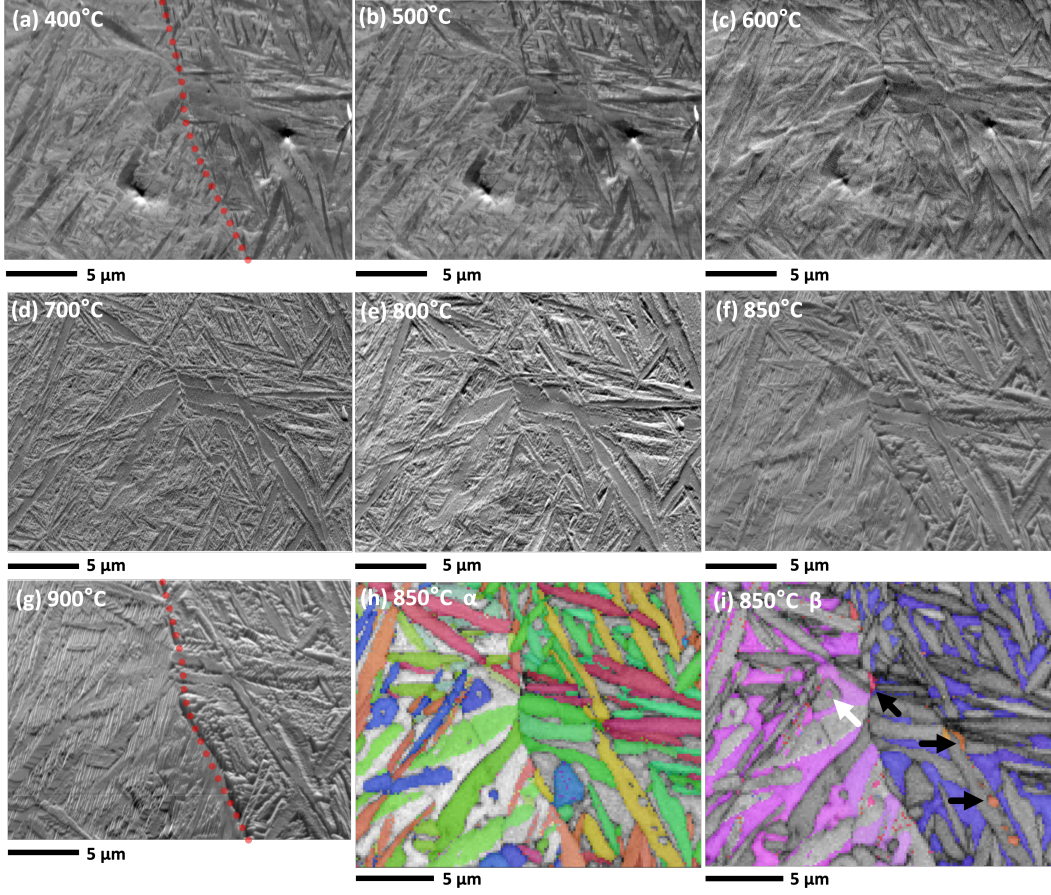


Figure 6: SEM images of microstructure evolution of L-PBF Ti-6Al-4V under stepwise heating (Figure 2). Forescatter micrographs at (a) 400°C, (b) 500°C, and (c) 600°C. Secondary electrons micrographs at (d) 700°C, (e) 800°C, (f) 850°C, and (g) 900°C. Measured α (h) and β (i) orientation map in Z-IPF (overlaid with band contrast image and using the colour scheme of Fig. 5e), showing the crystallographic texture at 850°C, with a white arrow indicating the β phase growth from the interior of the α' phase, and black arrows indicating the recrystallised high angle boundary (HAB) β phase. The red dotted line in (a) and (g) marks the location of the initial prior- β GB.

f_{β}^{end} is the β fraction at the end of the PF simulation, while H^{max} and H^{min} are the maximum and minimum measured hardness, respectively.

3.3 Phase-field simulations of microstructure evolution

Figure 9 shows the simulated evolution of α' and β volume fractions ($f_{\alpha'}$ and f_{β} , respectively) during the step-wise heat treatment, and the corresponding thermal history (PF input data). The microstructure evolution in regions 1 and 2, at the

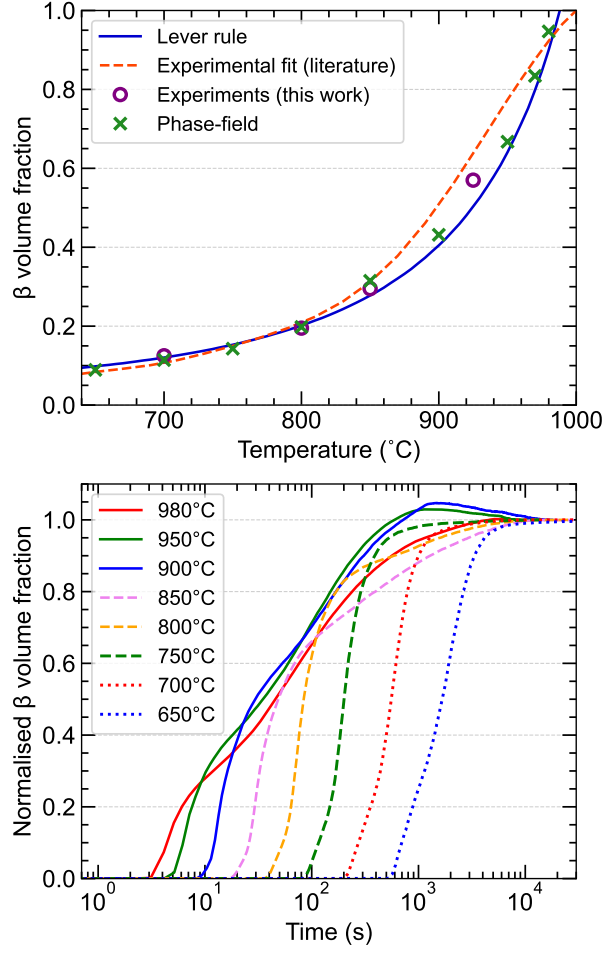


Figure 7: (Top) Equilibrium β volume fraction of Ti-6Al-4V at high temperature, comparing lever rule, experimental fit for traditionally manufactured Ti-6Al-4V [73], phase-field results, and our experimental results for L-PBF Ti-6Al-4V. (Bottom) Kinetics of β transformation computed with the phase-field model and normalised with respect to the final β fraction.

end of the 8 plateaus of the annealing process ($t = t_1$ to t_8 labeled in Figure 9) is shown in Figures 10 and 11. The solute (V) concentration map in both regions at the end of the 700 $^{\circ}\text{C}$ ($t = t_3$) and 800 $^{\circ}\text{C}$ ($t = t_4$) plateaus, is illustrated in Figure 12. The concentration c , and corresponding η_i , along a scanning line shown in Figure 10 (region 1), is presented in Figure 13. Stable α and metastable α' phases may be challenging to distinguish, since they share a similar crystal structure and close lattice parameters [31]. The main differences appear in their morphologies and the solute concentration, with α' typically exhibiting a fine lath structure and solute supersaturation beyond equilibrium. Yet, the supersaturation threshold to unambiguously determine α and α' regions is not clearly established. Here, in order

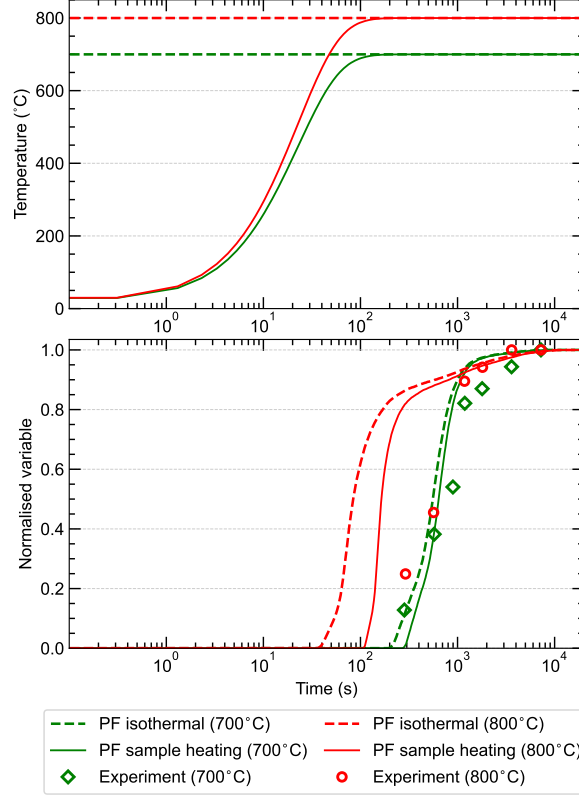


Figure 8: Temperature evolution (top) and kinetics of $\alpha' \rightarrow \alpha + \beta$ transformation computed with the phase-field model for region 1 (bottom), compared with experimental data [72] (y -axis: normalised β fraction from PF simulations; normalised hardness from experiments).

to distinguish α and α' phases, we use an *ad hoc* criterion and consider that a point within the α/α' region (i.e. where $\sum_i \eta_i > 0.99$) belongs to the metastable α' phase if its concentration is higher than $1.5c_\alpha^*$, where c_α^* is the V equilibrium concentration in the α phase at a given temperature. Finally, Figure 14 compares experimental (EBSD) maps and PF-simulated microstructures after 300 s at $T = 850^\circ\text{C}$ (i.e. $t_4 < t < t_5$) for regions 1 and 2.

