

**SYNTHESIS OF HIGH-PERFORMANCE MULTI-COMPONENT
METALLIC MATERIALS BY LASER ADDITIVE MANUFACTURING
VIA INTEGRATED MODELING AND SYSTEMATIC EXPERIMENTS**

by

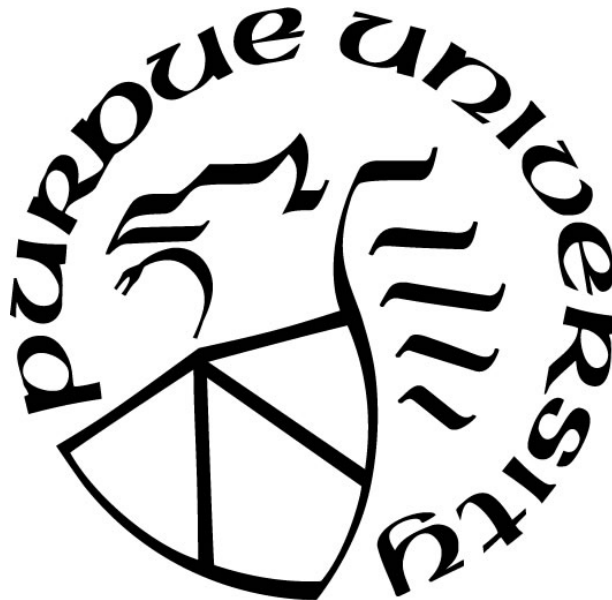
Shunyu Liu

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THE PURDUE UNIVERSITY GRADUATE SCHOOL
STATEMENT OF COMMITTEE APPROVAL

Dr. Yung C. Shin, Chair

School of Mechanical Engineering

Dr. Benxin Wu

School of Mechanical Engineering

Dr. Kejie Zhao

School of Mechanical Engineering

Dr. Lia A. Stanciu

School of Materials Engineering

Approved by:

Dr. Nicole L. Key

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ABSTRACT

This research aims at investigating the direct in-situ synthesis of high-performance multi-component alloys such as high entropy alloys, bulk metallic glasses, and metal matrix composites using the directed energy deposition (DED) process, and modeling the entire solidification and microstructure evolution of these alloys via a novel three-dimensional cellular automata-phase field (3D CA-PF) model. These alloys are currently the focus of significant attention in the materials and engineering communities due to their superior material properties. In the 3D CA-PF model, the growth kinetics including the growth velocity and solute partition at the local solid/liquid interface is calculated by the multi-phase and multi-component PF component, and the 3D CA component uses the growth kinetics as inputs to calculate the dendrite morphology variation and composition redistribution for the entire domain, which could save the computational cost more than five orders of magnitude compared to the PF modeling that can only be applied to small domains due to its heavy computational requirements. Coupled with the temporal and spatial temperature history predicted by the experimentally validated DED model, this computation-efficient 3D CA-PF model can predict the microstructure evolution within the entire macro-scale depositions, which is known to be nonuniform due to the particular nature of additive manufacturing (AM) processes.

To achieve the final goal of direct in-situ synthesis of five-component CoCrFeCuNi high entropy alloys (HEA), and modeling of the solidification and microstructure evolution during the DED process, the proposed research is carried out in progressive stages with the increasing complexity of alloy systems. First, a simple binary material system of Ti-TiC composite was studied. The thermodynamically-consistent binary PF model is used to simulate the formation mechanism of detrimental resolidified dendritic TiC_x . To capture the polycrystalline solidification, a grain index is introduced to link different crystallographic orientations for each grain. This PF model simulates the microstructure evolution of TiC_x in different zones in the molten pool by combining the temperature history predicted by the DED model. The simulated results provide the solution of limiting the free carbon content in the melt, according to which, the formation of TiC_x dendrites is successfully avoided by experimentally controlling the melting degree of premixed TiC particulates.

Second, the solidification, grain structure evolution, and phase transformation in the DED-built ternary Ti6Al4V alloy under the influences of thermal history are systematically simulated using the established simulation framework and a phase prediction model. The thermal history in a three-track deposition is simulated by the DED model. With such thermal information, the 3D CA model simulates the grain structure evolution on the macro-scale. The thermodynamically-consistent PF model predicts the local grain structure and concentration distributions of solutes Al and V on the micro-scale. The meso-scale CA-PF model captures the sub-grain microstructure evolution and concentration distributions of solutes within the entire molten pool. The dendritic morphology is captured within the large β grains. When the temperature drops below the β -transus temperature, the solid-state phase transformation of $\beta \rightarrow \alpha/\alpha'$ is studied by the phase prediction model. Based on the predicted volume fractions of α' and α , the microhardness is also successfully assessed using rules of mixtures.

Third, the material system is expanded to a four-component ZrAlNiCu bulk metallic glass composite, whose raw composition is prepared by premixing the four pure elemental metals. The DED model is employed to obtain the temperature field and heating/cooling rates in single-track ZrAlNiCu bulk metallic glass composite, which provides insights for microstructure evolution. By delicate control of the material composition and utilization of the thermal history of the DED process, an amorphous-crystalline periodic structure is produced with in-situ formed crystalline particulates embedded in the amorphous matrix. This crack-free microstructure is successfully maintained within bulk parts, where a high fraction of the amorphous phase and crystalline phases are produced in the fusion zone and heat-affected zone, respectively. The large volume percentage of the amorphous phase contributed to the hardness, strength, and elastic modulus of the composite while the various soft crystalline phases improve the ductility by more than three times compared to monolithic metallic glasses. Nanoindentation tests are also performed to study the deformation behavior on the micron/sub-micron length scale.

Fourth, the material system is expanded to a five-component CoCrFeNiTi HEA alloy. Three CoCrFeNiTi HEA alloys with different compositions are designed and synthesized from premixed elemental powders via the DED process. Through a delicate design of composition and powder preparation, different microstructures are formed. H3-Co24.4Cr17.4Fe17.5Ni24.2Ti16.5 is mainly composed of a soft face-centered cubic (FCC)- γ phase while σ -FeCr, δ -NiTi₂, and a small amount of Ni₃Ti₂ are precipitated and uniformly distributed in the FCC matrix for H1-

Co_{22.2}Cr_{16.1}Fe₁₉Ni_{21.8}Ti_{20.9} and H2-Co_{25.9}Cr₁₅Fe₁₇Ni_{20.8}Ti_{21.3}. With a large percent of the secondary phases, H1 exhibits a hardness value of about 853 HV_{0.5}. These HEA alloys display a high oxidation resistance comparable to Inconel 625 superalloy. A detailed evaluation of the hardness, oxidation resistance, and wear resistance of these HEAs are conducted as compared with those of a reference HEA and two popular anti-wear steels.

Finally, a novel 3D Cellular Automata-Phase Field (CA-PF) model that can accurately predict the dendrite formation in a large domain, which combines a 3D CA model with a 1D PF component, is developed. In this integrated model, the PF component reformulated in a spherical coordinate is employed to accurately calculate the local growth kinetics including the growth velocity and solute partition at the solidification front while the 3D CA component uses the growth kinetics as inputs to update the dendritic morphology variation and composition redistribution throughout the entire domain. Taking advantage of the high efficiency of the CA model and the high fidelity of the PF model, the 3D CA-PF model saves the computational cost more than five orders of magnitude compared to the 3D PF models without losing much accuracy. By coupling the thermodynamic and kinetic calculations into the PF component, the CA-PF model is capable of handling the microstructure evolution of any complex multi-component alloys. Al-Cu binary alloys with 2 wt.% and 4 wt.% Cu are first used to validate the 3D CA-PF model against the Lipton-Glicksman-Kurz analytical model and a 3D PF model. Then, the 3D CA-PF model is applied to predicting the dendrite growth during large-scale solidification processes of directional solidification of Al-30wt.%Cu and laser welding of Al-Cu-Mg and Al-Si-Mg alloys.

1. INTRODUCTION

1.1 Background

Additive Manufacturing (AM) has a broad capability in synthesizing advanced metallic materials. Currently, it has been widely used to fabricate various engineering materials, like steels [1-3], titanium alloys [4, 5], aluminum alloys [6-8], etc., which significantly minimizes material waste and reduces the manufacturing cost because of its net-shaping capability [9, 10]. The directed energy deposition (DED) such as blown-powder and wire-feed AM processes also find their wide application in building composites and functionally graded materials since they can feed various materials simultaneously [11-14]. Instead of premixing the reinforced secondary phases to the matrix powders, some secondary phases can also be introduced by in-situ synthesis [14, 15], as AM processes produce a peak temperature of more than 2500 K in the molten pool resulting from the highly concentrated energy created by the focused laser beam or electron beam [1, 16-19]. In addition, this high temperature also makes AM suitable for dealing with materials with high melting temperatures, such as ceramics and refractory elements [20]. In addition to the high temperature, AM processes are also able to produce a cooling rate of $10^3 - 10^6$ K/s [13, 21-24], which is higher than the critical cooling rate of most titanium-based, copper-based, and zirconium-based metallic glasses [25, 26], making AM applicable to synthesizing some metallic glasses [19, 27-29]. Moreover, the profound quenching effect resulting from the high cooling rate is beneficial to stabilizing phase structure and restricting element diffusion. Consequently, AM processes exhibit great advantage in direct synthesis of novel multi-principal component high entropy alloys (HEA) [30-34], which are mainly composed of solid solution phases [35, 36].

Despite the great advantages in geometry and composition control, material properties of final products are the key factors determining AM processes as qualified manufacturing techniques in lieu of traditional methods; therefore, it is vital to understand the microstructure evolution in AM-built products since microstructure governs the products' property. For example, HEA's property is highly dependent on the formed phases [36, 37]. Table 1.1 summarizes the hardness of typical phases found in HEA [37]. As the yield strength of a metallic material can be estimated to be one-third of its hardness [38], the hardness value can be used to approximate the strength condition. In addition to the phase-type, the distribution and morphology of the phase, as well as

the grain size, also affect the strength and hardness [39]. Otto et al. [40] reported the effect of grain size on the yield strength of CoCrFeMnNi HEA. When the grain size was increased from 4.4 μm to 50 μm , the yield strength dropped by about 190 MPa, while about 40 MPa dropped further when the grain was coarsened to 155 μm .

Table 1.1. Hardness for typical phases [37].

Phase	Typical phases	Hardness (HV)
Valence compounds	Carbides, borides, silicides	1000 – 4000
Intermetallic phases with complex structures	σ , Laves, η	650 – 1300
BCC and derivatives	BCC, B2, Heusler	300 – 700
FCC and derivatives	FCC, L12, L10	100 – 300

Microstructure is determined by the thermal history and processing attributes of manufacturing methods. For AM processes, the combined effect of power, scan speed, layer height, and hatch spacing results in complex multi-physics phenomena such as mass addition, laser-particle interaction, laser-substrate interaction, thermal and fluid dynamics in the molten pool, solidification, etc. The complex thermal behavior and rapid thermal cycles produce unique microstructure with fine grains and non-equilibrium phases [39, 41-43], which leads to improved hardness [39, 44, 45], strength [4, 30], wear resistance and corrosion resistance [45-47] but reduced Young's modulus, degraded ductility and fatigue toughness over some other fabrication methods [4, 48-51]. The directional growth of as-solidified grains aligning with the maximum temperature gradient direction [24, 52-56] are responsible for the anisotropy in tensile properties and impact toughness observed in AM-built products [4, 57]. Repeated thermal cycles experienced in the overlapping zone of adjacent tracks and layers are also responsible for producing non-uniform microstructure, resulting in variation in local microhardness [1, 58]. In order to establish an effective processing-microstructure-property relationship for the additively manufactured parts, it is vital to capture the microstructure evolution in response to the thermal history in AM processes.

1.2 Motivation

As microstructure study is vital in establishing the effective processing-microstructure-property relationship for a targeted material, a tremendous amount of experimental and simulation

research has been carried out to achieve this goal. Due to the intensive cost and time involved in experimental tests, numerical simulation has become a powerful tool in carrying out the microstructure prediction. In addition, numerical simulation can provide insights into experimental design and property control. Moreover, it also has the advantage of capturing in-process microstructure evolution in response to the transient thermal history, which is definitely beyond the capability of experimental study. Currently, the most popular simulation models that are widely adopted to predict the grain structure evolution are phase-field (PF) and cellular automata (CA) models, while the kinetic model is popular with the simulation of solid-state phase transformation.

