Rapid thermokinetics driven nanoscale vanadium clustering within martensite laths in laser powder bed fused additively manufactured Ti6Al4V

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\textbf{ABSTRACT}
This paper reports the computational approach adopted for thermo-diffusion kinetics to rationalize homogeneously distributed nanoscale vanadium-rich clusters formed within the martensite laths of Ti6Al4V alloy printed using laser powder bed fusion at an energy density of 52.08 J/mm\textsuperscript{3}. The computations were conducted using a finite element method based thermal model, which predicted extremely rapid thermokinetics associated with the thermal cycles experienced at any given location of LPBF-printed Ti6Al4V. The numerically estimated effective V diffusion length of 6.61 nm indicated kinetic-limited diffusion resulting in V nano-clusters and are in good agreement with the atom probe tomography data giving a value of half the inter-cluster spacing of 7 nm.

\textbf{IMPACT STATEMENT}
The computational approach adopted for thermo-diffusion kinetics comprehends homogeneously distributed vanadium nano-clusters within martensite laths of Ti6Al4V, printed by laser powder bed fusion, due to repetitive and extremely rapid thermokinetics.

1. Introduction
Laser powder bed fusion (LPBF) is an extensively used laser-based additive manufacturing (AM) technique \cite{1,2}. It involves inherently complex heat-treatment cycles associated kinetics that makes it difficult to understand and control microstructural/phase evolution in the printed component. Hence, the fundamental understanding of laser material interactions during laser-based AM processes is of paramount importance.

LPBF technique is widely explored for Ti6Al4V, a titanium alloy, due to its excellent set of characteristics in various fields. The microstructural evolution of such an alloy is mainly governed by the thermokinetics involving repetitive rapid heating-cooling cycles and steep thermal gradients during LPBF fabrication. Hence, the resultant LPBF-printed Ti6Al4V primarily exhibits metastable martensite $\alpha'$ phase within the prior columnar $\beta$ grains directionally and epitaxially grown along (100) direction \cite{3,4}. However, the complex spatial and temporal variations of thermokinetics associated with thermophysical processes, and laser parameters \cite{3,5–7} affect the extent of thermodynamic phase stability, crystallographic texture, and thermal stresses induced during the process, thereby quantitively affecting the extent of phase decomposition and crystallographic defects in the components \cite{7–9}.

The formation and decomposition of martensites ($\alpha'$ and $\alpha''$) and localization of $\beta$ stabilizing elements at various interfaces during AM fabrication of Ti6Al4V \cite{8–10} is mainly driven by the diffusion kinetics of Vanadium that is contingent on inherent thermokinetics associated with these processes. With this viewpoint, the present study identifies homogeneously distributed nanoscale V-rich clustering within martensite laths of LPBF-printed...
Ti6Al4V, and rationalizes this effect based on the complex thermo-diffusion kinetics involved in the processing, simulated via finite element method (FEM) based computational modeling. It correlates the computed thermal and diffusion kinetics results with the observed state of nano-structures in LPBF-printed Ti6Al4V. Although thermomechanical effects of LPBF on phase evolution were recognized, no attempts are made to report them here. Currently, separate in depth efforts are being pursued on this aspect that will be reported in future publication.

2. Materials and methods

Ti6Al4V blocks (10 × 10 × 15 mm$^3$) were printed in LPBF AconityMIDI system (CW, Nd:YAG laser, 1070 nm wavelength, 85 µm beam diameter, 800 mm/s scanning speed, and 150 W power resulting into energy density of 52.08 J/mm$^3$, build chamber oxygen content of 50 ppm) with the commercial grade-23 Ti6Al4V alloy powder (15 µm–45 µm particle size). Each layer of 30 µm thickness was deposited using bi-directional linear laser beam scans with a separation of 120 µm between the centers of consecutive laser scans along with rotation of 90° and 16 s delay time between each layer.

The microstructural examination of the LPBF-printed blocks was carried out in the nano scanning electron microscope (nano SEM) and 200kV FEI Tecnai G2 TF20$^{TM}$ Transmission Electron Microscopy (TEM). An Atom Probe Tomography (APT) for compositional partitioning was performed in Cameca LEAP 5000XS 3D Atom Probe Microscope at 30 K (50 nJ, 100 kHz pulse rate, and 0.5–1 detection rate in laser mode). The lift outs for TEM and APT were prepared using the FEI Nova 200 dual-beam focused ion beam (FIB).