4 Discussion

4.1 Experiments

The microstructure in as-built L-PBF Ti-6Al-4V (Figure 5), composed of fully acicular α' martensite, no detectable β phase, and a weak crystallographic texture, is quite typical for as-built L-PBF Ti-6Al-4V microstructures, and consistent with

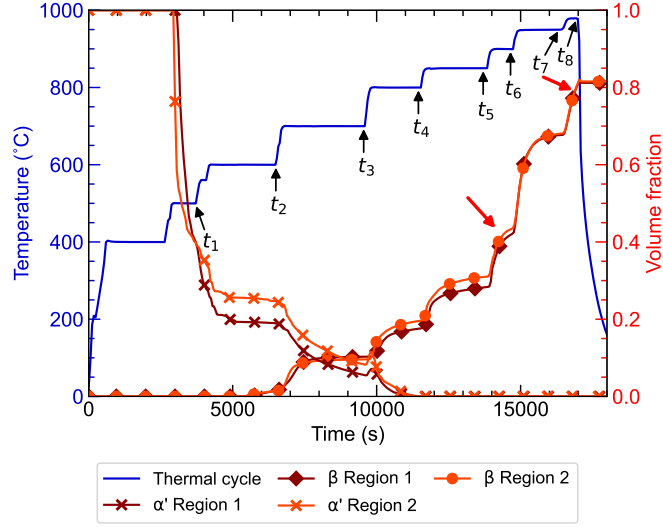


Figure 9: Temperature (left) and α' and β volume fraction (right) evolution during the heat treatment.

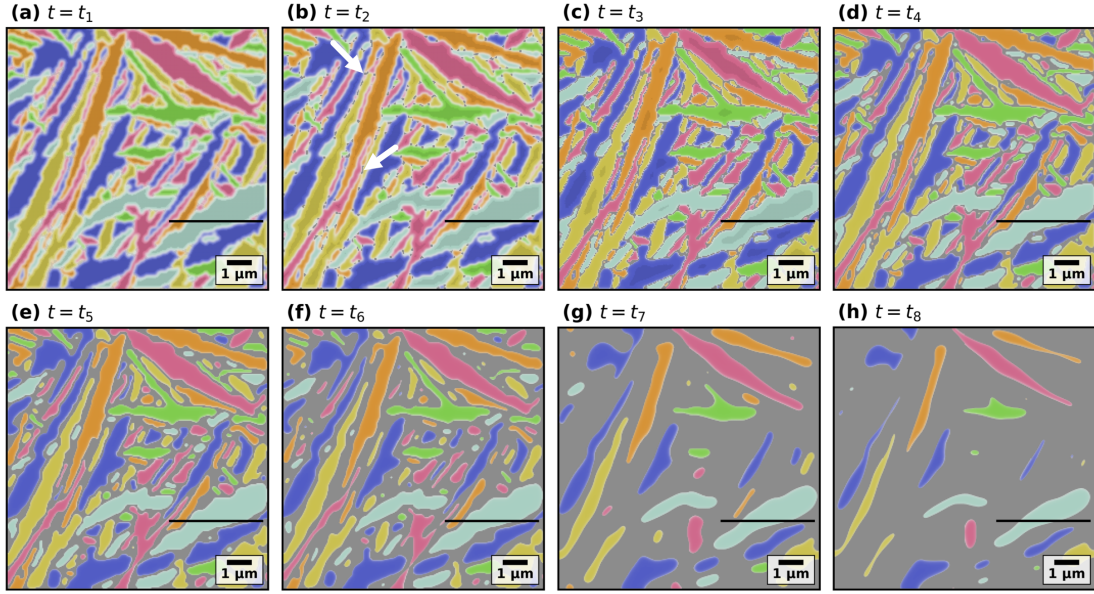


Figure 10: Simulation results of material microstructure in region 1 at the end of the isothermal plateaus at (a) 500°C, (b) 600°C, (c) 700°C, (d) 800°C, (e) 850°C, (f) 900°C, (g) 950°C, and (h) 980°C; colour maps show different phases and grains (β : grey, α : different colours for different variants, and α' : different shaded colours for different variants). The horizontal black line marks the location of the compositional line-scan of Figure 13. White arrows in (b) show some β nucleation sites along α' martensite lath boundaries.

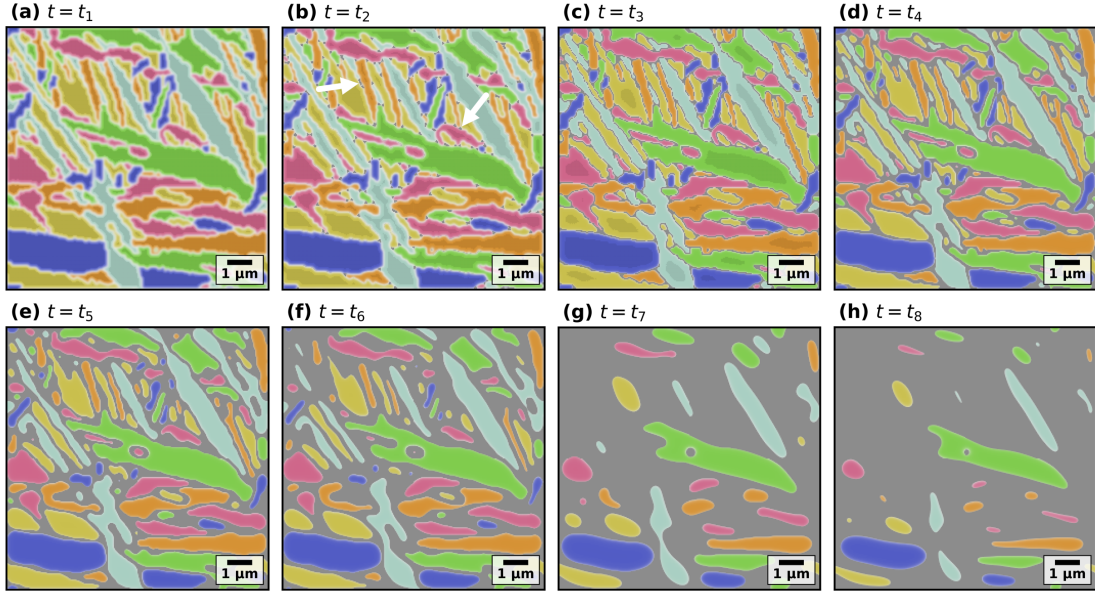


Figure 11: Simulation results of material microstructure in region 2 at the end of the isothermal plateaus at (a) 500°C, (b) 600°C, (c) 700°C, (d) 800°C, (e) 850°C, (f) 900°C, (g) 950°C, and (h) 980°C; colour maps show different phases and grains (β : grey, α : different colours for different variants, and α' : different shaded colours for different variants). White arrows showing some β nucleation sites along α' martensite lath boundaries.