To predict microstructure evolution in AM processes, the foremost important fact is that the microstructure prediction should be carried out in a 3D space since the AM processes are 3D such that the temperature field and solutal diffusion are also 3D. Although some 3D microstructure predictive models exist such as 3D CA and 3D PF, none of them can provide both high computation efficiency and physics-based fidelity at the same time. In addition, the spacial and temporal-dependent thermal history during AM processes must be extracted and incorporated into the microstructure predictive models since the as-built microstructure is determined by the thermal history in AM processes. Unfortunately, most microstructure prediction was conducted by assuming a constant temperature condition for simplicity, lacking practical usefulness due to the deviation from the real condition. Furthermore, in order to capture the microstructure evolution in AM processes, the simulation should be carried out at least in the smallest unit-single track of the AM processes. However, the single-track dimension of about 1 mm in width is still too large for PF modeling, which can only be executed on the micron-scale due to the high computational cost. Although the CA model can be applied to a large domain, CA models have the inherent limitation in revealing microstructure details and composition evolutions.

Applying the microstructure simulation models to a multi-component alloy system is another big challenge with regard to predicting the concentration evolution of each solute. Solute diffusion is one of the key factors dominating the microstructure evolution in both solidification and solid-state phase transformation. Currently, the only available predictive tool that can carry out the composition evolution is PF modeling. In order to accurately capture the composition evolution of each solute, the PF model must be coupled with the thermodynamic and diffusion mobility data of the alloy system. With the increase of component and phase numbers, the computational cost

increases exponentially. What's worse, for newly developed materials, e.g. HEA, the thermodynamic and diffusion mobility data that are used for PF modeling are both lacking.

Despite the abovementioned limitations, microstructure simulation of AM-built multi-component materials is necessary since high-performance multi-component materials are gaining increasing attention in both engineering and material communities due to their superior material properties. To catch up with the pace of the material community and to satisfy the requirements of industries, AM processes should be extended to more challenging material systems, e.g. HEA. Currently, most HEA alloys are fabricated by casting. A small number of HEA are produced by cold rolling and wrought. All these conventional manufacturing methods have shortcomings of high material waste, excessive manufacturing cost, long leading time, and limitation in geometry and dimension. Under such circumstances, AM processes provide a new window of opportunity for the fabrication of HEA with complex geometries. In addition, AM processes also have the advantage of in-situ synthesis of HEA with changeable compositions due to the flexibility in composition control. Furthermore, the rapid thermal cycle in AM processes is beneficial to stabilizing HEA's microstructure and improving HEA's properties due to the refined microstructure.

1.3 Literature Review

1.3.1 AM Fabrication of Ti-TiC and Microstructure Modeling

Titanium carbide (TiC) is a widely used reinforcement for Ti-based metal matrix composites due to its high hardness, good stability, respectable strength, and similar density to Ti [14, 59, 60]. The combination of these unique properties of TiC with the toughness and damage tolerance of the Ti matrix makes these composites attractive for usage as structural, wear and corrosion-resistant materials [61]. In the synthesis of composites, directed energy deposition (DED) has demonstrated a higher capability than traditional manufacturing techniques such as casting, forging and powder metallurgy. One dominant advantage of DED is its flexibility in both composition and geometry control as it can simultaneously feed reinforcement and matrix powders into the molten pool created via laser irradiation to provide requisite compositions and properties in addition to customized exterior shapes [12, 54].

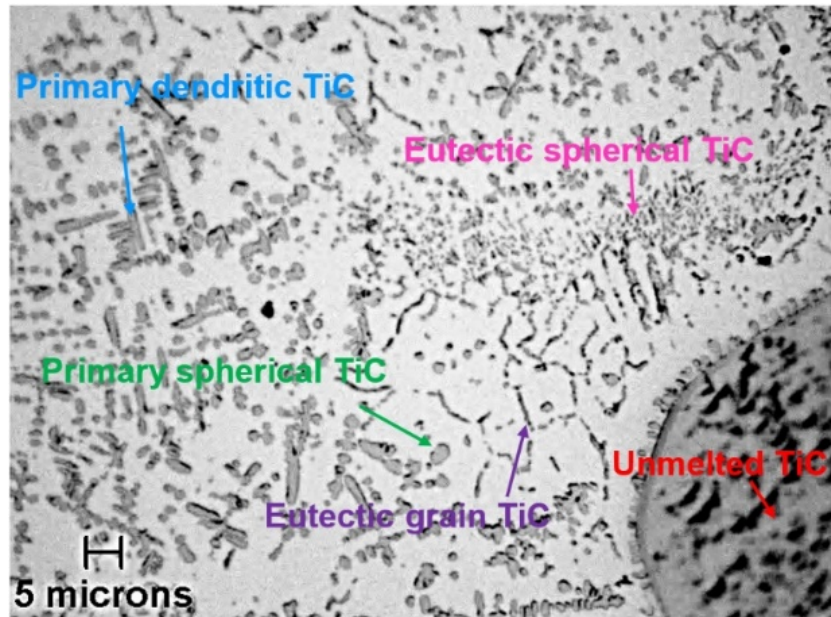


Figure 1.1. Morphologies of TiC in Ti6Al4V-15vol.%TiC composites deposited by the DED process with 250 W and 254 μm layer height.

Although TiC is thought to be thermodynamically stable in Ti and its alloys, partial melting and dissolution always occur to the premixed TiC particulates during the DED process [12, 14, 54]. As the temperature in the molten pool decreases, the dissolved C atoms will react with matrix Ti to form different morphologies of resolidified TiC_x precipitates from the Ti-C liquid [12, 54, 62]. Figure 1.1 shows five morphologies of TiC precipitates in a DED-built Ti6Al4V-TiC metal matrix composite. The big particle is unmelted TiC (UMC). The melting of the embedded TiC particles can be visually observed according to the boundary shape of the TiC particles. If the melting degree is high, many tiny columnar carbide grains attach to the UMC particles, and the boundary of the UMC particles displays a serrated shape as shown in Figure 1.1. The big spherical carbide particles, which are uniformly distributed in the microstructure, are the primary spherical TiC (PSC). According to the Ti-C binary phase diagram [63], the PSC resulting from the in-situ reaction of C and Ti first precipitates from the liquid at liquidus temperature. As the PSC stays in the liquid for a relatively long time, the particles grow large. If the melting degree of the embedded TiC particles is high, the primary dendritic TiC (PDC) will form. When the temperature decreases to the eutectic point, some eutectic TiC grains form. One is the eutectic grain TiC (EGC) that precipitates around the boundary of the prior β grains and exhibits a loop shape. Another is the eutectic spherical TiC (ESC), which displays a segregated small spherical morphology. In Ref.

[64], the ESC grains are found mainly gathering in the triple junction. The DED process will lead to a non-equilibrium solidification, where the liquidus and eutectic temperatures will be a little different from those in the equilibrium phase diagram.

The formation of PDC is harmful to the mechanical properties of Ti64-TiC MMCs since the dendritic grains will block the development of the strain, and it is easy for the dendrite tip to initiate cracks. Figure 1.2 shows the tensile test fracture morphology of Ti6Al4V-10vol.%TiC deposited with high energy input. Some bright dendritic TiC grains, indicated by the arrows, are clearly observed. These dendritic grains display a brittle cleavage fracture behavior and will change the fracture from ductile behavior to brittle behavior, rendering the composite loss of the ductility [65]. Dendritic growth depends on the thermal history of the DED process and the solute diffusion within the molten pool. The space-dependent temperature fields produced at different locations in the molten pool result in varied microstructures, which govern the mechanical properties of final products. For the optimization of material properties, a fundamental knowledge of the solidification process of resolidified TiC_x dendrites during the DED process is necessary. Due to the multi-physics and nonlinear nature of the DED process, numerical methods must be employed to study the thermal behavior. In the last two decades, a significant amount of research has been conducted to establish thermal modeling of the DED process [66-71]. However, all of these efforts dealt with pure metals and alloys rather than accounting for the reinforcements in composites.

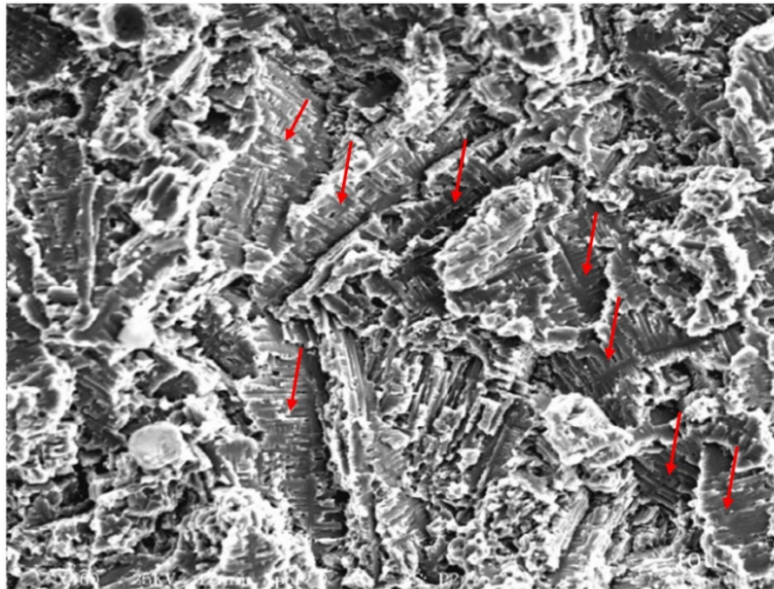


Figure 1.2. Tensile test fracture morphology of Ti6Al4V-10vol.%TiC built by the DED process with 350 W and 254 μm layer height reveals dendritic TiC grains indicated by arrows.

With regard to the simulation of dendritic grain structure, PF models have emerged as powerful tools for modeling microstructure evolution in various processes, such as rapid solidification [72], precipitate coarsening [73], microsegregation growth [74], sintering process [75], and dynamic loading [76]. In a PF model, states of a phase are defined by a phase variable, and the interface regions of two phases are described by the smoothly changing value of this phase variable. Microstructure evolves to minimize the total free energy of the system, which depends on both thermal and concentration fields. In order to gain insights into microstructure evolution in a realistic phase transformation process, PF models have been extended in combination with realistic thermodynamic and kinetic databases of materials [75, 77-79]. For disordered phases, the sub-regular solution (single-sublattice) models can be used to establish the thermodynamic database [78, 79], while multi-sublattice models must be adopted for ordered phases [75, 80, 81].

To capture a grain growth process that is close to the realistic situation, the polycrystalline growth of multiple grains should be carried out since most alloys have a polycrystalline structure. Currently, two methodologies are mainly adopted to simulate the polycrystalline growth. One method extends the number of phase variables to account for many grains of many different orientations (multi-phase PF model) [76], where each grain is assigned with a different phase field variable and a different crystallographic angle. Although the methodology is simple, this method involves considerable computation costs as it requires to solve a lot of phase-field variables that are equal to the grain numbers. As an alternative to using a large number of phase variables, orientation-field PF models were developed, which solve an extra time-dependent local crystallographic orientation equation [78, 79]. This method saves computational cost but the theory is a little more difficult to understand.

As for the solidification simulation of the dendritic of TiC_x , PF modeling should be coupled with the thermodynamic and diffusion mobility data of the Ti-C system in order to accurately predict the microstructure evolution and concentration evolution of TiC_x during the DED process. TiC_x has an ordered NaCl-type grain structure, where Ti atoms form a face-centered cubic (FCC) lattice with octahedral holes partially filled with C atoms, leaving some vacancies. Therefore, the molar fraction of C in TiC_x is 0.32 – 0.494 [80], and TiC_x can be treated as a solution phase and modeled with a two-sublattice model $(\text{Ti})_1(\text{C},\text{Va})_1$, where Ti atoms completely occupy one sublattice while C atoms and vacancies together occupy the other [80, 81]. To the author's best

knowledge, the dendritic growth of TiC_x has never been reported before, letting along the polycrystalline growth prediction of dendritic TiC_x .