Considering the inherent experimental and thermal sensing limitations of LPBF process, thermokinetics of the process was predicted using a FEM-based three-dimensional thermal model on the COMSOL platform. The designed model mainly dwells on monitoring the transient temperature distribution while influenced by the complex dynamics of the melt. The governing equations and boundary conditions of the model were adopted from the recent reports of the authors [3,11].

3. Results and discussion

Microstructural analysis of LPBF-printed Ti6Al4V, carried out via SEM, indicated martensitic ($\alpha'$) lath morphology as shown in Figure 1(a,b). These images also reveal a high density of internal twinning and other planar faults within the $\alpha'$ laths (Figure 1(a,b)). While such internal twinning is possible in martensitic laths to accommodate the lattice invariant shear, typical martensites in quenched samples of bulk Ti6Al4V do not exhibit such a high density of internal twinning. Such a high density of defects is likely to arise due to the extremely rapid thermokinetics associated with the LPBF process,
as recently reported by the authors with an inclusive computational model developed for the LPBF process [3]. Based on adaptation of this computational model in the current study, the thermokinetic aspects involved a rapid cooling rate ranging from $2.56 \times 10^7$ K/s to $4.82 \times 10^5$ K/s and steep thermal gradients ranging from $1.58 \times 10^7$ K/m to $1.48 \times 10^6$ K/m during solidification of the alloy. Such a rapid thermokinetics is likely to generate severe thermal stresses, which are partially relieved by these twins and planar defects. Further characterization was performed with TEM to confirm the phases present in LPBF-printed Ti6Al4V. The inset in Figure 1(c) shows the diffraction pattern recorded from [101 \bar{1}] HCP zone axis, which confirmed the presence of martensitic $\alpha'$ phase. The bright-field micrograph shown in Figure 1(c) exhibits multiple martensite laths but no evidence of any retained $\beta$ phase formation within or at lath interface. This indicates the complete transformation of prior parent $\beta$ phase into a martensite microstructure under extremely rapid cooling rates.

LPBF process is associated multiple heating-cooling cycles at varying kinetics. Such intrinsic thermal cycles can affect the thermodynamic state of the $\alpha'$ phase during LPBF printing. With this perception, APT characterization was carried out to detect any evidence for the onset of martensitic decomposition. The APT sample lift-out using FIB was made such that multiple inter-lath interfaces were included, and the data from two representative reconstructions are shown in Figures 2 and 3. Figure 2(a) shows the V ions map within a 5nm slice of the three-dimensional (3D) reconstruction, which clearly reveals V-rich nano-clusters within the martensite lath. The iso-concentration surface of 6 at.% V with Ti ions (Figure 2(b)) displays the spherical/ellipsoidal morphology of these V-rich nano-clusters. Composition profiles in the form of a proximity histogram constructed across 6 at.% V iso-surface (Figure 2(c)), reveals that while V content in the clusters has increased by 16 at.% and Ti content decreases by 16 at.%, there is no significant difference between the Al content of the matrix and clusters. Based on thermodynamic considerations, there is a strong driving force for rejection of V, a strong $\beta$ stabilizer in Ti alloys, from the supersaturated martensitic $\alpha'$ laths. This results in a cross-diffusion of Ti and V due to their similar diffusion coefficients within the $\alpha/\alpha'$ phases in the Ti-Al-V system [12]. Relatively lower diffusion coefficient of Al may cause insignificant diffusion in the same system rendering constant concentration throughout the $\alpha'$ lath [12]. Considering the region of stable V concentration within the nano-cluster, the average radius of these clusters was obtained to be 1.88 nm (Figure 2(c)). Accordingly, the volume percent of V nano-cluster within a martensite lath was measured as 10.31%.

This dataset allowed computing inter-cluster spacing as $\sim 14$ nm assuming an average uniform equidistant distribution of V nano-clusters within the laths.

Similar V enrichment was detected in a second APT reconstruction capturing an inter-lath interface (Figure 3(a)) with V ions map of 5nm slice of the 3D reconstruction. Figure 3(b) shows full 3D reconstruction with V ions and a cylinder across which a concentration profile of each element was obtained as presented in Figure 3(c). The plot clearly reveals the V enrichment at the inter-lath interface by $\sim 5$ at.% and a corresponding decrease in Ti content. The fluctuations in the composition of matrix are due to V clustering within the laths. Thus, the APT investigation indicated uniform nano-clustering of V within the martensite lath and enrichment at the lath boundary.