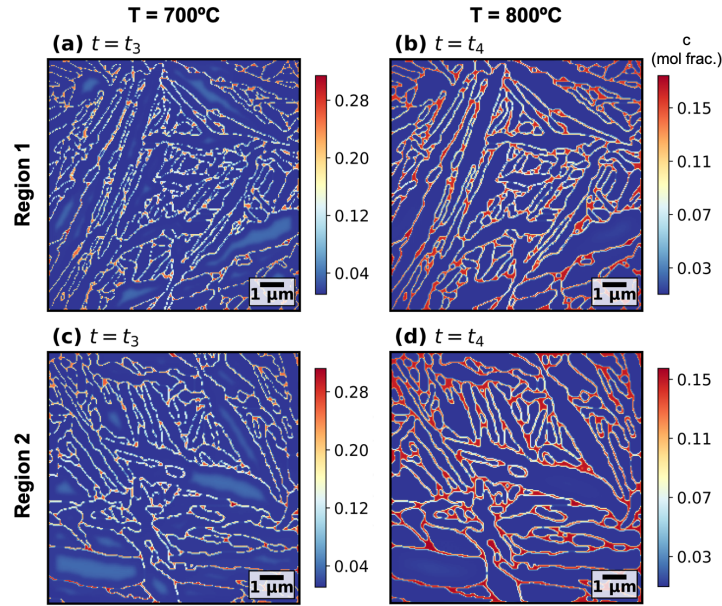


Figure 12: Simulation results of V concentration, in mole fraction, for regions 1 (a,b) and 2 (c,d) at the end of the isothermal plateaus at 700°C (a,c) and 800°C (b,d).

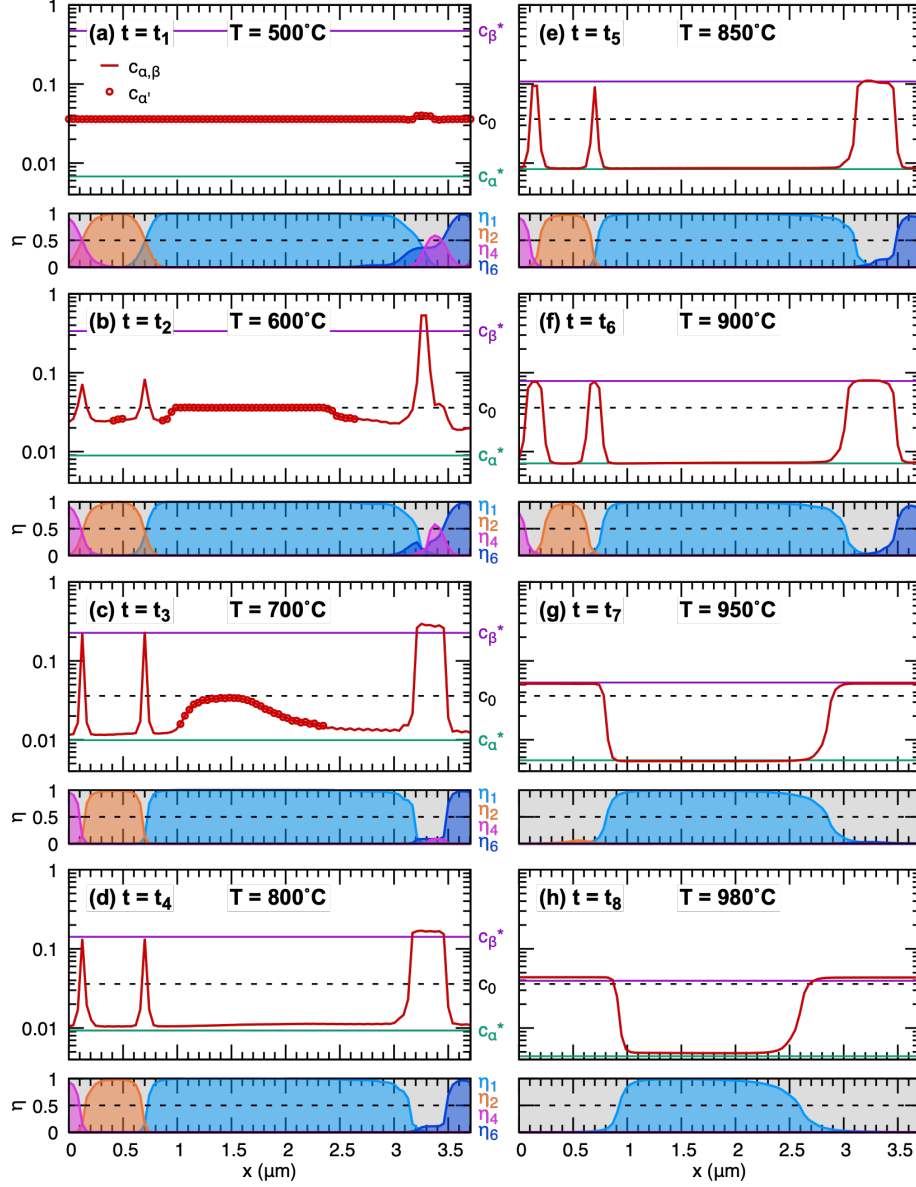


Figure 13: Compositional scans along the black horizontal line of region 1 in Figure 10 at different times/temperatures. Each panel (a-h) shows (top) the V concentration, in mole fraction (red line, with symbols for α' regions) compared to nominal, c_0 , and equilibrium, c_α and c_β , concentrations, as well as (bottom) order parameters, η_i , along the same line.

previously reported results [36, 69]. The formation of the α' martensite in the as-built microstructure (Figure 5) can be attributed to the fast cooling of the melt pool during L-PBF. High-speed thermal imaging measurements suggest that the effective cooling rate experienced in the L-PBF Ti-6Al-4V melt pool is of order

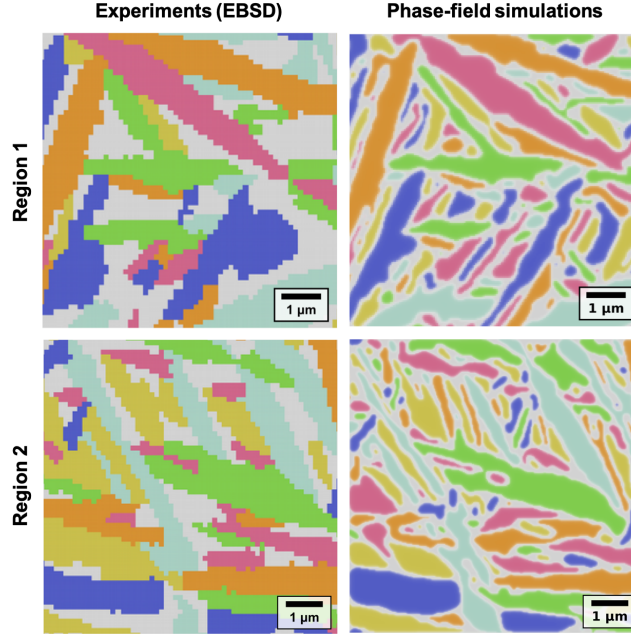


Figure 14: Computational simulation results compared to experimental microstructures in region 1 and region 2, after 300 s of isothermal annealing at 850°C.

10^6 °C/s [108], while the *in-situ* XRD analysis suggests an overall cooling rate of around 10^4 °C/s [71], both being far beyond the critical cooling rate required to form metastable martensite upon cooling (410°C/s) [109]. Recent research suggests that, under such high cooling rates, nano-scale β stripes may be preserved in the as-built microstructure alongside the dominant α' martensite [21]. However, such nano-scale β phases are too small to be detected by SEM or XRD [21].

During the thermal treatment, the microstructure does not exhibit any visible change at 400°C and 500°C (Figure 6(a)-(b)). At this low temperature, recovery of the sub-grain structure occurs, which includes relaxation of the residual stress, annihilation and rearrangement of the dislocations [110]. Such a recovery process was evidenced recently, via *in-situ* high-energy XRD, by the reduction of XRD peak width (Full Width at Half Maximum, FWHM) in all observed grain orientations at 497°C [111]. This recovery occurs without the migration of any high-angle grain boundaries and will not trigger any evolution in the microstructural constituents [63, 110]. Therefore, no visible changes can be noticed in the foreshatter electron micrographs.

Visible changes can be observed at higher temperatures. Coarsening of the microstructure starts being noticeable at 600°C (Figure 6(c)), leading to the emergence of topographical changes. At 700°C (Figure 6(d)), the grain structure appears clearly, and the boundary of each α/α' grain is well marked. Solute diffusion

and elements partitioning become significant at elevated temperature, which leads to the decomposition of α' into $\alpha + \beta$ [36, 63]. Visible changes in the topography of the grain boundary are attributed to the nucleation and growth of the β phase, which takes place on the boundary of the newly formed α [36]. Previous studies reported martensite start temperatures M_s^* ranging from 580°C to 700°C, affected by multiple factors, such as the dislocation density, residual stress, and supersaturation in V [28, 112, 113, 114]. The initial appearance of the β phase was previously captured by *in-situ* high-energy XRD analysis of L-PBF Ti-6Al-4V at 640°C [111], which supports our *in-situ* observations.