1.3.2 AM Fabrication of Ti6Al4V and Microstructure Modeling

Ti6Al4V alloy, also known as TC4 or Ti64, is an $\alpha+\beta$ titanium alloy with high strength, low density, high fracture toughness, excellent corrosion resistance and superior biocompatibility [82, 83]. Recognized as the most popular titanium alloy, Ti6Al4V is enjoying almost half of the market share of titanium products used in the world today. Ti6Al4V alloy was originally developed for aircraft structural applications in the 1950s. This lightweight and yet strong alloy saves weight in highly loaded structures and is hence extremely suitable for jet-engine, gas turbines and many airframe components [84-87]. While the aerospace industry still dominates the Ti6Al4V demand [85-88], other application fields such as marine, automobile, energetic, chemical and biomedical industries have also found their wide acceptance during the last half-century. The low density, high strength, high corrosion resistance, and biocompatibility are attractive attributes of Ti6Al4V for use as bridges and implants [83, 89-93]. Its applications have also been extended to the marine and chemical industries due to its high corrosion resistance to most corrosive acids and alkalis [83, 94-96].

Despite the high demand, manufacture of Ti6Al4V products is always challenging due to its poor thermal conductivity [97], the propensity to strain hardening [98, 99] and active chemical reactivity to oxygen [100]. Conventional manufacture of Ti6Al4V products relies on forging, casting and rolling of bulk feedstock materials, followed by subsequent machining to final shapes and dimensions. These traditional manufacturing processes always inevitably result in high material waste, excessive manufacturing cost and long leading time [101, 102]. Under such circumstances, additive manufacturing (AM), advanced manufacturing technology of producing near-net shaping structures directly from CAD models by adding materials in a track-by-track and layer-by-layer fashion, offers its beneficial capability for fabrication of Ti6Al4V products with geometric complexities [87, 101].

In addition to the improved manufacturing flexibility, AM processes are also capable of refining microstructure and producing particular phases due to the multi-physics phenomena and thermal cycles since microstructure is highly dependent on thermochemical and thermomechanical

processing. In AM processes, Ti6Al4V will go through the $\alpha/\beta \rightarrow \beta \rightarrow \text{liquid} \rightarrow \beta \rightarrow \alpha/\alpha'$ phase transformation sequence in the fusion zone (FZ). Upon solidification of the molten pool, the strong epitaxial growth of β grains from the molten pool bottom will lead them into columnar shape with the long axis aligned with the maximum temperature gradient direction [24, 52-55]. The high aspect ratio of β grains is responsible for the notable anisotropy observed in tensile properties [4]. In the following solid-state $\beta \rightarrow \alpha/\alpha'$ transformation, laser-based AM processes such as directed energy deposition (DED) and selective laser melting (SLM) are reported to produce cooling rates higher than 10^4 K/s [22-24, 43], which lead to a complete α' phase in the FZ [41-43]. The fine α' martensite is beneficial to mechanical strength but degrades the ductility [4]. In addition, α' martensite is more corrosion resistant than α/β two-phase microstructure [103]. For the purpose of optimizing products' properties, modeling microstructural evolution in response to processing features and thermal histories has become a cost-effective method for process control and microstructure design.

Microstructure consists of grains and phases. The most popular predictive tools for simulating the as-solidified β -grain structure in AM-built titanium alloys are cellular automata (CA) and phase-field (PF) models. CA models simulate the grain growth via a cellular automata-algorithm and own intrinsic advantages in scalability and simplicity as well as a much lower calculation requirement. Dezfoli et al. [104] established an integrated model to combine a 3D finite element model with a CA model to study the β -grain solidification during laser melting of Ti6Al4V. The solidified grains exhibited a columnar shape with a tilt angle towards the laser movement direction. Shi et al. [55] also employed a 3D CA model to simulate the as-solidified grain structure and texture of β grains in the single-track Ti6Al4V built by selective laser melting (SLM). The increased scan speed was reported to lead the grains mainly normal to the scan direction. Yang et al. [105] used a 2D CA model to simulate solidification in SLM-built multi-layer Ti6Al4V depositions, and six evolution types of β grains were simulated; however, the simulation could not capture the 3D grain morphology due to the limitation of 2D models. Although all these publications predicted the competitive growth pattern of β grains successfully, they failed to reveal detailed dendritic grain structure due to the limitations of CA modeling. Additionally, CA models are also unable to predict composition diffusion during microstructure evolution.

PF modeling is known for its physics-based fidelity in uncovering grain structure details and composition evolution despite the high computational cost. Sahoo and Chou [106] used PF modeling to simulate Ti6Al4V solidification during an electron beam melting (EBM) process and studied the effect of temperature gradient and scan speed on the dendritic morphology change. Gong and Chou's work [107] further revealed the positive influence of undercooling on dendrite growth. Liu and Wang [108] incorporated the PF modeling with the thermal lattice Boltzmann method to simulate the β -grain solidification during the SLM process for Ti6Al4V. The latent heat turned out to have a large influence on the formation of secondary arms and must be considered to provide more realistic kinetics of dendrite growth. All these publications revealed local dendritic details for the as-solidified β grains, but the simulations were limited to only micro-scale or meso-scale due to the expensive computation cost of PF modeling. In addition, all these PF models assumed the ternary Ti6Al4V alloy as a pseudo-binary alloy by treating Al and V together as one solute. Since the solute distribution is the dominant factor for the dendrite growth, this simplification deviates from the real composition evolution.

As for the solid-state phase transformation during AM processes of Ti6Al4V, the FZ and heat-affected zone (HAZ) with regard to the heating and cooling cycles should be considered separately. Note that the isotherm of $T_{\beta\text{-trans}}$ (about 1269K) defines the HAZ boundary. In the heating cycle, the material in the FZ is subjected to melting while diffusion-controlled $\alpha \rightarrow \beta$ transformation takes place in the HAZ since the peak temperature is between $T_{\beta\text{-trans}}$ and the liquidus temperature (T_{liquidus}), but this transformation is highly incomplete due to the high heating rate [109, 110]. In the cooling cycle, the decomposition of β phase is governed by the temperature and cooling rate. A high cooling rate larger than 410 K/s passing the martensite start temperature (M_s , around 1053 K) results in a complete diffusionless $\beta \rightarrow \alpha'$ martensitic transformation. For the cooling rate in the range of 410 – 20 K/s, a mixture of diffusionless-transformed massive α and diffusion-controlled α phases is formed instead [111, 112]. The massive α was reported to have a similar formation mechanism, composition, and crystal structure to α' martensite such that it was always treated as the same phase as α' [111-113]. The primary formation mechanism of a diffusionless process is displacive [114], which is considered instantaneously [115]; however, the diffusion-controlled transformation follows a nucleation and growth mode. Ahmed and Rack [112]

reported two nucleation sites for the α phase during slow cooling from above $T_{\beta\text{-trans}}$: the thin layer of α grain boundary nucleates at the β -grain boundaries while α platelets nucleate within the β grains. The growth of α phase is mainly driven by the diffusion of vanadium and aluminum.

Compared with the grain size, phase has more dominant effects on property determination. To quantify the volume fractions of α and α' in the final microstructure, the JMAK model (Johnson–Mehl [116], Avrami [117] and Kolmogorov [118]) has been widely used to describe the diffusion-controlled $\alpha \rightarrow \beta$ and $\beta \rightarrow \alpha$ transformations in Ti6Al4V, while the Koistinen–Marburger law [119], an empirical principle depending on the undercooling, is popular with the diffusionless transformation of martensitic α' . JMAK equations are formulated based on the temperature-dependent parameters extracted from Temperature-Time-Transformation (TTT) curves, so the classic JMAK model is theoretically only applicable to isothermal processes [120]. To apply the JMAK model to cooling cycles [111, 121, 122], a fictive time concept is commonly introduced based on the additivity principle [123, 124]. Salsi et al. [113] have adopted the JMAK model with the additivity principle to simulate the $\beta \rightarrow \alpha$ transformation during AM processes. Instead of employing the fictive time, Kherrouba et al. [125] used linear regression to calculate the kinetic parameters from a single DSC curve; however, this improved approach was still an adaption of the JMAK model. The classic JMAK model is also limited to the complete transformation of a single phase. Murgau et al. [111] extended the JMAK model to account for the incomplete transformation of two α variants: grain boundary α and Widmanstätten α by handling them subsequently within every fictive time step. Considering the fast thermal cycles and inhomogeneous transformation in laser processes, Ashby and Easterling [114] proposed a simple 1D diffusive model for the incomplete diffusion-controlled transformation in the heating cycle during laser surface hardening of carbon steels; while in the cooling cycle for diffusionless transformation, the formed martensite content was approximated as a function of cooling rate. Hahn et al. [126] adapted this model for vanadium diffusion to study the microstructure and hardness development under the influence of laser surface hardening conditions for Ti6Al4V. A similar model was also used by Crespo and Vilar [127] to study the phase transformation kinetics in Ti6Al4V built by laser powder deposition. In this paper, the Ashby and Easterling's model is adopted to describe the solid-state phase transformation in DED-built Ti6Al4V.

1.3.3 Synthesis of Bulk Metallic Glasses by AM

The disordered long-range atomic arrangement and the absence of defects such as grain boundaries, dislocations and stacking faults endow the bulk metallic glasses (BMG) with exceptional strength, elastic limit, hardness, corrosion and wear resistance [128-133]. However, most BMG parts exhibit extreme macroscopic brittleness during room temperature deformation, which limits their structural applications [130]. The mechanisms behind the lack-of-plasticity result from work softening [134] and shear localization that lead to the formation and fast propagation of a dominant shear band throughout BMG components [135, 136]. One of the most practical ways to address this challenge is to embed secondary phases into the amorphous matrix such that the secondary phases promote multiple shear bands [137-139], and also act as obstacles retarding their propagation [140, 141]. The secondary phases are generally introduced through in-situ and ex-situ reactions, depending on whether the secondary phases are formed during solidification of the metallic melt or are externally added to the system [138].

In-situ synthesis of bulk metallic glass composites (BMGC) requires intermediate cooling rates to directly form micro/nanocrystals [140-142] or repeated heating that partially transforms the amorphous phase to crystalline phases [143]. The amorphous matrix generally contributes to the overall strength while the uniformly embedded crystals improve plasticity. For example, a $\text{Zr}_{65}\text{Cu}_{15}\text{Ni}_{10}\text{Al}_{10}$ BMGC exhibited a high ductility of about 25% due to nanocrystallization during the compression test [144]. An investigation on MgCuYZn BMGC (amorphous-46% crystalline) revealed an increased plastic strain of $\sim 18\%$ under compression loads compared to its monolithic glassy matrix [145]. The enhanced plasticity was attributed to the precipitation of Mg flakes as the leading phase. Sun et al. [137] obtained an impressive result in a recent study that they achieved an engineering tensile strain of $10.2 \pm 3.7\%$ and a fracture strength of 1450 ± 119 MPa in copper cast ZrCu-based BMGC reinforced with the in-situ formed metastable B2 phase. In addition to the large tensile ductility, this deformation-induced martensitic transformation of B2 also improved work-hardening significantly [134]. Actually, these metastable crystalline phases reinforced BMGC are known as shape memory BMGC [146-148].

Externally added secondary phases are alloy particles [148], metal powders [149, 150], ceramic particles [151] or polymer phases [152]. As long as the secondary phases are able to promote multiple shear bands, they are still beneficial to improving the ductility even if they lack

ductility. For example, Shanthi et al. [151] successfully synthesized $\text{My}_{67}\text{Zn}_{28}\text{Ca}_5$ BMGC reinforced with 0.66–1.5 vol% of nano-alumina particulates using the disintegrated melt deposition technique. The embedded alumina reinforcements were found to have no significant effect on the glass-forming ability of the amorphous matrix but they improved micro-hardness, fracture strength and failure strain of the monolithic BMG counterpart. Zhang et al. [149] added Ta powders to the $\text{Zr}_{48}\text{Cu}_{36}\text{Ag}_8\text{Al}_8$ alloy to form the Ta-reinforced BMGC. The homogeneously distributed 10 at.% Ta particles resulted in 31% plastic strain.