In conventional tempering heat treatment or AM processes involving slower kinetics, V being a strong $\beta$
stabilizer, tends to diffuse towards inter-lath interfaces, since these are potent heterogeneous nucleation sites for β phase nucleation during the tempering of martensitic α’ [8,9,13]. However, under the diffusion constraints due to rapid thermokinetics, it may not be possible for the V atoms within the supersaturated martensitic laths to diffuse over the long distances required to reach the inter-lath interfaces. Therefore, the V atoms tend to homogeneously cluster within the α’ laths, or decorate possible lattice defects and α’/α’ inter-lath interfaces, with their distribution being determined by the diffusion distances permitted by the rapid thermokinetics (Figures 2 and 3).

There are two previous reports, based on APT results, clearly showing the formation of V-rich regions in SLM-printed Ti6Al4V, one using 170 W powder and a travel speed of 1.2 m/s [8], and a second report employing energy densities of 77 J/mm³ and 145 J/mm³ with a preheated stage at 473 K [9]. However, both these studies reported V-rich one- and two-dimensional features (rod-like and films) within the APT reconstructions. V enrichment at planar interfaces such as twin boundaries, as well as at linear defects such as dislocations, within the α’ laths, was reported [8]. Similarly, formation of V-rich films at α’/α’ inter-lath interfaces, resulting in the nucleation of β at these interfaces has also been reported [9]. There are two fundamental differences between these previous observations and the ones reported in the present paper. Firstly, while the previously reported APT observations [8,9] have indicated local V enrichment only at heterogeneous defects and interfaces, the present study clearly revealed homogeneously distributed nanoscale V-rich spheroidal clusters within the martensitic α’ laths in addition to V-rich films at α’/α’ inter-lath interfaces. Secondly, in the present case the TEM diffraction results did not indicate the presence of any β phase or α’ martensitic phase in the sample. The relatively high degree of V enrichment (~16 at.% higher than the matrix) within the nano-clusters could potentially result in local lattice distortions and formation of embryonic β regions inside the martensitic α’ laths. However, the evidence for such local lattice distortions requires high resolution TEM/STEM investigations which is the subject of future studies. Further, it should be noted that the relatively lower energy density of 52.08 J/mm³ without preheating the stage was employed in the present study. Therefore, it is likely to have comparatively rapid kinetics, as mentioned earlier, affecting diffusion lengths and defect density [9].

The thermokinetics experienced by any given location within a given layer of LPBF-printed Ti6Al4V block was computationally predicted using the computational model presented in Figure 4. This thermokinetics experienced by a given location is presented as thermal patterns P₁, P₂, P₃, P₄, . . . due to fabrication of subsequent layers. Thermal pattern P₁ consists of a collection of thermal cycles corresponding to sequential laser tracks during fabrication of a given build layer. When the laser moves to build another layer above the given layer, the same location in the previously built layer experiences the thermal pattern P₂ with reduced heat intensity and this trend continues while building subsequent layers (Figure 4(a)). These thermal patterns are separated with the interlayer delay time (tᵢ), which is a time gap between building of two consecutive layers (Figure 4(a)). As the instantaneous highest temperatures reached during thermal cycles in thermal patterns P₁ and P₂ are higher than the melting of point (1877 K) of Ti6Al4V, the first melting event at a given location in cycle C₁ occurs during fabrication of the first layer followed by remelting in C₂ during fabrication of the second layer (Figure 4(a)). The remelting during
Figure 4. Numerically predicted thermokinetics results showing (a) thermal history experienced by any given location during LPBF printing of Ti6Al4V, and (b) magnified view of the selected thermal cycles from (a), (c) cumulative diffusion length of V corresponding to each heating-cooling cycle shown in (b), (d) Schematic showing probable diffusion distance of V atoms based on their inter-cluster spacing.

thermal cycle $C_2$ wipes out the thermal history generated previously during fabrication of the first layer, and new $\alpha'$ laths are generated under the rapid cooling rate, which remains above $10^5$ K/s. During fabrication of subsequent layers, highest instantaneous temperatures in the thermal cycles associated with the thermal pattern $P_3, P_4, \ldots$ remain below the melting point of Ti6Al4V (Figure 4(a)). Some of these thermal cycles are likely to initiate the transient solid-state diffusion of V manifesting in the form of uniformly distributed V-rich nano-clusters within the $\alpha'$ laths (Figures 2 and 3). This transient diffusion of V was analyzed considering the above-described thermokinetics of the LPBF process.