At higher temperature, e.g., 800°C (Figure 6(e)), we expect the original α' to be nearly fully decomposed [36] and we observed a further coarsening of the α phase. A notable growth of the β phase can be observed at 850°C as seen in the measured β orientation map (Figure 6(i)). At this temperature, regions that consist of β phases appear with a specific stepped topography in the secondary electron micrographs (Figure 6(f)). This topography might result from the bcc structure of the β phase. The β phase can be observed both at the α boundary and in the interior of the α phase, as indicated by the white arrow in Figure 6(i). The observed inner β regions might stem from nucleation at lattice defects located within the α/α' phase. This is consistent with recent studies suggesting that, beyond nucleation at vanadium-enriched grain/lath boundaries, the β phase can also nucleate along lattice defects within α/α' phases [31, 22, 59]. The most likely underlying causes of such nucleation events are (i) the high density of lattice defects (e.g. dislocations, stacking faults, twin boundaries) reported to form in Ti-6Al-4V processed at high cooling rates [11, 28, 29, 36], and (ii) the local V enrichment at one-dimensional lattice defects such as dislocations and dissociated (partial) dislocations, acting as precursor nucleation sites for the β phase [31, 22]. The proportion of β -phase nucleating within the bulk α/α' phase remains low compared to that nucleation along grain/lath boundaries (Figure 6(i)). Therefore, in spite of the rudimentary description of nucleation in the present model, we expect the resulting discrepancies to be relatively small.

Recrystallised high-angle boundary (HAB) β phase can also be observed in the orientation map, as indicated by the black arrows in Figure 6(i). This recrystallisation process cannot usually be produced in traditional manufactured Ti-6Al-4V via simple heating [115]. Therefore, it is a unique feature of the additively manufactured Ti-6Al-4V. Recent research suggests that this recrystallisation may be triggered by the stored energy of deformation in the as-built microstructure, which is typically expressed by the large dislocation densities found after L-PBF [59].

The microstructure at 900°C is shown in Figure 6(g). An increase of the area covered by stepped topography can be observed when compared to a lower temperature, which evidences the increase of β phase in the $\alpha + \beta$ matrix, as

the temperature approaches the β transus temperature. However, the prior- β grain boundary is nearly intact and unchanged at 900°C (see red dotted line in Figure 6(g) marking the location of the initial prior- β GB). It is consistent with results from other studies, which reported that heat treatment at a temperature below β transus has limited influence on the prior- β structure of L-PBF Ti-6Al-4V [36, 69].

4.2 Model validations

The comparison of PF-predicted, theoretical (lever rule), and experimentally assessed β volume fraction (Figure 7) serves as a validation of our model and parameters for thermodynamic equilibrium. As expected, a temperature increase clearly reduces the incubation time and increases the transformation rate. Notably, the $f_\beta(t)$ curves slightly deviate from the smooth sigmoidal shape characteristic of Avrami kinetics, due to the additional effect of the microstructure (e.g., accounting for interfacial energies and kinetics), particularly at high temperatures undergoing a relatively more complex interplay of solute diffusion and interface kinetics.

The different thermal paths (Figure 8) influence mostly the early onset of the transformation, but they nonetheless result in clearly distinct kinetics, since transformation kinetics (e.g. Avrami plots) are usually represented in logarithmic scale. Accounting for the heating up of the sample leads, as expected, to a slower transformation, and to a good agreement with experiments. This validates that the values considered for mobilities M in Eq. (6) (see Appendix A.2) and L in Eq. (7) (see Sec. 2.2.4) are reasonable. We could have achieved a better match between experiments and simulations by further adjusting the mobilities, but, given the degree of uncertainties associated with the experimental data, we chose to keep the atomic mobilities as developed in Ref. [102] (see Appendix A.2) and to not modify the interface mobility L any further. Notably, in Figure 8, the agreement between PF results and experimental measurements is better for the 700°C case than for the 800°C case, which we attribute to differences in α' initial microstructures. The experimental data relates to wrought and water-quenched samples and, as mentioned in [10], coarser α' martensite laths are generally obtained in comparison with L-PBF processed samples. Therefore, fewer nucleation sites are expected for the β phase, resulting in a slower kinetics of the transformation, even more marked at high temperatures where β nuclei grow more rapidly.

4.3 Martensite decomposition in post-AM heat treatments

The temperature plateau at 400°C does not induce any noticeable transformation (Figure 9), either ($\alpha' \rightarrow \alpha$) or ($\alpha' \rightarrow \alpha + \beta$). At 500°C, there still is no significant sign of β nucleation (i.e. $\sum_i \eta_i$ remains close to 1), but the diffusion of V is now

fast enough to initiate the transformation of α' into α (see Figure 9). Higher temperatures ($T \geq 600^\circ\text{C}$) lead to the formation of β , first nucleating along α' martensite lath boundaries at $T = 600^\circ\text{C}$ (white arrows in Figs 10b and 11b), then growing as thin layers between the laths at $T = 700^\circ\text{C}$ and 800°C (panels c and d), as reported in various studies [13, 61, 63, 65, 66]. At $T = 850^\circ\text{C}$ (Figs 10e and 11e), remaining α regions, now fully transformed from α' , are still occupying nearly 70% of the domain (see Figure 9), and are fully surrounded by β layers. As the temperature increases further above 850°C (Figs 10f-h and 11f-h), the remaining α progressively transforms into β , as diffusion is now sufficiently fast to reach near-equilibrium phase fractions within the isothermal plateaus.

The evolution of the β fraction (Figure 9) exhibits multiple sigmoid-like plateaus as the annealing temperature evolves. At 600°C the β volume fraction ($f_\beta < 0.015$) remains far from equilibrium ($f_\beta^* \approx 0.09$) due to the low mobilities of V and interfaces at such low temperature and to the short annealing times. Once at $T \geq 700^\circ\text{C}$, the V concentration in β is close to equilibrium (c_β^*), which decreases as the temperature increases (see Figure 13). However, at 900°C and 980°C , the isothermal plateaus are too short to reach full equilibrium, which can be seen in the still significant slope of the $f_\beta(t)$ curve at t_6 and t_8 , indicated with red arrows in Figure 9. As expected, the time derivative of f_β indicates that the transformation rate increases with temperature, for the most part due to the increase of V mobility and interface mobility. The transformation rate in region 1, initially slower at low T , becomes higher than that of region 2 above 900°C , which we attribute to the initially finer α' martensitic microstructure of region 1 (Figure 4).

The V concentration along the scanning line of region 1 (Figure 13) shows that the stable α and martensitic α' phases coexist at 600°C and 700°C (with $c_{\alpha'}$ labelled with symbols when $c > 1.5c_\alpha^*$). At 700°C , thin α' laths have been completely converted to α but the thicker ones are only partially transformed. This appears clearly in Figure 12, as well as Figures 10 and 11 (panels c), where we applied a darker colour shade in regions corresponding to α' (i.e. where $c > 1.5c_\alpha^*$). This partial $\alpha' \rightarrow \alpha$ transformation is attributed to the limited annealing times, thus not allowing the diffusion of V across the entire thicker laths, given the moderate diffusivity at this temperature. Indeed, since the $\alpha' \rightarrow \alpha$ transformation has already started at $T = 600^\circ\text{C}$ (see Figures 9 and 13), one would expect it to be completed provided a sufficient annealing time. Finally, at $T \geq 800^\circ\text{C}$, thicker laths are completely transformed into α and their V composition remains very close to equilibrium (c_α^*).

Importantly, our simulations confirm that, for the considered annealing times, the microstructure conserves a (ultra)fine $\alpha + \beta$ microstructure inherited from the initial α' lath structures (Figure 4) at 850°C , while nearly all the α' martensite has transformed into an equilibrium α phase from $T = 800^\circ\text{C}$. By increasing the

annealing temperature above 850°C, small α grains transform into β and larger α grains undergo further coarsening (hinting at an evolution toward a globularisation regime). These results are all consistent with previous experiments showing that below 400°C only stress relaxation occurs [66], while phase transformation takes place above 550°C [66], but that 2h of annealing time may still not be sufficient to complete the $\alpha' \rightarrow \alpha + \beta$ transformation even at 700°C or 800°C [35], while microstructural coarsening is only evident at 900°C and above [36], and with globularisation occurring for heat treatments usually involving temperatures above 800°C (most often above 900°C) [69, 47, 116, 117].