The most commonly used processing method for BMGC is casting with externally added particles, fibers and springs [153-157] or in-situ precipitated crystals [157-159]; however, casting has intrinsic limitations in dimension and intricacy. Even for the world's largest BMG alloy made from $\text{Pd}_{42.5}\text{Cu}_{30}\text{Ni}_{7.5}\text{P}_{20}$, the critical casting diameter was still limited to 80 mm due to requisite high cooling rates [160]. Therefore, layer-by-layer additive manufacturing (AM) processes, such as DED, apparently have significant advantages in the fabrication of large-scale and complex BMGC [132, 161, 162]. In addition to the ex-situ introducing of secondary phases to the precursor materials [163], the unique thermal behavior of DED also offers great potential for the in-situ fabrication of BMGC [132, 161, 162, 164, 165]. The high cooling rate ($10^3 - 10^6$ K/s) produced in FZ is sufficient for the formation of amorphous phase [4, 13, 132, 161, 166] while in-process “tempering” experienced in HAZ transforms the amorphous phase to crystals [132, 161, 167, 168]. Consequently, a crystal reinforced BMGC with an amorphous-crystalline periodic structure is naturally in-situ formed.

The commonly used raw materials for AM built BMGC are prealloyed amorphous powders [161, 169, 170], which lack the flexibility in composition adjustment. Gas atomization of pre-alloyed amorphous powders also increases cost and requires longer lead time. Moreover, additive manufacturing of these pre-alloyed amorphous powders will produce a complete amorphous phase in the FZ [169, 170], which is not desirable for plasticity improvement [169]. Recently, Ye and Shin [132] successfully used premixed pure metal powders in lieu of pre-alloyed amorphous powders to build BMGC via the DED process, paving a new cost-effective way for the manufacture of BMGC using AM processes.

1.3.4 Synthesis of High Entropy Alloys by AM

HEA are multi-component alloys that are composed of five or more principal elements with the concentration of each element being between 5 at.% and 35 at.% [171]. Some trace elements can also be added to HEA to enhance their properties [172]. Although HEA has been recognized only in the past 15 years, more than 37 elements have been used to prepare more than 400 HEA [36]. Unlike traditional Fe, Ti, Ni, or Al-based alloys that contain only one principal element, the multi-principal elements in HEA increase the mixing entropy and also offer a high potential for achieving versatile outstanding properties such as high strength and toughness, exceptional wear and corrosion resistance, excellent high-temperature resistance, and superior functional (magnetic, electrical, and thermal) properties [35, 36]. The high configurational entropy of HEA favors the formation of simple face-centered cubic (FCC), body-centered cubic (BCC), and hexagonal close-packed (HCP) solid solutions, followed by complex intermetallic phases like Sigma and Laves phases. Miracle and Senkov [36] made a summary of the phase types of the reported HEA and listed that the solid solution microstructures occupy 48% of the totally reported microstructures, the mixtures of solid solutions and intermetallic components are 42%, and the left 10% is pure intermetallic phases.

As phases and uniform microstructure play a dominant role in the HEA products' properties, manufacturing methods should be granted priority with regard to the microstructure optimization. Conventional fabrication of HEA mainly relies on casting; however, as-cast parts always suffer from segregation, decompositions/inhomogeneities, pores, and non-uniform microstructure [173-175]. To homogenize the microstructure and remove defects, post-processing such as cold rolling, forging, or annealing treatment must be carried out to tailor the properties [176]. Instead, AM processes are particularly advantageous in synthesizing HEA since the quenching effect resulting from the rapid thermal cycles (10^3 – 10^6 K/s cooling rate) is particularly advantageous for forming super-saturated solid solution phases and stabilizing HEA's phase structure [13, 21-24]. Besides, the high cooling rate also leads to a refined microstructure, which improves the microhardness and strength due to the mechanism of grain refinement strengthening [4, 39]. Moreover, AM processes, particularly the blown-powder AM techniques, have the advantage of direct in-situ synthesis of HEAs with changeable compositions due to the flexibility in composition control [12, 19, 177]. Due to the multi-component feature of HEA, powder-based feedstock materials are

popular for AM processing of HEAs. In general, the feedstock powders are classified into two categories: gas atomized prealloyed powders and premixed elemental powders.

The prealloyed powders are prone to producing a more uniform composition in the as-built state. For example, Brif et al. [32] used selective laser melting (SLM) to directly synthesize FeCoCrNi HEA from the prealloyed powders. X-ray diffraction (XRD) results showed a single BCC solid solution with a uniform chemical composition in the as-built parts, which exhibited comparable strength and ductility to stainless steels. Li et al. [33] also used SLM to fabricate the equiatomic prealloyed FeCoCrNiMn HEA with an emphasis on its non-equilibrium microstructure evolution and mechanical properties. The refined grain and the formed σ phase synergistically improved the mechanical properties as compared with conventionally solidified HEA. Kuncce et al. [39] used the Laser engineered net shaping (LENS), a DED process, to produce thin-walled samples of AlFeCoCrNi HEA from prealloyed powders. The as-built part exhibited an average microhardness of approximately 543 HV_{0.5}, which was approximately 13% higher than that of the as-cast counterpart. Shiratori et al. [178] also worked on AlFeCoCrNi HEA using the electron beam melting (EBM) technique via prealloy powders. In addition to the disordered body-centered cubic (BCC) and ordered B2 phases, an FCC phase was also observed at the grain boundaries of the B2/BCC mixture, which was attributed to the preheating effect of EBM. The as-built specimens exhibited much higher ductility than the cast specimen without a significant loss of strength.

Compared with prealloyed compositions, premixed elemental powders have higher flexibility over a large range of chemical compositions, cheaper, and also require much shorter lead time for preparation. Kuncce et al. [179] reported the studies on the structure and hydrogen storage properties of the ZrTiVCrFeNi HEA that was directly synthesized from premixed elemental powders via the LENS process. The as-built part processed a chemical composition close to the nominal composition, whose homogeneity was further improved after an annealing process. Haase et al. [180] used the laser metal deposition (LMD) process to synthesize CrMnFeCoNi HEA from elemental powders. A denser microstructure with less segregation was produced compared to the cast part. Chen et al. [181] premixed Al_xCoFeNiCu_{1-x} HEA elements with changeable x ratios ($x = 0.25, 0.5, 0.75$) and synthesized these HEA via the LMD process. The XRD and electron backscatter diffraction (EBSD) results revealed that with an increase in Al content and a decrease in Cu content, a change in crystal structure from a predominantly FCC to a combined FCC and BCC structure was formed, leading to an elevated hardness. The

abovementioned compositions are mostly composed of elements with lower melting points and the difference in melting points among all elements is small, which make the AM manufacturing process easier.

When coming to the refractory elements, direct synthesis of premixed elemental powders become more challenging because of the high melting temperatures of refractory elements and the large difference in melting points among them (e.g. Ti has a melting temperature of 1668 °C while Ta has a melting point of 3017 °C resulting in a large difference of 1350 °C) [182-185]. Therefore, some special strategies must be adopted to address the unmelting and potential inhomogeneity in composition with these refractory elements. Dobbels et al. [34] employed a two-step scanning strategy-low laser power deposition that yielded low evaporation of the powder stream and high power remelting that homogenized composition during the LMD synthesis of $\text{Ti}_{25}\text{Zr}_{50-x}\text{Nb}_{0-x}\text{Ta}_{25}$ HEA from elemental powders. Zhang et al. [186] deposited a TiZrNbMoW HEA coating from premixed elemental powders using plasma spraying followed by laser remelting such that the aforementioned issues with refractory elements were successfully avoided.

The literature review in this section clearly shows the capability of various AM processes in direct synthesis of HEA as coating and bulk parts. Both of the prealloyed and premixed feedstock compositions exhibit particular advantages to be used as precursor materials. The prealloyed powder is prone to producing a more uniform composition in the as-built state while the premixed method is beneficial to provide fast synthesis and flexibility over a large range of chemical compositions. With regard to the refractory elements with a high melting temperature, the premixing method may encounter difficulty in melting. However, the introduction of some particular strategies to AM processes can solve the issue.

1.3.5 Microstructure Prediction Modeling

Simulation study always has two targeted goals: accuracy and efficiency. As discussed in Section 1.3.1 and 1.3.2, the most powerful predictive tools for microstructure prediction is PF modeling and CA modeling. PF modeling has physics-based fidelity and is also able to predict dendritic details for the grain morphology and concentration evolution during various thermal processes despite the high computational cost. CA modeling has high computational efficiency but lacks physics-based fidelity. For modified CA models, they can also capture the dendritic

morphology in AM processes [187] and welding cases [188, 189]. In addition to PF and CA models, the Monte Carlo (MC) model has also been used to predict the grain size and distribution [190, 191]. However, the MC model does not allow for direct coupling of thermal and microstructure predictive models and also does not account for texture or anisotropy as well as lacks physics-based fidelity [191].

Microstructure evolution is governed by the temperature field and solute diffusion [192], and the solute diffusion rate is also temperature-dependent [193]; therefore, it is essential to couple the microstructure predictive tools with thermal models. Compared with the MC model, both the CA model and the PF model can incorporate the thermal models. However, the intensive computational cost of PF modeling limits its application only on the meso-scale and micron-scale. As for the AM processes, even though the smallest unit-the single track, has a dimension on the millimeter-scale, which is far beyond the computational capability of PF modeling. As a result, PF modeling can only provide “snapshot-like” local microstructure prediction in different zones in the molten pool [13], making it unable to capture the influence of the large temperature gradient within the entire molten pool on the microstructure evolution. The most dominant influence of large temperature gradient on the grain morphology is the unique texture resulting from the directional growth. For example, the as-solidified β grains in AM-built Ti6Al4V present an elongated morphology of columnar shape due to the alignment of the preferred growth direction with the maximum temperature gradient direction (Section 1.3.2). Similar directional growth is also prevalent in AM-built and welded various steel materials [194, 195].

Unlike the PF modeling, the CA models have an inherent advantage of capturing grain texture in response to the thermal history in a large domain. Rappaz and Gandin [196, 197] first coupled the CA model with the finite element (FE) model to obtain the thermal field and the grain structure of an Al-Si alloy. Pavlyk and Diltthey [198] developed an integrated 2D CA-FE scheme to simulate the dendrite growth in a laser welding pool, where the FE component was used to capture the macroscopic heat and fluid flow in the molten pool. The simulated dendrite arm spacing was much larger than the experimental observation. Yin and Felicelli [187] improved the 2D CA-FE model and used it to simulate the dendrite growth during the solidification of binary Fe-C alloy in the LENS process. Gandin et al. [199] further developed a 3D CA-FE model to predict the dendritic grain structure formed during solidification in binary alloys controlled by solute diffusion. Dezfoli et al. [104] also established an integrated 3D CA-FE model to study the β -grain

solidification during the laser melting of Ti6Al4V. It should be noted that the FE modeling involved in the abovementioned integrated CA-FE models do not capture the AM or welding processes accurately since almost all of them assumed a fixed heating source instead of a moving heating source. Shi et al. [55] simulated a moving heating source for the SLM process and solved the 3D temperature field in the molten pool using a hybrid finite element and finite volume formulation on an unstructured grid. Under such circumstances, Tan and Shin et al. [195] developed a more realistic multi-scale 3D integrated simulation framework to simulate the microstructure evolution in laser keyhole welding of AISI304 stainless steel. The fluid flow and heat transfer in the keyhole and the molten pool were solved using a macro-scale computational fluid dynamics model. Moreover, the calculated 3D temperature field was incorporated to predict the resultant 3D microstructure, which showed good agreement with experimental results.