A transition from diffusion-limited phase transformation to kinetic-limited phase transformation is associated with local non-equilibrium diffusion effects in the bulk material due to rapid thermokinetics [14,15]. Based on inherent rapid heating ($2.31 \times 10^5 - 6.71 \times 10^7$ K/s) and cooling rates ($2.56 \times 10^7\ K/s - 4.82 \times 10^5\ K/s$) in the present study, the kinetic-limited diffusion length is likely to be at atomic to nanometer scale. Considering the diffusion during both heating and cooling events of the thermal cycles, the solution to Fick’s second law of diffusion with varying diffusion coefficient ($D$) can provide concentration spread with distance and time. With its general solution form the diffusion length ($x$) can be computed over a period of time ($t$) at a constant temperature using Equation (1).

$$x = \sqrt{Dt}.$$  

(1)

However, since the diffusion coefficient varies with temperature, Equation (1) needs to be expressed differently, considering the variable diffusion coefficient. The diffusion coefficient $D(T)$ is a function of temperature usually expressed in the Arrhenius form as Equation (2).

$$D(T) = D_0 \exp \left(\frac{-Q}{RT}\right).$$  

(2)

With the above relation and temperature-time relationship obtained through thermokinetic predictions (Figure 4(a)), the diffusion coefficient dependance on time was obtained, which allowed integrating Equation (1) over a period of time varying from $t_1$ to $t_2$ to obtain the diffusion length.

$$x^2 = \int_{t_1}^{t_2} D(t) \, dt.$$  

(3)

The above integration was solved using a basic numerical method to obtain the diffusion length of V during heating and cooling events of thermal cycles. The diffusion data corresponding to V in hexagonally closed packed phase $\alpha$ in Ti–Al–V system was considered from the recent literature [12]. These diffusion calculations were conducted
for only those thermal cycles that reached instantaneous temperature above 773 K and below the β solvus temperature (1268 K), since V diffusion is insignificant below this temperature [12]. From Figure 4(a), it can be seen that after the thermal cycle C2 that forms α′ laths, only thermal cycles triggering diffusion of V are C3, C4, C5, C6, and C7. Parts of these cycles above 773 K are magnified in Figure 4(b). The diffusion length corresponding to both heating and cooling events of the thermal cycles triggering diffusion of V are shown in Figure 4(c). This dwell time of the heating-cooling cycles are predicted in the range of 0.25–1.05 ms above 773 K. Furthermore, the diffusion distance corresponding to the heating events of all thermal cycles are relatively shorter than during the cooling events (Figure 4(c)). This is due to more rapid heating rate compared to the cooling rates.

The computationally predicted average total diffusion length of V atoms from resulting thermal cycles was 6.61 nm (Figure 4(c)). This numerically predicted value nearly matches the half V inter-cluster spacing of ∼7 nm experimentally determined from the APT analysis. As schematically depicted in Figure 4(d), the region of V atoms lying in the region halfway between clusters is likely to diffuse towards the surrounding V nano-clusters, representing the overall diffusion length. Although the numerically calculated diffusion lengths are closely comparable to the experimentally measured diffusion length, multiple factors associated with non-equilibrium diffusion due to rapid thermokinetics may lead to the difference in their values. In addition to kinetic-limited diffusion, the stresses and defect generated, and stored energy during prior thermal cycles (C1, C2) can potentially assist in the clustering of the V atoms. Furthermore, the presence of elastic strain gradient surrounding dislocations or solutes adds to the chemical potential gradient to drive the diffusion. This effect can also accelerate the diffusion and cluster formation rate due to additional stress-induced drift [15]. Thus, the effective non-equilibrium diffusion length can be longer when compared to the equilibrium diffusion.

In summary, the onset of martensitic decomposition via formation of V-rich nano-clusters, revealed by atom probe tomography, was detected in the LPBF-printed Ti6Al4V at an energy density of 52.08 J/mm³. APT results revealed a uniform distribution of V-rich nano-clusters with ∼16 at.% concentration within the martensite laths and at inter-lath interfaces. A numerical thermokinetic model predicted a cooling rate in the range 2.56 × 10⁷ to 4.82 × 10⁵ K/s and thermal gradients of 1.58 × 10⁷ to 1.48 × 10⁶ K/m. The predicted thermal history of the LPBF-printed Ti6Al4V rationalizes the partial tempering effect on martensite forming V-rich nano-clusters. The numerically predicted effective diffusion length of V of 6.61 nm was found to be in good agreement with the experimentally measured half inter-cluster spacing (∼7 nm) indicating kinetically limited diffusion.

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**Disclosure statement**

No potential conflict of interest was reported by the author(s).

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