Finally, regarding the comparison between experimental and simulated microstructures at $T = 850^\circ\text{C}$ (Figure 14), our simulations capture well the fact that thinner laths were transformed into β phase and that α conserved a lath shape inherited from the α' martensite. As already apparent in Figure 7, the volume fractions of β phase are in reasonable agreement between simulation (region 1: $f_\beta = 0.289$, region 2: $f_\beta = 0.281$) and experiments (region 1: $f_\beta = 0.26$, region 2: $f_\beta = 0.18$), which is relatively close to equilibrium ($f_\beta^* \approx 0.31$). The discrepancy in region 2 is attributed primarily to dimensionality, since the experimental f_β is measured from a single 2D EBSD slice and simulations are also two-dimensional. Another difference observed in Figure 14 is the propensity of the PF model to grow β phase homogeneously along all α' lath boundaries, hence resulting in a β layer fully surrounding the remaining α grains, while the EBSD maps still contains grain boundaries between different α grains. In addition to the already-mentioned dimensionality, here we also attribute this discrepancy to the rudimentary treatment of β nucleation in the model – or, more precisely, the lack of a specific nucleation algorithm, as we let β nucleate spontaneously at grain boundaries, triggered by fluctuations from the interpenetration term in the free energy (Eq. (4)). As a result, simulations tend to predict a continuous nucleation of β along the martensitic lath boundaries, ultimately resulting in a relatively finer microstructure than observed in experiments.

5 Summary, Conclusions and Perspectives

We performed a joint experimental-computational study of martensite decomposition during post-printing heat treatment of L-PBF additively manufactured Ti-6Al-4V alloy. Our original experiments made use of *in-situ* electron microscopy and diffraction (EBSD) analysis during heat treatment up to nearly β -transus temperature. Our simulations rely on a FFT-based GPU-accelerated phase-field model of microstructure evolution, using experimental EBSD maps of as-built Ti-6Al-4V and experimental temperature history as input.

Our *in-situ* experiments confirmed or revealed that:

- The microstructure of L-PBF processed Ti-6Al-4V alloy is fully martensitic (α'), with a weak texture mostly due to the several possible lath orientations emerging from prior- β grains (up to 12 variants per β grain). Possible other phases, such as small β grains [21, 22] or precipitates [23] were not observed – but they might have been too small to unambiguously identify with the techniques employed here (SEM, EBSD, XRD).
- At low annealing temperature ($T = 400^\circ\text{C}$ or 500°C), while some relaxation of residual stresses or annihilation/rearrangement of dislocations might have occurred, the topology of the microstructure did not exhibit any significant change. Visible microstructure evolution occurred only at $T \geq 700^\circ\text{C}$.
- Nucleation of β phase primarily takes place along the boundaries of α' laths. However, traces of β phase nucleating within α/α' region, rather than at lath boundaries, suggests possible β nucleation sites along lattice defects (e.g. dislocations, twins, sub-grain boundaries, etc.) [22, 59].
- While it substantially alters the α' lath structure within the prior- β grain, a near β -transus temperature does not seem to significantly change the topology of the β grain structure.

From the modelling and simulations perspective:

- We proposed a phase-field model, kept relatively simple by the adoption of experiment/evidence-motivated assumptions, in particular considering (i) a pseudo-binary alloy approximation, (ii) isotropic interfaces, and (iii) 2D simulations. Thermodynamic description of phases (free energies and mobilities) were directly taken from the literature (with almost no adjusted parameters). Simulations were accelerated by an original FFT-based resolution algorithm and GPU parallelisation. We used the model to simulate the evolution of experimentally characterised microstructures (using EBSD maps as initial conditions) and experimentally imposed/measured thermal history.
- Despite its simplicity, the model captures the salient features of the $\alpha' \rightarrow \alpha + \beta$ transformation, such as: (i) a martensite decomposition visibly starting around 600°C with a small amount of β phase formed along α' grain boundaries, (ii) a transformation kinetics leading to near-equilibrium fractions of α and β phases at the end of the isothermal plateaus at $T \geq 700^\circ\text{C}$, (iii) a reasonable direct comparison of EBSD maps at $T = 850^\circ\text{C}$ (Figure 14) – however with slightly finer predicted microstructure, attributed to the primitive modeling of β nucleation (or, more precisely, a lack thereof).
- Our simulations complemented the *in-situ* experimental characterisation, in particular by providing the spatiotemporal evolution of solute (V) within

the inspected regions. This allowed, for instance, to ascertain that, for the considered temperature-time profile, the full decomposition of α' into an $\alpha + \beta$ structure was complete at $T \approx 800^\circ\text{C}$.

This work emphasizes the advantage of relatively simple phase-field models, which provide a deeper description of phase transformation kinetics than classical mean-field (e.g. Avrami-based) models commonly employed to analyse martensite decomposition in additively manufactured Ti-6Al-4V [72, 73, 74]. Indeed, PF models provide not only fractions of phase, but also the morphological evolution of the microstructure. Such information may be critical, for instance in the production of ultrafine $\alpha + \beta$ microstructures with outstanding mechanical properties.

Limitations of the simulations carried out here pertain most importantly to the dimensionality of the simulations (2D) and to some fairly restrictive model assumptions, in particular neglecting the effects of mechanics (e.g. strain energy contributions) and anisotropy of bulk crystalline phases and interfaces. A more advanced treatment of β nucleation [118], possibly accounting for the spatial distribution of defects (e.g. dislocation) and their effect on the local concentration fields and contribution to the nucleation energy barrier, could also allow to achieve a greater agreement with experiments.

Potential perspectives from this work are manifold, some of which are already the focus of work in progress. The model could be used to assess whether and how a different solute concentration across α' laths (as evidenced recently [119]) might affect the kinetics of martensite decomposition. It could also be used to explore the effect of minor compositional changes [120] or non-conventional heat treatments, e.g. cyclic heat treatments [69, 121] or intrinsic heat cycling during the printing process [11, 12, 27, 34]. Our ongoing efforts focus on the incorporation of anisotropic elastic terms, in order to better account for the underlying crystal structure and grain orientations. Such extension, combined with further thermodynamic description of possible metastable phases, could for instance allow studying in greater detail the still debated reaction path between α' and $\alpha + \beta$, e.g. addressing the potential intermediate formation of a non-equilibrium α -like phase with a hcp structure but a composition close to that of the β phase [122].

By including a more proper description of mechanical effects, an underlying objective is to ultimately use microstructures predicted from virtual processing into a micromechanics framework also based on FFT spectral methods [123] in order to simulate their mechanical behaviour and predict their mechanical properties. Furthermore, while here we chose to use experimental martensitic microstructures as initial conditions, the proposed model could greatly benefit from a coupling (upstream) with models capable of predicting the morphology of martensitic microstructures emerging from L-PBF of Ti-6Al-4V (e.g. [124]) and (downstream) with models capable to assess the mechanical properties of resulting heterogeneous

microstructure (e.g. [82, 125]). Our ambition is that such an integrated predictive framework could lead to the design of original thermal treatments to maximise the mechanical properties of L-PBF Ti-6Al-4V, but also to the design of novel Ti-based alloys. Ultimately, this concerted effort from the multiscale modeling community shall allow to take full advantage of additive manufacturing and post processing routes, and accelerate the synergistic development of novel alloys and manufacturing technologies, e.g. in the aeronautical and biomedical sectors.

CRediT Author Contribution Statement

A.D. Boccardo: Investigation (Computational); Methodology; Formal analysis; Software; Validation; Funding acquisition; Writing - original draft. **Z. Zou:** Investigation (Experimental); Methodology; Formal analysis; Writing - original draft. **M. Simonelli:** Investigation (Experimental); Methodology; Formal analysis; Funding acquisition; Supervision; **M. Tong:** Conceptualization; Supervision; **J. Segurado:** Conceptualization; Supervision; **S.B. Leen:** Conceptualization; Funding acquisition; Supervision; **D. Tournet:** Conceptualization; Methodology; Funding acquisition; Supervision; Writing - original draft. **All:** Writing - Review & Editing.

Data availability

The data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study. However, any shareable piece of source code, file, or post processing script will be gladly shared upon request to the corresponding author.