Another shortcoming with the abovementioned integrated CA-FE modeling work is the lack of or inaccurate calculation of the concentration evolution. Although some publications considered the concentration evolution, it was calculated using numerical approximation instead of accurate calculation using PF models. To fill this gap, PF modeling must be involved and it should be coupled with the thermodynamic and diffusion mobility data of the studied alloy system. However, PF modeling cannot be applied to the entire molten pool due to the limitation in PF's high computational cost. To address this issue, Tan et al. [194, 200] proposed a new integrated CA-PF model, which takes the advantage of high computation efficiency of the CA model and physics-based fidelity of the PF model such that it effectively alleviates the shortcoming of both models. As a result, this CA-PF model successfully extended the simulation domain to the entire molten pool and was capable of producing a quantitative prediction of dendrite morphology with an affordable computational cost, and has been applied to predict the microstructure of multi-component alloys in the DED process and laser conduction welding processes [194, 200]. In this CA-PF model, the 1D PF component calculates the growth kinetics including the growth velocity and solute partition at the solid/liquid interface for the 2D CA component, and the CA component calculates the dendritic morphology variation and concentration redistribution in the solid and liquid as well as the solid/liquid interface. This CA-PF model successfully captures the sub-grain morphology on the meso-scale under the influence of the thermal history in the molten pool; however, the established CA-PF model is only a 2D model.

2D models obviously have limitations in carrying out the real microstructure evolution in a 3D process like AM processes, where both the temperature field and solute diffusion are 3D. In 2D PF modeling, diffusion is limited to one plane, i.e., solutes must diffuse directly away from the interface. Kundin et al. [201] recently presented 2D results of simulated secondary dendrite arm spacing during the SLM process as compared to the measured value in experimental observation. However, they stated that their results should be verified in 3D due to the “non-trivial” differences between 2D and 3D simulations. To address the shortcoming of 2D PF modeling, George and Warren [202] first developed the 3D PF model but applied it to simulate the isothermal dendrite growth in a binary alloy. Chen et al. also developed an adaptive mesh 3D PF model in simulating the equiaxed dendrite solidification [203] and cellular grain growth [204], but their simulations were also limited to isothermal or assumed temperature gradient fields. Bailey et al. [205] did a comparative assessment of microstructure predictions during laser welding of Al 6061 via 2D and 3D PF models in a recent publication. They confirmed the limitation of 2D modeling and reported that the 3D simulation is much more accurate than 2D simulation in predicting grain morphology, solutal concentration, and growth velocity since the temperature gradient and solute diffusion are 3D. The differences between 2D and 3D results are more significant if the extracted plane is away from the temperature gradient. In addition, the authors also combined the 3D PF model with a validated multi-physics laser welding model to predict the temperature field and dendrite growth during laser welding of Al 6061 alloy. Although the simulation was carried out only in a $20\text{ }\mu\text{m} \times 14\text{ }\mu\text{m} \times 8\text{ }\mu\text{m}$ region, it took 60 days of computation time on 20 2.6 GHz processors.

In order to carry out the realistic microstructure evolution in the entire molten pool of AM processes, a 3D model that can balance both accuracies in predicting grain structure morphology and concentration evolution, and efficiency in performing the simulation in a large domain at an affordable cost is the focus of the microstructure prediction for AM processes.

1.4 Research Objectives

1.4.1 In-situ Synthesis of Multi-component Metallic Materials by AM

To find out the method to synthesize ultimate five-component HEA by AM, the research was carried out progressively from two-component alloys to five-component HEA as:

- i. Two-component Ti-TiC composite
- ii. Three-component Ti6Al4V
- iii. In-situ synthesis of four-component BMG
- iv. In-situ synthesis of five-component HEA

Instead of using prealloyed compositions, the premixing of pure elemental metals was adopted to synthesize BMG and HEA, which has high flexibility in changing compositions. In order to solve the unmelting and inhomogeneous composition issues, some strategies were applied to the preparation of precursor materials. For example, high-energy ball milling was used to change the size and shape of elemental metal powders. A delicate composition control was also performed to produce the actual composition close to the target composition.

1.4.2 3D Microstructure Prediction by a Novel 3D CA-PF Model

While approaching the final goal of developing a novel 3D CA-PF model to predict 3D microstructure evolution during solidification of AM processes, the microstructure prediction was carried out from simple two-component alloys via 2D modeling first as follows:

- i. 2D PF modeling of binary alloy Ti-TiC and ternary alloy Ti6Al4V
- ii. 3D CA modeling of ternary alloy Ti6Al4V
- iii. 2D CA-PF modeling of ternary alloy Ti6Al4V
- iv. 3D CA-PF modeling of binary Al-Cu and ternary AlCuMG and AlSiMg alloys

To develop a computationally efficient and physics-accurate 3D CA-PF model, the CA component is a 3D model while the PF component is a 1D model that only calculates the local growth kinetics in the solidification front in a 3D space. In addition, the PF model is coupled with the thermodynamic and diffusion mobility data of the realistic alloy system to capture the concentration evolution of each solute accurately.

1.5 Dissertation Outline

To achieve the final goal of direct in-situ synthesis of five-component HEA alloys and modeling of the solidification and microstructure evolution during AM processes via a novel 3D CA-PF model, the proposed research has been carried out in progressive stages. Since HEA has five principal elements, the outline is arranged by increasing the component number of the studied materials at different stages. Each stage falls into one chapter. In total, the report consists of six chapters: 1. Introduction; 2. Directed Energy Deposition of Binary Ti-TiC Composites and Microstructure Modeling; 3. Directed Energy Deposition of Ternary Ti6Al4V and Microstructure Modeling; 4. Directed Energy Deposition of Quaternary ZrCuNiAl Bulk Metallic Glass Composites; 5. Directed Energy Deposition of Quinary CoCrFeNiTi High Entropy Alloys; 6. A Novel 3D CA-PF Modeling of Computationally Efficient Microstructure Prediction during Solidification in a Large Domain. The following is a brief explanation of the six chapters:

Chapter 1 Introduction:

This chapter provides an overall background, discusses the motivation with the synthesis of HEA with AM processes and limitations in the simulation of microstructure evolution, and explains the research objectives and novelty of this dissertation. In addition, a thorough literature review of AM fabrication of binary Ti-TiC and ternary Ti6Al4V, and AM synthesis of ZrCuNiAl bulk metallic glasses and novel CoCrFeNiTi high entropy alloys, as well as microstructure prediction modeling is given. In order to acquire the final goal, the staged research plan and progress are also introduced.

Chapter 2 Directed Energy Deposition of Binary Ti-TiC Composites and Microstructure Modeling:

In this chapter, a simple binary alloy system of Ti-TiC composite is first introduced. To improve the mechanical properties of this composite, the formation mechanism of detrimental resolidified dendritic TiC_x was studied via a thermodynamically-consistent binary PF model, which was coupled with the thermodynamic and diffusion mobility data of the Ti-C system. The growth pattern of resolidified dendritic TiC_x at different locations in the molten pool under the influences of temporal and spatial thermal history predicted by a validated DED model was

presented. The simulated results provided the solution of limiting the free carbon content in the melt to control the formation of detrimental TiC_x , according to which an experimental design was performed on Ti6Al4V-TiC composites to control the melting degree of premixed TiC particulates, which validated the simulation results as the formation of TiC_x dendrites was successfully avoided.

Chapter 3 Directed Energy Deposition of Ternary Ti6Al4V and Microstructure Modeling:

Chapter 3 provides a complete and systematic modeling study of the solidification, grain structure evolution, and phase transformation in the DED-built ternary Ti6Al4V alloy by combining the DED model, the 3D CA model, the 2D multi-phase and multi-component PF model, the integrated 2D CA-PF model, as well as a phase prediction model. The multi-track DED process and thermal history within the depositions were simulated by the DED model. With such thermal information, the 3D CA model simulated the grain structure evolution during the solidification of β grains in response to the movement of the laser beam on the macro-scale. The PF model incorporated the thermodynamic and cross diffusion mobility data of the Ti-Al-V system and predicted the local grain structure and concentration distributions of solutes Al and V during the competitive growth of β grains on the micro-scale. By coupling the growth kinetics produced by 1D PF modeling to the 2D CA model, the sub-grain microstructure evolution and concentration distributions of solutes were successfully predicted. When the temperature dropped below the β -transus temperature, the solid-state phase transformation of $\beta \rightarrow \alpha/\alpha'$ was studied by the phase prediction model based on the local heating/cooling rates predicted by the DED model. According to the predicted volume fractions of α' and α , the microhardness was successfully assessed for any given position in the deposition using rules of mixtures.

Chapter 4 Directed Energy Deposition of Quaternary ZrCuNiAl Bulk Metallic Glass Composites:

In this chapter, the material system is expanded to a four-component ZrAlNiCu bulk metallic glass composite, whose raw composition was prepared by pre-mixing the four pure metals. The DED model was also employed to obtain the temperature fields and heating/cooling rates in single-track ZrAlNiCu bulk metallic glass composite, which provided insights for microstructure evolution. By delicate control of the material composition and utilization of the thermal history of the DED process, an amorphous-crystalline periodic structure was produced with in-situ formed

crystalline particulates embedded in the amorphous matrix. This crack-free microstructure was successfully maintained within bulk parts, where a high fraction of the amorphous phase and crystalline phases were produced in the fusion zone and amorphous zone, respectively. The large volume percentage of the amorphous phase contributed to the hardness, strength, and elastic modulus of the composite while the various soft crystalline phases improve the ductility by more than three times compared to pure metallic glasses. Nanoindentation tests were also performed to study the deformation behavior on the micron/sub-micron length scale.

Chapter 5 Directed Energy Deposition of Quinary CoCrFeNiTi High Entropy Alloys:

Similar to the synthesis of ZrCuNiAl bulk metallic glass composites (Chapter 4), premixed elemental powders were also used to directly in-situ synthesize three CoCrFeNiTi HEA alloys with different atomic ratios using a single-step DED process. This composition was selected due to its superior anti-wear performance, excellent oxidation resistance, and great high-temperature stability [206]. By using the elemental powders and taking advantage of the high flexibility of AM in composition control, CoCrFeNiTi HEA alloys with varied atomic ratios can be directly in-situ synthesized into customized structures. To handle the potential incomplete melting issue in this synthesis process, flake-shaped powders with a small particle size were also adopted instead of the two-step approaches used by earlier researchers. Composition design, microstructure, hardness, and oxidation resistance were studied and discussed thoroughly.

Chapter 6 A Novel 3D CA-PF Modeling of Computationally Efficient Microstructure Prediction during Solidification in a Large Domain:

In this chapter, the 2D CA-PF model is further expanded to a novel 3D CA-PF model, which consists of a 3D CA component and a 1D PF component. The growth kinetics including the growth velocity and solute partition at the solid/liquid interface was calculated by the 1D PF component in a spherical coordinate, while the 3D CA component used the growth kinetics calculated by the PF model as inputs to calculate the dendritic morphology variation and concentration redistribution within the entire CA domain. To capture the dendritic morphology at the solid/liquid interface for a 3D grain, the 1D PF component was derived in a spherical coordinate. Coupling the PF component with the thermodynamic data and kinetic calculations of a material system, this 3D

CA-PF model can predict the dendrite growth of any complex multi-component alloys on a large-scale domain for various solidification processes. The model was first validated against the Lipton-Glicksman-Kurz (LGK) analytical model and a 3D PF model of Al-Cu binary alloys and then applied to large-scale solidification processes of directional solidification of Al-30wt.%Cu and laser welding of Al-Cu-Mg and Al-Si-Mg alloys. In addition to the drastic saving in computational cost over the PF modeling, quantitatively accurate results were also obtained compared to the experimental microstructure.

2. DIRECTED ENERGY DEPOSITION OF BINARY Ti-TiC COMPOSITES AND MICROSTRUCTURE MODELING

In this chapter, the formation mechanism of TiC_x is uncovered by developing an improved thermodynamically-consistent PF model. In this improved PF model, a grain index is introduced to track the crystallographic orientation of each grain to reflect the polycrystalline growth pattern of TiC_x dendrites. The thermodynamic database of ordered TiC_x is established using a two-sublattice model. Since the modification avoids the use of multiple phase-field variables, the calculation efficiency will be dramatically improved. Influences of temperature fields on the microstructure evolution of resolidified dendritic TiC_x in different zones in the molten pool are carried out with temporal and spatial temperature fields in the molten pool predicted by the validated DED model. The accuracy of the model is validated with a direct comparison to the experimental microstructure of TiC_x in DED synthesized Ti-40vol.%TiC composite and the phase diagram for composition. How to control the resolidified dendritic TiC_x is revealed based on the simulation results, according to which an experimental design is carried out using Ti6Al4V-TiC to control the formation of dendritic TiC_x with the intent to verify the simulation results.