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A Redlich-Kister Polynomials

A.1 Chemical free energy

Chemical potentials of the alloying elements in α and β phases were calculated at different temperatures in the range from 400°C to 1000°C using ThermoCalc (database: TCNI8) and then approximated by cubic polynomials:

$$\mu_{Ti}^{\alpha} = 6.5215 \times 10^{-6} T^3 - 3.6174 \times 10^{-2} T^2 - 12.930 T - 2.1944 \times 10^3 \quad (10)$$

$$\mu_V^{\alpha} = 6.5307 \times 10^{-6} T^3 - 3.4676 \times 10^{-2} T^2 - 11.591 T - 1.9335 \times 10^3 \quad (11)$$

$$\mu_{Al}^{\alpha} = 6.4497 \times 10^{-6} T^3 - 3.5642 \times 10^{-2} T^2 - 12.247 T - 3.2008 \times 10^3 \quad (12)$$

$$\mu_{Ti}^{\beta} = 6.8957 \times 10^{-6} T^3 - 3.5142 \times 10^{-2} T^2 - 20.431 T - 4.5117 \times 10^3 \quad (13)$$

$$\mu_V^{\beta} = 6.5306 \times 10^{-6} T^3 - 3.4675 \times 10^{-2} T^2 - 13.991 T - 2.0665 \times 10^3 \quad (14)$$

$$\mu_{Al}^{\beta} = 6.4407 \times 10^{-6} T^3 - 3.5627 \times 10^{-2} T^2 - 15.268 T - 7.8040 \times 10^3 \quad (15)$$

Redlich-Kister coefficients of the excess term in α and β phases, extracted from Ref. [96], except for $L_{AlTi_0}^{\beta}$ that was recalibrated (see Section 2.2.2), are:

$$L_{TiV_0}^{\alpha} = 20000 \quad (16)$$

$$L_{AlTi_0}^{\alpha} = -133500 + 39 T \quad (17)$$

$$L_{AlTi_1}^{\alpha} = 750 \quad (18)$$

$$L_{AlTi_2}^{\alpha} = 17500 \quad (19)$$

$$L_{TiV_0}^{\beta} = 10500 - 1.5 T \quad (20)$$

$$L_{TiV_1}^{\beta} = 2000 \quad (21)$$

$$L_{TiV_2}^{\beta} = 1000 \quad (22)$$

$$L_{AlTi_0}^{\beta} = -118500 + 33.5 T \quad (23)$$

$$L_{AlTi_1}^{\beta} = 6000 \quad (24)$$

$$L_{AlTi_2}^{\beta} = 21200 \quad (25)$$

$$L_{AlV_0}^{\beta} = -95000 + 20 T \quad (26)$$

$$L_{AlV_1}^{\beta} = -6000 \quad (27)$$

A.2 Atomic mobility

Atomic mobility of alloying elements in phase $\varphi \in (\alpha, \beta)$, extracted from Ref. [102], are:

$$M_{Ti}^\varphi = \exp \left[\frac{\Delta G_{Ti}^\varphi}{RT} \right] \frac{1}{RT} ; \quad M_V^\varphi = \exp \left[\frac{\Delta G_V^\varphi}{RT} \right] \frac{1}{RT} ; \quad M_{Al}^\varphi = \exp \left[\frac{\Delta G_{Al}^\varphi}{RT} \right] \frac{1}{RT} \quad (28)$$

where:

$$\Delta G_{Ti}^\alpha = c_{Ti} \Delta G_{Ti,Ti}^\alpha + c_V \Delta G_{Ti,V}^\alpha + c_{Al} \Delta G_{Ti,Al}^\alpha \quad (29)$$

$$\Delta G_{Ti,Ti}^\alpha = -291755.355 - 115.51861 T \quad (30)$$

$$\Delta G_{Ti,V}^\alpha = -298988.939 - 333.55846 T \quad (31)$$

$$\Delta G_{Ti,Al}^\alpha = -111539.54 - 141.61855 T \quad (32)$$

$$\Delta G_V^\alpha = c_{Ti} \Delta G_{V,Ti}^\alpha + c_V \Delta G_{V,V}^\alpha + c_{Al} \Delta G_{V,Al}^\alpha \quad (33)$$

$$\Delta G_{V,Ti}^\alpha = -262867.416 - 95.5291479 T \quad (34)$$

$$\Delta G_{V,V}^\alpha = -270101.0 - 313.569 T \quad (35)$$

$$\Delta G_{V,Al}^\alpha = 0 \quad (36)$$

$$\Delta G_{Al}^\alpha = c_{Ti} \Delta G_{Al,Ti}^\alpha + c_V \Delta G_{Al,V}^\alpha + c_{Al} \Delta G_{Al,Al}^\alpha \quad (37)$$

$$\Delta G_{Al,Ti}^\alpha = -311534.815 - 95.17706 T \quad (38)$$

$$\Delta G_{Al,V}^\alpha = 0 \quad (39)$$

$$\Delta G_{Al,Al}^\alpha = -131319.0 - 121.277 T \quad (40)$$

and:

$$\begin{aligned} \Delta G_{Ti}^\beta &= c_{Ti} \Delta G_{Ti,Ti}^\beta + c_V \Delta G_{Ti,V}^\beta + c_{Al} \Delta G_{Ti,Al}^\beta + c_{Al} c_{Ti} \Delta G_{Ti,Al,Ti}^\beta \\ &\quad + c_{Ti} c_V [\Delta G_{Ti,Ti,V_0}^\beta + \Delta G_{Ti,Ti,V_1}^\beta (c_{Ti} - c_V)] \end{aligned} \quad (41)$$

$$\Delta G_{Ti,Al}^\beta = -104715.111 - 267.14 T \quad (42)$$

$$\Delta G_{Ti,Ti}^\beta = -153362.077 - 126.135031 T \quad (43)$$

$$\Delta G_{Ti,V}^\beta = -331128.104 - 65.0814985 T \quad (44)$$

$$\Delta G_{Ti,Al,Ti}^\beta = -139719.202 + 294.400646 T \quad (45)$$

$$\Delta G_{Ti,Ti,V_0}^\beta = 234932.489 - 219.426462 T \quad (46)$$

$$\Delta G_{Ti,Ti,V_1}^\beta = -261099.972 \quad (47)$$

$$\begin{aligned}\Delta G_V^\beta &= c_{Ti} \Delta G_{V,Ti}^\beta + c_V \Delta G_{V,V}^\beta + c_{Al} \Delta G_{V,Al}^\beta + c_{Al} c_{Ti} \Delta G_{V,Al,Ti}^\beta \\ &\quad + c_{Ti} c_V [\Delta G_{V,Ti,V_0}^\beta + \Delta G_{V,Ti,V_1}^\beta (c_{Ti} - c_V)]\end{aligned}\quad (48)$$

$$\Delta G_{V,Ti}^\beta = -179114.192 - 107.062681 T \quad (49)$$

$$\Delta G_{V,Al}^\beta = 0 \quad (50)$$

$$\Delta G_{V,V}^\beta = -322244.697 - 75.7262222 T \quad (51)$$

$$\Delta G_{V,Al,Ti}^\beta = 421533.074 - 629.054528 T \quad (52)$$

$$\Delta G_{V,Ti,V_0}^\beta = 163888.616 - 38.4124933 T \quad (53)$$

$$\Delta G_{V,Ti,V_1}^\beta = -54096.709 \quad (54)$$

$$\begin{aligned}\Delta G_{Al}^\beta &= c_{Ti} \Delta G_{Al,Ti}^\beta + c_V \Delta G_{Al,V}^\beta + c_{Al} \Delta G_{Al,Al}^\beta + c_{Al} c_{Ti} \Delta G_{Al,Al,Ti}^\beta \\ &\quad + c_{Ti} c_V \Delta G_{Al,Ti,V}^\beta\end{aligned}\quad (55)$$

$$\Delta G_{Al,Ti}^\beta = -159367.966 - 125.405247 T \quad (56)$$

$$\Delta G_{Al,Al}^\beta = -110721.0 - 266.41 T \quad (57)$$

$$\Delta G_{Al,V}^\beta = 0 \quad (58)$$

$$\Delta G_{Al,Al,Ti}^\beta = -348892.407 + 280.179819 T \quad (59)$$

$$\Delta G_{Al,Ti,V}^\beta = -261912.01 - 157.174295 T \quad (60)$$

B Numerical Methods

B.1 Cahn-Hilliard equation

After applying a backward Euler implicit time discretisation, Eq. (6) is written as:

$$(c^{(t+\Delta t)} - c^{(t)}) - V_m^2 \Delta t \nabla \cdot \left[\frac{M^{(t+\Delta t)}}{V_m} \nabla \left(\frac{\partial f_c^{(t+\Delta t)}}{\partial c} - \kappa_c \nabla^2 c^{(t+\Delta t)} \right) \right] = 0 \quad (61)$$

For the sake of clarity, the unknown field $c^{(t+\Delta t)}$ will be referred to as c . The differential equation above is non-linear and will be solved iteratively by successive linearisations using the Newton method. To this aim, the concentration field at iteration $(j+1)$ is written as $c_{(j+1)} = c_{(j)} + \delta c$, where $c_{(j)}$ is the concentration at previous iteration j , and δc is the increment of the concentration in this new iteration, now used as the unknown of the problem.

Evaluating Eq. (61) at iteration $(j+1)$ and linearising

$$M_{c_{(j+1)}} = M_{(c_{(j)} + \delta c)} \approx M_{c_{(j)}} + \delta c \frac{dM_{c_{(j)}}}{dc} \quad (62)$$

and

$$\frac{\partial f_{c_{(j+1)}}}{\partial c} = \frac{\partial f_{c_{(j)} + \delta c}}{\partial c} \approx \frac{\partial f_{c_{(j)}}}{\partial c} + \delta c \frac{\partial^2 f_{c_{(j)}}}{\partial c^2} \quad (63)$$

we obtain:

$$(c_{(j)} + \delta c - c^{(t)}) - V_m \Delta t \nabla \cdot \left[\left(M_{c_{(j)}} + \frac{dM_{c_{(j)}}}{dc} \delta c \right) \nabla \left(\frac{\partial f_{c_{(j)}}}{\partial c} + \frac{\partial^2 f_{c_{(j)}}}{\partial c^2} \delta c - \kappa_c \nabla^2 (c_{(j)} + \delta c) \right) \right] = 0 \quad (64)$$

Neglecting the high order terms related to δc , the following linear partial differential equation is obtained, whose solution gives δc that allows to compute $c_{(j+1)}$:

$$\begin{aligned} \delta c - V_m \Delta t \nabla \cdot \left[M_{c_{(j)}} \nabla \left(\frac{\partial^2 f_{c_{(j)}}}{\partial c^2} \delta c - \kappa_c \nabla^2 \delta c \right) + \frac{dM_{c_{(j)}}}{dc} \delta c \nabla \left(\frac{\partial f_{c_{(j)}}}{\partial c} - \kappa_c \nabla^2 c_{(j)} \right) \right] = \\ (c^{(t)} - c_{(j)}) + V_m \Delta t \nabla \cdot \left[M_{c_{(j)}} \nabla \left(\frac{\partial f_{c_{(j)}}}{\partial c} - \kappa_c \nabla^2 c_{(j)} \right) \right] \end{aligned} \quad (65)$$

By definition of the Fourier transform, the gradient and Laplacian of a field f are, respectively:

$$\widehat{\nabla f} = i \boldsymbol{\xi} \widehat{f} \quad (66)$$

$$\widehat{\nabla^2 f} = -\|\boldsymbol{\xi}\|^2 \widehat{f} \quad (67)$$

with i the imaginary unit, $\boldsymbol{\xi}$ the frequency vector, $\|\boldsymbol{\xi}\|^2$ the square of the frequency gradient, and $\widehat{}$ denotes the Fourier transform of the affected variable.

The previous differential equation can be transformed to the Fourier space, resulting in:

$$\begin{aligned}
& \widehat{\delta c} - V_m \Delta t \, i \boldsymbol{\xi} \cdot \mathcal{F} \left\{ M_{c(j)} \mathcal{F}^{-1} \left[i \boldsymbol{\xi} \left[\mathcal{F} \left(\frac{\partial^2 f_{c(j)}}{\partial c^2} \mathcal{F}^{-1}(\widehat{\delta c}) \right) + \kappa_c \|\boldsymbol{\xi}\|^2 \widehat{\delta c} \right] \right] + \right. \\
& \left. \frac{dM_{c(j)}}{dc} \mathcal{F}^{-1}(\widehat{\delta c}) \mathcal{F}^{-1} \left[i \boldsymbol{\xi} \left(\widehat{\frac{\partial f_{c(j)}}{\partial c}} + \kappa_c \|\boldsymbol{\xi}\|^2 \widehat{c}_{(j)} \right) \right] \right\} = (\widehat{c}^{(t)} - \widehat{c}_{(j)}) + \\
& V_m \Delta t \, i \boldsymbol{\xi} \cdot \mathcal{F} \left\{ M_{c(j)} \mathcal{F}^{-1} \left[i \boldsymbol{\xi} \left(\widehat{\frac{\partial f_{c(j)}}{\partial c}} + \kappa_c \|\boldsymbol{\xi}\|^2 \widehat{c}_{(j)} \right) \right] \right\}
\end{aligned} \tag{68}$$

The resulting equation is linear and can be solved after discretisation using some algebraical linear solver combined with a preconditioner, as presented in Appendix B.3

B.2 Allen-Cahn equation

Using a semi-implicit formulation, the $\partial f_c / \partial \eta_i$ terms are computed considering their value at the previous time step (explicit part) and the Laplacian of η_i is computed at the current time step (implicit part). After applying time discretisation, Eq. (7) is written as:

$$(\eta_i^{(t+\Delta t)} - \eta_i^{(t)}) + \frac{L}{V_m} \Delta t \left(\frac{\partial f_c^{(t)}}{\partial \eta_i} - \kappa_\eta \nabla^2 \eta_i^{(t+\Delta t)} \right) = 0 \tag{69}$$

For the sake of clarity, the unknown fields $\eta_i^{(t+\Delta t)}$ will be referred to as η_i . The previous differential equations can be transformed to the Fourier space, resulting in:

$$\widehat{\eta}_i \left(1 + \frac{L}{V_m} \Delta t \kappa_\eta \|\boldsymbol{\xi}\|^2 \right) = \widehat{\eta}_i^{(t)} - \frac{L}{V_m} \Delta t \widehat{\frac{\partial f_c^{(t)}}{\partial \eta_i}} \tag{70}$$

At each time $t + \Delta t$, the right hand side term of equation (70) depends only on values of the previous time step and therefore can be solved directly in Fourier space for each frequency, leading to

$$\widehat{\eta}_i = \frac{\widehat{\eta}_i^{(t)} - \frac{L}{V_m} \Delta t \widehat{\frac{\partial f_c^{(t)}}{\partial \eta_i}}}{\left(1 + \frac{L}{V_m} \Delta t \kappa_\eta \|\boldsymbol{\xi}\|^2 \right)} \tag{71}$$

B.3 Preconditioning and resolution

The discretised Eq. (68) corresponds to a linear algebraical equations $\widehat{\mathcal{A}}_{c_{(j)}}(\widehat{\delta c}) = \widehat{b}_{c_{(j)}}$ in which the linear operator is

$$\begin{aligned} \widehat{\mathcal{A}}_{c_{(j)}}(\cdot) = & (\cdot) - V_m \Delta t \, i\boldsymbol{\xi} \cdot \mathcal{F} \left\{ M_{c_{(j)}} \mathcal{F}^{-1} \left[i\boldsymbol{\xi} \left[\mathcal{F} \left(\frac{\partial^2 f_{c_{(j)}}}{\partial c^2} \mathcal{F}^{-1}(\cdot) \right) + \kappa_c \|\boldsymbol{\xi}\|^2(\cdot) \right] \right] + \right. \\ & \left. \frac{dM_{c_{(j)}}}{dc} \mathcal{F}^{-1}(\cdot) \mathcal{F}^{-1} \left[i\boldsymbol{\xi} \left(\widehat{\frac{\partial f_{c_{(j)}}}{\partial c}} + \kappa_c \|\boldsymbol{\xi}\|^2 \widehat{c}_{(j)} \right) \right] \right\} \end{aligned} \quad (72)$$

and the right-hand-side (independent term) corresponds to

$$\widehat{b}_{c_{(j)}} = (\widehat{c}^{(t)} - \widehat{c}_{(j)}) + V_m \Delta t \, i\boldsymbol{\xi} \cdot \mathcal{F} \left\{ M_{c_{(j)}} \mathcal{F}^{-1} \left[i\boldsymbol{\xi} \left(\widehat{\frac{\partial f_{c_{(j)}}}{\partial c}} + \kappa_c \|\boldsymbol{\xi}\|^2 \widehat{c}_{(j)} \right) \right] \right\} \quad (73)$$

The linear system defined by these equations for each time step can be solved by an iterative Krylov method, e.g. the Conjugate Gradient method, thus avoiding to form and store the matrix representing the linear operator. To accelerate the convergence of the iterative solver, an approximate inverse operator is used as preconditioner in the preconditioned conjugate gradient method (PCG) [97]. Following the procedure of Ref. [98], the preconditioner operator $\widehat{\mathcal{M}}_{c_{(j)}}$ is defined as:

$$\widehat{\mathcal{M}}_{c_{(j)}}(\cdot) = (\cdot) \left[1 + V_m \Delta t \overline{M}_{c_j} \left(\overline{\frac{\partial^2 f_{c_{(j)}}}{\partial c^2}} \|\boldsymbol{\xi}\|^2 + \kappa_c \|\boldsymbol{\xi}\|^4 \right) \right] \quad (74)$$

where $\overline{M}_{c_{(j)}}$ and $\overline{\partial^2 f_{c_{(j)}}/\partial c^2}$ are the average values of $M_{c_{(j)}}$ and $\partial^2 f_{c_{(j)}}/\partial c^2$ over the domain.