2.1 Model Description

Modeling of the solidification process of resolidified TiC_x in DED manufactured Ti-TiC composite was carried out by combining a DED model and a PF model. The DED model simulates mass addition, laser-powder interaction, heat transfer, and molten pool dynamics throughout the deposition process. Temperature-dependent material properties were considered in the DED model to predict deposition geometry and thermal behavior. Temperature histories within the molten pool were extracted as inputs for equilibrium thermodynamic calculations using the TiC_x thermodynamic database, which was established using a two-sublattice model. This database was then incorporated into the PF model, which was developed to capture the solidification process of resolidified TiC_x . A grain index was introduced to the PF model to track the growth of each grain. The flow chart of computational models was illustrated in Figure 2.1.

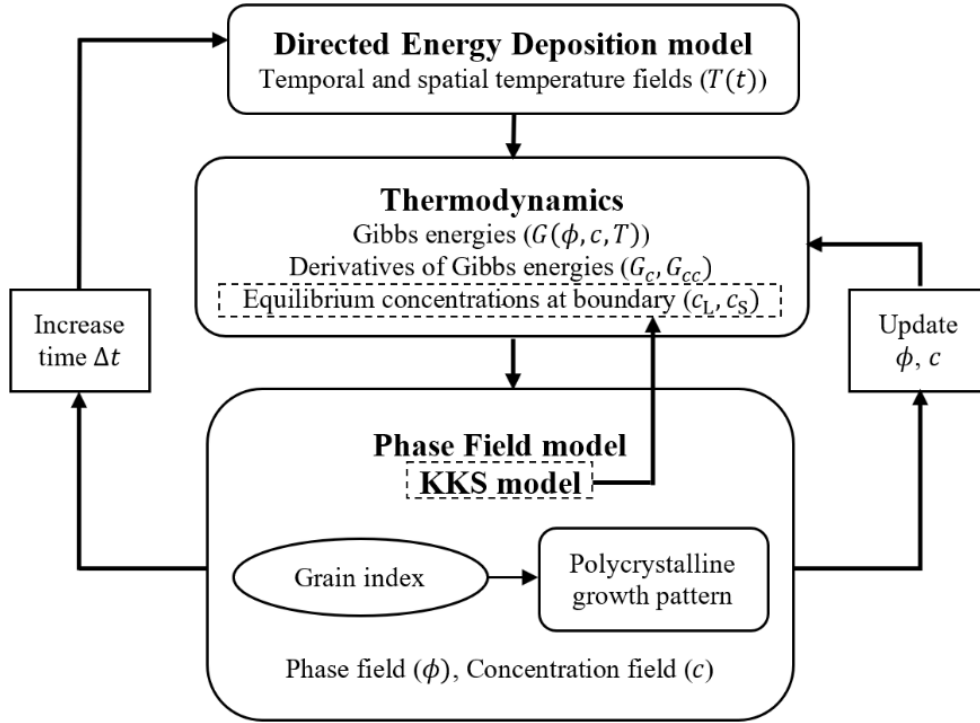


Figure 2.1. Flow chart of computational models.

2.1.1 3D DED Model for Thermal History in DED-built Ti-TiC

The DED model was developed by the authors' group [67, 68], and has been validated by various materials. In this chapter, the DED model was applied to the DED process of Ti-TiC. The physical phenomena associated with the DED process such as mass addition, laser-particle interaction, powder capture efficiency as well as thermal and fluid dynamics in the molten pool are captured by the governing equations for continuity, momentum, energy, and levelset, as shown in Eq. (2.1) – Eq. (2.8). The levelset equation is utilized to track the distance from the free surface due to mass addition, and the free surface is denoted by $\phi = 0$. More details for these equations can be found in Refs. [67, 68, 207].

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \vec{V}) = \dot{S}_{\text{mass}} \quad (2.1)$$

$$\frac{\partial (\rho \vec{V})}{\partial t} + \nabla \cdot (\rho \vec{V} \vec{V}) = -\nabla \bar{P} + \nabla \cdot \left(\bar{\tau} \right) + \vec{S}_{\text{mom}} \quad (2.2)$$

$$\frac{\partial (\rho h)}{\partial t} + \nabla \cdot (\rho \vec{V} h) = \nabla \cdot (k \nabla T) + \dot{S}_{\text{energy}} \quad (2.3)$$

$$\frac{\partial(\rho\varphi)}{\partial t} + \nabla \cdot (\rho \vec{V} \varphi) = \dot{S}_{\text{levelset}} \quad (2.4)$$

Together with:

$$\dot{S}_{\text{mass}} = (\rho_g - \rho_m) \delta(\varphi) \frac{\partial \varphi}{\partial t} \quad (2.5)$$

$$\vec{\dot{S}}_{\text{mom}} = -\frac{\mu_m}{K} \vec{V} - \vec{e} \cdot (\gamma \vec{n} \kappa - \nabla_s \gamma) \delta(\varphi) + \rho \vec{g} \beta (T - T_r) + \vec{V} (\rho_g - \rho_m) \delta(\varphi) \frac{\partial \varphi}{\partial t} \quad (2.6)$$

$$\dot{S}_{\text{energy}} = \left[\alpha q_{\text{laser}}'' + q_{\text{powder}}'' + h_c (T - T_0) - \sigma \varepsilon (T^4 - T_0^4) \right] \delta(\varphi) + \left[\rho (h_g - h_m) + h (\rho_g - \rho_m) \right] \delta(\varphi) \frac{\partial \varphi}{\partial t} \quad (2.7)$$

$$\dot{S}_{\text{levelset}} = -\rho F_p |\nabla \varphi| + \dot{S}_{\text{mass}} \varphi \quad (2.8)$$

where $\dot{S}_{\text{mass}}$, $\vec{\dot{S}}_{\text{mom}}$, $\dot{S}_{\text{energy}}$, and $\dot{S}_{\text{levelset}}$ are source terms of mass, momentum, energy and levelset governing equations. $\delta(\varphi)$ in Eq. (2.5) – Eq. (2.7) is the derivative of the Heaviside function, which allows the source terms to be distributed across the interface; therefore, the last terms in Eq. (2.5) – Eq. (2.7) represent the physical processes associated with material deposition along with the moving interface. In Eq. (2.6), the first term donates the damping force when fluid passes through a mushy zone. The second term describes the free surface forces including the capillary and Marangoni forces. The third term is buoyancy force. In Eq. (2.7), the first term is heat flux at the interface resulting from laser energy addition, powder addition, convection, and radiation while the second term is the energy change resulting from the phase change associated with mass and enthalpy change during the moving of interface. The nomenclature for all the variables in Eq. (2.1) – Eq. (2.8) is summarized in Table 2.1.

For this study, the DED model was utilized to simulate the DED process of Ti-40vol.%TiC composite. Since the thermal and physical properties of this composite were unknown, rules of mixtures were adopted to obtain the material properties. Table 2.2 and Table 2.3 present the material properties of pure Ti, TiC, C and, the calculated properties of Ti-40vol.%TiC, respectively. The solid specific heat and thermal conductivity for TiC were obtained via a linear curve fit of the property data from [208]. A similar calculation was also applied to obtain the expressions of these two properties for Ti-40vol.%TiC.

Table 2.1. Nomenclature for the variables in the DED model.

Symbol	Variable	Symbol	Variable
t	Time	κ	Surface curvature
ρ	Density	β	Thermal expansion coefficient
ρ_g	Gas density	T_r	Reference temperature
ρ_m	Metal density	T_0	Ambient temperature
h	Enthalpy	α	Absorptivity
h_g	Gas enthalpy	ε	Emissivity
h_m	Metal enthalpy	σ	Stephen-Boltzmann constant
$\vec{V}$	Velocity	h_c	Convective heat transfer coefficient
$\vec{P}$	Pressure	$\vec{e}$	Unit vector
T	Temperature	$\vec{n}$	Normal vector
$\vec{\tau}$	Stress tensor	$\vec{g}$	Gravitational vector
k	Thermal conductivity	γ	Surface tension
ϕ	Levelset variable	q''_{laser}	Laser intensity
μ_m	Liquid viscosity	q''_{powder}	Energy flux due to powder addition
K	Liquid isotropic permeability	F_p	Free surface velocity due to mass addition

Table 2.2. Material properties of pure Ti, TiC and C for the DED model.

Property	Units	Ti		TiC	C
		Solid phase	Liquid phase	Solid phase	Liquid phase
Density	kg/m ³	4520 [209]	4520 [209]	4910 [208]	1600 [210]
Specific heat	J/(kg·K)	453.34+0.15T [211]	702.78 [211]	-10 ⁻⁴ T ² +0.5373T -442.32 [208]	2164.74 [210]
Thermal conductivity	W/(m·K)	14.99 + 34.65 exp (-6.57×10 ⁻³ T) [211]	1.40×10 ⁻² T [211]	-3×10 ⁻⁶ T ² +0.0199T+17.044 [208]	290 [210]
Liquid viscosity	kg/(m·s)	-	0.003 [211]	-	-
Thermal expansion coefficient	1/K	8.75×10 ⁻⁶ [212]	-	5.9×10 ⁻⁶ [213]	-
Absorptivity	-	0.45 [214]	-	0.69 [215]	-
Emissivity	-	0.555 [216]	-	0.79 [217]	-
Latent heat of fusion	J/kg	4.19×10 ⁵ [218]	-	10 ⁶ [208]	-
Melting temperature	K	1943 [211, 219]	-	3340 [208]	-
Surface tension	N/m	-	1.64 [211]	-	-
Surface tension temperature coefficient	N/(m·K)	-	-2.38×10 ⁻⁴ [211]	-	-

Table 2.3. Calculated material properties of Ti-40vol.% based on rules of mixtures for the DED model.