For every time step, the iterations are performed until $\widehat{c}_{(j+1)}$ is converged. Since $M_{c_{(j+1)}}$ and $\partial f_{c_{(j+1)}}/\partial c$ were linearised in Eq. (64), Eq. (61) is only satisfied for $c_{(j+1)}$ after convergence. The difference between left and right hand sides of Eq. (61) is used as a residual,

$$\text{Res}_{(j)} = \mathcal{F}^{-1} \left\{ \frac{\widehat{c}_{(j+1)} - \widehat{c}^{(t)}}{V_m^2 \Delta t} - i\boldsymbol{\xi} \cdot \mathcal{F} \left\{ \frac{M_{c_{(j+1)}}}{V_m} \mathcal{F}^{-1} \left[i\boldsymbol{\xi} \left(\widehat{\frac{\partial f_{c_{(j+1)}}}{\partial c}} + \kappa_c \|\boldsymbol{\xi}\|^2 \widehat{c}_{(j+1)} \right) \right] \right\} \right\}. \quad (75)$$

The absolute error for the current value of $\widehat{c}_{(j+1)}$ is then given by the norm of the residual $\text{Err}_{(j)} = \int_V \text{Res}_{(j)}^2 dV$ and the equation converges when this error becomes smaller than the tolerance.

Variable time stepping is performed in the following way. When a large number of iterations is reached in the Newton method ($j_{\text{Newton}} > it_{\text{max}}$, with $it_{\text{max}} = 200$) and the solution is not converged, Δt is reduced by a factor of 2 in order to stabilise the algorithm. The time step is also reduced by a factor of 2 when the PCG exceeds a high number of iterations ($j_{\text{PCG}} > it_{\text{max}}$). When the number of iterations is below it_{max} , the new value of time step is computed as $\Delta t^{(t+\Delta t)} = \tau \Delta t^{(t)}$, where τ is a time step factor computed as $\tau = \min(\tau_{\text{algorithm}})$, with $\tau_{\text{algorithm}} = (it_{\text{target}}/it_{\text{algorithm}})^{0.3}$, $it_{\text{target}} = 25$ the target number of iterations to get convergence, $it_{\text{algorithm=Newton}}$ the number of iterations needed to get the solution in the previous time step by the Newton method, and $it_{\text{algorithm=PCG}}$ the maximum number of iterations needed by the PCG method to converge in the previous time step.

B.4 Algorithms

The resolution scheme of the complete system of equations is presented in Algorithm 1 and the resolution of the concentration field in Algorithm 2.

Algorithm 1: Phase-Field resolution algorithm for 2D domain

Fields initialisation;
Time discretisation $[0, r\Delta t, \dots, t_{\max}]$, for $r \in \mathbb{Z}$;
Space discretisation $x \leftarrow [0, s\Delta x, \dots, l_x]$, $y \leftarrow [0, s\Delta y, \dots, l_y]$, for $s \in \mathbb{Z}$;
 ξ and $\|\xi\|^2$ with Eqs. (8) and (9), respectively;
while $t < t_{\max}$ **do**
 Concentration field computation:
 $c^{(t+\Delta t)}$ with Algorithm 2;
 Phase field computation:
 $\frac{\partial f_c^{(t)}}{\partial \eta_i}$;
 $\widehat{\frac{\partial f_c^{(t)}}{\partial \eta_i}} \xleftarrow{\mathcal{F}} \frac{\partial f_c^{(t)}}{\partial \eta_i}$;
 $\widehat{\eta}_i^{(t+\Delta t)} \leftarrow \frac{\widehat{\eta}_i^{(t)} - \frac{L}{V_m} \Delta t \frac{\partial f_c^{(t)}}{\partial \eta_i}}{\left(1 + \frac{L}{V_m} \Delta t \kappa_\eta \|\xi\|^2\right)}$;
 $\eta_i^{(t+\Delta t)} \xleftarrow{\mathcal{F}^{-1}} \widehat{\eta}_i^{(t+\Delta t)}$;
end
Output generation;

Algorithm 2: c resolution algorithm for 2D domain

Variable initialisations:

$$\text{Err}_{tol} \leftarrow 10^{-10};$$

$$\widehat{c}_{(j=1)}^{(t+\Delta t)} \xleftarrow{\mathcal{F}} c^{(t)};$$

while $\text{Err}_{(j)} > \text{Err}_{tol}$ **do**

$$\begin{aligned} & M_{c_{(j)}}^{(t+\Delta t)}; \frac{dM_{c_{(j)}}^{(t+\Delta t)}}{dc}; \\ & \frac{\partial f_{c_{(j)}}^{(t+\Delta t)}}{\partial c}; \frac{\partial^2 f_{c_{(j)}}^{(t+\Delta t)}}{\partial c^2}; \\ & \frac{\partial f_{c_{(j)}}^{(t+\Delta t)}}{\partial c} \xleftarrow{\mathcal{F}} \frac{\partial f_{c_{(j)}}^{(t+\Delta t)}}{\partial c}; \end{aligned}$$

$$\begin{aligned} \widehat{b}_{c_{(j)}}^{(t)} & \leftarrow (\widehat{c}^{(t)} - \widehat{c}_{(j)}^{(t+\Delta t)}) + V_m \Delta t \, i\xi \cdot \mathcal{F} \left\{ M_{c_{(j)}}^{(t+\Delta t)} \mathcal{F}^{-1} \left[i\xi \left(\frac{\partial f_{c_{(j)}}^{(t+\Delta t)}}{\partial c} + \right. \right. \right. \\ & \left. \left. \left. \kappa_c \|\xi\|^2 \widehat{c}_{(j)}^{(t+\Delta t)} \right) \right] \right\}; \end{aligned}$$

$$\begin{aligned} \widehat{\Delta c}_{(j)}^{(t+\Delta t)} & \leftarrow \widehat{\mathcal{A}}_{c_{(j)}}^{-1} (\widehat{b}_{c_{(j)}}^{(t+\Delta t)}) \text{ computed with PCG method and } \widehat{\mathcal{M}}_{c_{(j)}} \text{ with} \\ & \text{Eq. (74);} \end{aligned}$$

$$\widehat{c}_{(j+1)}^{(t+\Delta t)} \leftarrow \widehat{c}_{(j)}^{(t+\Delta t)} + \widehat{\Delta c}_{(j)}^{(t+\Delta t)};$$

$$c_{(j+1)}^{(t+\Delta t)} \xleftarrow{\mathcal{F}^{-1}} \widehat{c}_{(j+1)}^{(t+\Delta t)};$$

$$\text{Res}_{(j)} \xleftarrow{\mathcal{F}^{-1}}$$

$$\frac{(\widehat{c}_{(j+1)}^{(t+\Delta t)} - \widehat{c}^{(t)})}{V_m^2 \Delta t} - i\xi \cdot \mathcal{F} \left\{ \frac{M_{c_{(j+1)}}^{(t+\Delta t)}}{V_m} \mathcal{F}^{-1} \left[i\xi \left(\frac{\partial f_{c_{(j+1)}}^{(t+\Delta t)}}{\partial c} + \kappa_c \|\xi\|^2 \widehat{c}_{(j+1)}^{(t+\Delta t)} \right) \right] \right\};$$

$$\text{Err}_{(j)} \leftarrow \int_V \text{Res}_{(j)}^2 dV;$$

$$j \leftarrow j + 1;$$

end

$$c^{(t+\Delta t)} \leftarrow c_{(j)}^{(t+\Delta t)};$$

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