Property	Units	Solid phase	Liquid phase	Rules of mixtures
Density	kg/m ³	4676	4676	$\rho_{\text{mix}} = \rho_{\text{Ti}} \cdot V_{\text{Ti}} + \rho_{\text{TiC}} \cdot V_{\text{TiC}}$ [220] $\rho_{\text{mix}} = \rho_{\text{Ti}} \cdot V_{\text{Ti}} + \rho_{\text{C}} \cdot V_{\text{C}} + \rho_{\text{TiC}} \cdot V_{\text{TiC}}$
Specific heat	J/(kg·K)	$-6 \times 10^{-5} T^2 +$ $0.3127T + 448.7$ 1	$-9.618 \times 10^{-6} T^2$ $+0.0517T + 684.$ 285	$C_{\text{S mix}} = \frac{c_{\text{STi}} \cdot \rho_{\text{STi}} \cdot V_{\text{STi}} + c_{\text{STiC}} \cdot \rho_{\text{STiC}} \cdot V_{\text{STiC}}}{\rho_{\text{STi}} \cdot V_{\text{STi}} + \rho_{\text{STiC}} \cdot V_{\text{STiC}}}$ $C_{\text{L mix}} = \frac{c_{\text{LTi}} \cdot \rho_{\text{LTi}} \cdot V_{\text{LTi}} + c_{\text{LC}} \cdot \rho_{\text{LC}} \cdot V_{\text{LC}} + c_{\text{STiC}} \cdot \rho_{\text{STiC}} \cdot V_{\text{STiC}}}{\rho_{\text{LTi}} \cdot V_{\text{LTi}} + \rho_{\text{LC}} \cdot V_{\text{LC}} + \rho_{\text{STiC}} \cdot V_{\text{STiC}}}$
Thermal conductivity	W/(m·K)	$0.0016T + 19.71$ 8	$0.0195T -$ 2.6924	$K_{\text{S mix}} = K_{\text{STi}} \cdot \frac{2K_{\text{STi}} + K_{\text{STiC}} - 2V_{\text{STiC}} \cdot (K_{\text{STi}} - K_{\text{STiC}})}{2K_{\text{STi}} + K_{\text{STiC}} + V_{\text{STiC}} \cdot (K_{\text{STi}} - K_{\text{STiC}})}$ [220] $K_{\text{L mix}} = K_{\text{LTi-TiC}} \cdot \frac{2K_{\text{LTi-TiC}} + K_{\text{STiC}} - 2V_{\text{STiC}} \cdot (K_{\text{LTi-TiC}} - K_{\text{STiC}})}{2K_{\text{LTi-TiC}} + K_{\text{STiC}} + V_{\text{STiC}} \cdot (K_{\text{LTi-TiC}} - K_{\text{STiC}})}$ where $K_{\text{LTi-TiC}} = K_{\text{LTi}} \cdot \frac{2K_{\text{LTi}} + K_{\text{LC}} - 2V_{\text{LC}} \cdot (K_{\text{LTi}} - K_{\text{LC}})}{2K_{\text{LTi}} + K_{\text{LC}} + V_{\text{LC}} \cdot (K_{\text{LTi}} - K_{\text{LC}})}$
Liquid viscosity	kg/(m·s)	-	0.003	
Thermal expansion coefficient	1/K	7.61×10^{-6}	-	$\alpha_{\text{mix}} = \alpha_{\text{Ti}} \cdot V_{\text{Ti}} + \alpha_{\text{TiC}} \cdot V_{\text{TiC}}$ [221]
Absorptivity	-	0.546	-	$A_{\text{mix}} = A_{\text{Ti}} \cdot V_{\text{Ti}} + A_{\text{TiC}} \cdot V_{\text{TiC}}$
Emissivity	-	0.649	-	$\varepsilon_{\text{mix}} = \varepsilon_{\text{Ti}} \cdot V_{\text{Ti}} + \varepsilon_{\text{TiC}} \cdot V_{\text{TiC}}$
Latent heat of fusion	J/kg	6.63×10^5	-	$L_{\text{mix}} = \frac{L_{\text{Ti}} \cdot \rho_{\text{Ti}} \cdot V_{\text{Ti}} + L_{\text{TiC}} \cdot \rho_{\text{TiC}} \cdot V_{\text{TiC}}}{\rho_{\text{Ti}} \cdot V_{\text{Ti}} + \rho_{\text{TiC}} \cdot V_{\text{TiC}}}$
Liquidus temperature	K	1943	-	
Solidus temperature	K	1933		
Surface tension	N/m	-	1.64	
Surface tension temperature coefficient	N/(m·K)	-	-2.38×10^{-4}	

Note: The solid phase consists of 60 vol.% solid Ti and 40 vol.% solid TiC. When TiC melts, the Ti-C chemical bond breaks, and becomes free Ti and C. As approximately 32 vol.% TiC is dissolved, the molten pool consists of 16 vol.% liquid C, 76 vol.% liquid Ti and 8 vol.% unmelted solid TiC

Since the embedded TiC particulates were not dissolved completely (Figure 2.2), the molten pool consists of Ti-C liquid and suspended unmelted TiC (UMC) particles. Therefore, liquid properties of Ti-40vol.%TiC should consider UMC particles. Figure 2.2(a) reveals that the size of UMC particles is approximately in the range of 0.5–100 μm , and UMC occupies only about 8.1 vol.%. In various sources of literature [220, 222, 223], reinforcements in such a low volume fraction are isolated from each other, and hence the resultant composites will exhibit a low amount of physical property change by modeling via rules of mixtures approximation, independent of the actual configuration of the composite. Additionally, the liquid viscosity, surface tension and its temperature coefficient were assumed to be equal to those of liquid Ti because UMC has a much less influence on these properties than liquid Ti. Similarly, the effect of UMC on the liquidus temperature of the composite was ignored, which was assumed to be equal to the melting temperature of Ti while the solidus temperature of the composite was assumed 10 K lower since the realistic value is unknown. Additionally, the liquid phase was assumed to have a same density as the solid phase to maintain the numerical stability.

To perform the simulation, a 3D computational domain was created to include a bottom domain of Ti6Al4V substrate ($12 \times 5 \times 12 \text{ mm}^3$) and a top domain of gas ($12 \times 3 \times 12 \text{ mm}^3$) where the Ti-40vol.%TiC powder precursor was fed through. The whole domain was discretized by a uniform mesh ($50 \times 33 \times 50 \mu\text{m}^3$) in the deposition region ($6 \times 1 \times 2.5 \text{ mm}^3$) and a non-uniform mesh elsewhere. The initial temperature of the substrate was set at 300 K, which was quite close to the actual ambient temperature in the solver that uses a dual-time stepping method [224]. A time step of 10^{-5} s was used for time advancement with 25 pseudo time steps per physical time step to obtain a converged solution. The simulation lasted 0.16 s to ensure pseudo-steady-state was reached before stopping the simulation.

2.1.2 2D Binary Phase-field Model for Polycrystalline Solidification of TiC_x

For solidification of TiC_x , the system can be treated as a binary system where C is the solute and Ti is the solvent. Although a binary PF model is described in the current work, it can be extended to multi-phase and multi-component studies [75, 78, 79].

The molar Gibbs energy for a binary alloy system can be simplified as:

$$G(\phi, C, T) = \int_V \left[\frac{G_m(\phi, C, T)}{V_m} + \frac{\varepsilon^2}{2} |\nabla \phi|^2 \right] dV \quad (2.9)$$

where G is the total Gibbs free energy of the system, G_m is the molar free energy density, T is the temperature in the molten pool of Ti-40vol.% TiC deposition predicted by the DED model, ε is the gradient energy coefficient and V_m is the molar volume which is assumed to be constant. ϕ is the phase variable, ranging smoothly from 0 in the liquid to 1 in the solid over the liquid/solid interface. C is the concentration of carbon, and therefore $1 - C$ is the concentration of Ti.

The molar free energy density $G_m(\phi, C, T)$ is defined as:

$$G_m(\phi, C, T) = \frac{1}{V_m} \left\{ h(\phi) G_m^S(\phi, C_S, T) + [1 - h(\phi)] G_m^L(\phi, C_L, T) \right\} + \omega g(\phi) \quad (2.10)$$

together with:

$$h(\phi) = \phi^3 (6\phi^2 - 15\phi + 10) \quad (2.11)$$

$$g(\phi) = \phi^2 (1 - \phi)^2 \quad (2.12)$$

where G_m^S and G_m^L are the molar free energy density of the solid and liquid phase, respectively. C_S and C_L are the local equilibrium compositions on the solid and liquid sides at the liquid/solid interface. ω is the height of the double-well potential $g(\phi)$. $h(\phi)$ is a monotonous polynomial. To calculate C_S and C_L , the KKS model is adopted, which defines the liquid/solid interface as a mixture of two phases with the same chemical potential μ , but different compositions as [225]:

$$C = h(\phi) C_S + [1 - h(\phi)] C_L \quad (2.13)$$

$$\mu = \frac{\partial G_m^S(C_S)}{\partial C_S} = \frac{\partial G_m^L(C_L)}{\partial C_L} \quad (2.14)$$

It should be noted that the current PF model utilizes the standard diffuse interface instead of the “thin-interface” where an anti-trapping current term is introduced in order to eliminate the solute trapping effect [226-228]. Solute trapping is a phenomenon that solute atoms have the driving force but do not have the time to diffuse back to liquid, thus being trapped in solid. However, the solid TiC_x has a higher C concentration than liquid such that the carbon in TiC_x does

not “need” to diffuse back to liquid, thus resulting in little solute trapping. Secondly, thin-interface models work under the assumption of negligible solute diffusivity in the solid phase (D_s) as compared to D_L in liquid phase. On the contrary, D_s of carbon in TiC_x is a function of temperature [229] and is only about one order smaller than D_L at high temperatures, and thus cannot be ignored. The high D_s will further reduce the solute trapping effect at the interface, although solute trapping actually exists in rapid solidification processes such as laser processing [230, 231].

Governing equations for PF and concentration variables with diffuse interface can be derived as:

$$\begin{aligned} \frac{\partial \phi}{\partial t} &= -L_\phi \frac{\delta G}{\delta \phi} \\ &= L_\phi \left\{ \nabla \cdot \varepsilon^2 \nabla \phi + \frac{1}{V_m} h'(\phi) \left[G_m^L(C_L) - G_m^S(C_S) - (C_L - C_S) G_{mC_L}^L(C_L) \right] - \omega g'(\phi) \right\} \end{aligned} \quad (2.15)$$

$$\frac{\partial C}{\partial t} = \nabla \cdot \frac{D(\phi)}{G_{mCC}} \nabla G_{mC_L}^L(C_L) = \nabla \cdot [D(\phi) \nabla C] + \nabla \cdot [D(\phi) h'(\phi) (C_L - C_S) \nabla \phi] \quad (2.16)$$

where L_ϕ is the interface mobility. The notations $G_{mC_L}^L$, G_{mC} and G_{mCC} mean the first and second derivatives, namely $G_{mC_L}^L = \partial G_m^L / \partial C_L$, $G_{mC} = \partial G_m / \partial C$, and $G_{mCC} = \partial^2 G_m / \partial C^2$. To simulate the growth of an asymmetrical dendrite, a noise term $n = 0.4rg(\phi)$ is added to the liquid/solid interface. r is a random number between -1 and +1 [232]. D is the diffusivity and is determined to be the fraction-weighted average of D_s and D_L as:

$$D(\phi) = h(\phi) D_s + [1 - h(\phi)] D_L \quad (2.17)$$

When the interfacial free energy anisotropy is considered, ε becomes [74]:

$$\varepsilon(\theta) = \varepsilon_0 \left\{ 1 + \delta \cos[k(\theta - \theta_0)] \right\} \quad (2.18)$$

where ε_0 is the average value of ε , δ is the anisotropy strength and k is the symmetric mode number. ε_0 and ω are parameters associated with the interface energy σ and interface width 2λ as $\varepsilon_0 = \sqrt{3\sigma \cdot 2\lambda / \alpha}$ and $\omega = 6\sigma\alpha / 2\lambda$ [74], where α is a constant related to the interface thickness. θ is the angle between the orientation of a vector perpendicular to the liquid/solid interface and

the X axis, and $\theta = \arctan\left(\frac{-\partial\phi_p/\partial y}{-\partial\phi_p/\partial x}\right)$. θ_0 is the preferential crystallographic orientation angle relative to X axis.

Simulation of grain growth relies on θ_0 to produce the crystallographic orientation. For polycrystals with different preferential orientations, each grain has different θ_0 . The traditional method extends the number of phase variables to account for many grains of many different orientations (multi-phase PF model) [76, 233], that is, to create an independent phase field equation and assign θ_0 for each grain, which involves considerable computation costs. As an alternative to using a large number of phase variables, orientation-field PF models were developed, which solve an extra time-dependent local crystallographic orientation equation [78, 79].

The current PF model adopts the idea of the multi-phase PF model, but makes some modifications to reduce the calculation cost from the numerical aspect. Instead of using multiple phase variables, the core idea of this improved model is to use only one phase variable ϕ , and solve only one phase-field equation (Eq. (7)) but assigns different θ_0 values for different grains. A grain index is hence introduced to distinguish grains and θ_0 becomes a series of randomly or deliberately selected numbers that are linked to the grain index as:

$$\{\theta_0\} = \{\theta_{0_1}, \theta_{0_2}, \dots, \theta_{0_l}, \dots, \theta_{0_N}\} \quad (2.19)$$

where N is the total number of grains and l is the grain index that has the number from 1 to N. θ_{0_l} is the crystallographic orientation of the l th grain. As a grain grows, the index number of the first neighbor grids in the liquid ahead of the grain interface is updated for each time step to maintain its growth orientation. However, due to the truncation error and floating precision in the numerical calculation, the index will overgrow the grain. Therefore, the index must be restricted to grow with the phase variable. After preliminary tests, $\phi = 0.2$ proves to be a suitable threshold for updating the index number.

$$l_{i,j} = \begin{cases} \max\{l_{i+1,j}, l_{i-1,j}, l_{i,j+1}, l_{i,j-1}\}, & \phi > 0.2 \\ 0, & \phi \leq 0.2 \end{cases} \quad (2.20)$$

Eq. (2.20) describes the algorithm to update the index number at each grid in the domain, where i and j are the grid index in the X and Y direction in a 2D domain, respectively.

Before coupling the temperature field from the DED model, a presumed isothermal solidification of TiC_x at 2800 K was first simulated to test the accuracy of the PF model. After incorporating the temperature field, a constant temperature was assumed for the whole PF domain at each time step because the PF domain is much smaller than the grid size of the DED model. To perform the PF simulation, the governing equations were discretized on uniform grids using an explicit finite difference method. Zero flux boundary conditions were applied. The nucleation process was not considered in the current work, but modeling of nucleation can be found in Ref. [234]. Instead, rhombic seeds of 8×8 grids with the calculated initial carbon concentration of 24 mol.% (Figure 2.4) were randomly inserted in the domain. In order to simulate ensembles of multiple grains on a larger domain at an acceptable cost, a high-performance parallel computing MPI algorithm was developed to process the phase-field code. Additionally, larger grid spacing (3.0×10^{-8} m) and time step (1.5×10^{-8} s) were utilized for the isothermal solidification while smaller grid spacing (1.0×10^{-8} m) and time step (0.5×10^{-8} s) were set for the non-isothermal cases to stabilize the calculation. The physical properties of the Ti-C system and computational parameters for the PF model are summarized in Table 2.4.

Table 2.4. Physical properties of the Ti-C system and computational parameters for the phase-field model.

Parameters	Symbol	Value	Unit
Grid spacing	$\Delta x, \Delta y$	1.5×10^{-8} or 3×10^{-8}	m
Time step	Δt	0.5×10^{-8} or 1.5×10^{-8}	s
Interface width	2λ	$2\Delta x$	m
Anisotropy strength	δ	0.13	-
Symmetric mode number	k	4	
Phase field mobility	L_ϕ	8×10^{-5}	$\text{m}^4/\text{s} \cdot \text{J}$
Height of the double-well potential	ω	1.32×10^8	J/m^3
Average gradient energy coefficient	ε	2.216×10^{-4}	$(\text{J}/\text{m})^{1/2}$
Initial concentration	C_0	24	mol. %
Diffusivity in liquid phase	D_L	1.4×10^{-10}	m^2/s
Diffusivity in solid phase	D_S	*	m^2/s
Interface energy	σ	0.6	J/m^2
Molar volume	V_m	1.22×10^{-5}	m^3/mol

Note*: $D_S = \exp(26.3 - 148.5C_S + 150.3C_S^2 - 310000/RT)$ when the temperature (T) is above 1468 K while $D_S = \exp(-21.2 - 174000/RT)$ when T is below 1468 K [229], where R is gas constant.

To calculate the initial concentration of C in the Ti-C liquid (C_0 in Table 2.4), an image processing procedure was performed. At first, the optical micrograph was transformed into a black and white binary image to make the UMC particles more defined via Photoshop software. Matlab codes were then developed to calculate the 2D area fraction and the size distribution of UMCs based on the binary image. The Dream 3D software was finally employed to create a 3D view of the Ti-TiC composite and to calculate the volume fraction of UMCs using the 2D information. In this process, the UMC particle was assumed elliptical to simplify the calculation. Figure 2.2 illustrates the image processing procedure, and five images were processed to obtain an average volume fraction of UMC particles. The calculation result reveals that approximately 32 vol.% premixed TiC was dissolved under the current DED condition. The dissolved TiC became free Ti and C. Since the premixed 60 vol.% Ti was completely melted, the calculated mole ratio of carbon in the Ti-C liquid is about 0.24.

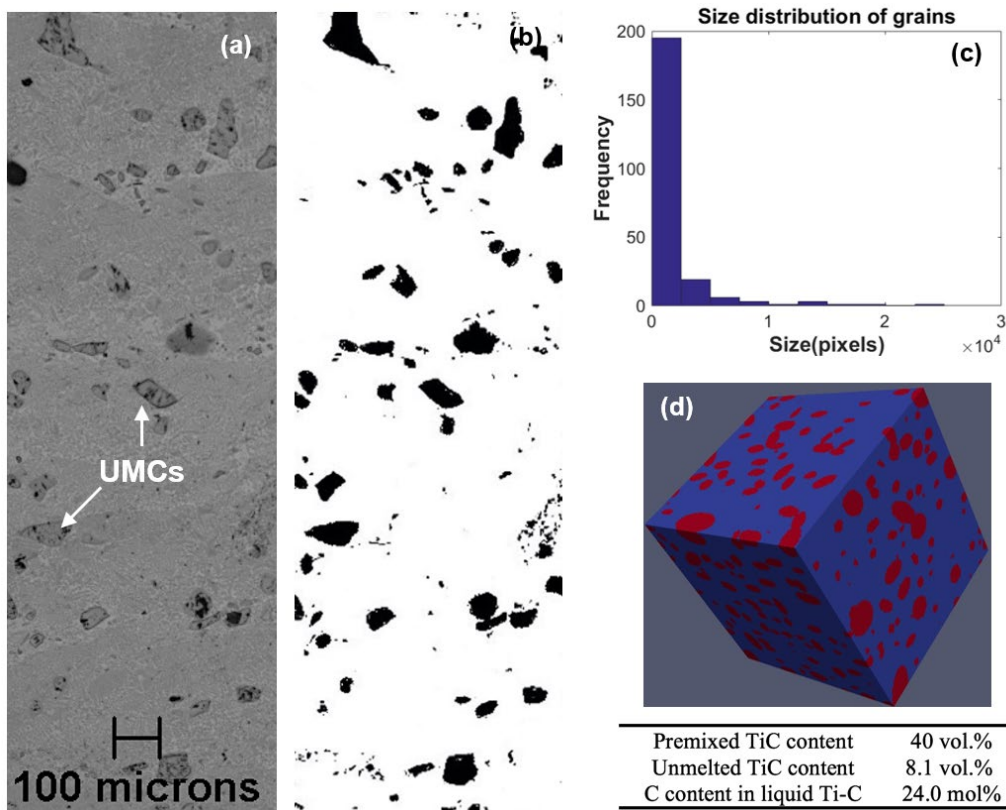


Figure 2.2. The image processing procedure to calculate the molar fraction of C in Ti-C liquid: (a) optical micrograph, (b) white and black binary image with unmelted TiC particles highlighted, (c) size distribution of unmelted TiC particles, (d) 3D view of the Ti-TiC composite. UMCs indicate unmelted TiC particles.

2.1.3 Thermodynamic Data of Ti-C System

In a multi-component system, the molar Gibbs energy for a given phase is determined by its constitution, temperature, and pressure. For AM processes, the pressure is set to be equal to the standard atmosphere pressure, whose influence on the Gibbs energy can be ignored; therefore, the molar Gibbs energy of a phase is only a function of constitution and temperature and can be written as:

$$G_m^\varphi = G_o^\varphi + G_{\text{mix}}^{\text{ideal}} + G_{\text{mix}}^{\text{ex}} \quad (2.21)$$

where φ indicates phase, G_o^φ is the contribution from the mechanical mixture of pure components to the Gibbs energy, $G_{\text{mix}}^{\text{ideal}}$ is the ideal mixing contribution, $G_{\text{mix}}^{\text{ex}}$ is the excess energy caused by the non-ideal interaction between different components.

According to the phase to be ordered or disordered, a sublattice model or a standard solution model is adopted to calculate its Gibbs energy. For a disordered phase, including solid solution phases and liquid, the expression for each term can be written as:

$$G_o^\varphi = \sum_{k=1}^M X_k {}^\circ G_k^\varphi \quad (2.22)$$

$$G_{\text{mix}}^{\text{ideal}} = RT \sum_{k=1}^M X_k \ln X_k \quad (2.23)$$

$$G_{\text{mix}}^{\text{ex}} = \sum_{k=1}^{M-1} \sum_{l=k+1}^M X_k X_l \sum_{n=0}^{M-1} [L_{kl,n} (X_k - X_l)^n] + G^{xs} \quad (2.24)$$

where X_k is the molar fraction of component k , M is the component number in the system, G^{xs} is the higher-order energy term in $G_{\text{mix}}^{\text{ex}}$. For a ternary alloy, G^{xs} has the following expression:

$$G^{xs} = X_1 X_2 X_3 L^{ter} \quad (2.25)$$

- **TiC_x Phase**

TiC_x has an NaCl-type structure, where Ti atoms form a face-centered-cubic (FCC) lattice with octahedral holes partially filled with C atoms, leaving some vacancies. Therefore, the molar fraction of C in TiC_x is 0.32–0.494 [80], and TiC_x can be treated as a solution phase and modeled with a two-sublattice model (Ti)₁(C,Va)₁, where Ti atoms completely occupy one sublattice while

C atoms and vacancies together occupy the other [80, 81]. The Gibbs energy expression for the TiC_x is [80]:

$$G_m^\delta = X_{\text{Ti}} G_{\text{Ti}}^\delta + X_{\text{C}} G_{\text{C}}^\delta \quad (2.26)$$

$$G_{\text{Ti}}^\delta = {}^\circ G_{\text{Ti:Va}}^\delta + RT \ln(1 - y_{\text{C}}) + y_{\text{C}}^2 \times L_{\text{C,Va}} \quad (2.27)$$

$$G_{\text{C}}^\delta = {}^\circ G_{\text{Ti:C}}^\delta - {}^\circ G_{\text{Ti:Va}}^\delta + RT \ln(y_{\text{C}} / (1 - y_{\text{C}})) + (1 - 2y_{\text{C}}) \times L_{\text{C,Va}} \quad (2.28)$$

$$y_{\text{C}} = X_{\text{C}} / (1 - X_{\text{C}}) \quad (2.29)$$

where δ indicates TiC_x . G_m^δ is the total free energy of the TiC_x phase. ${}^\circ G_{\text{Ti:C}}^\delta$ and ${}^\circ G_{\text{Ti:Va}}^\delta$ are Gibbs energies of the stoichiometric TiC and FCC Ti in their standard states. The parameter $L_{\text{C,Va}}$ represents the interaction between carbon atoms and vacancies in the C-vacancy sublattice. y_{C} is the site fraction of carbon in the C-vacancy sublattice, while X_{C} is the mole ratio of C in TiC_x .

• *Liquid Phase*

The liquid phase is treated as a disordered solution phase. The molar Gibbs energy for the disordered system takes the simple solution model as [80, 81]:

$$G_m^{\text{L}} = X_{\text{Ti}} {}^\circ G_{\text{Ti}}^{\text{L}} + X_{\text{C}} {}^\circ G_{\text{C}}^{\text{L}} + RT(X_{\text{Ti}} \ln X_{\text{Ti}} + X_{\text{C}} \ln X_{\text{C}}) + X_{\text{Ti}} X_{\text{C}} \left[{}^\circ L_{\text{Ti,C}}^{\text{L}} + {}^1 L_{\text{Ti,C}}^{\text{L}} (X_{\text{C}} - X_{\text{Ti}}) \right] \quad (2.30)$$

where X_{Ti} and X_{C} denote the mole ratio of Ti and C in the liquid phase, and ${}^\circ G_{\text{Ti}}^{\text{L}}$ and ${}^\circ G_{\text{C}}^{\text{L}}$ are the Gibbs energy of liquid Ti and C in their standard states. The first two terms on the right-hand side of Eq. (2.30) describe the mechanical mixture of the components, the third term indicates the ideal mixing Gibbs energy and the last term is the excess Gibbs energy. The expressions of standard Gibbs energy terms and interaction parameters can be found in Scientific Group Thermodata Europe (SGTE) element database [235] and Ref. [80], respectively.

2.2 Experimental Setup and Design

Ti-40vol.%TiC composites were built to verify the accuracy of the developed thermodynamically-consistent PF model, while Ti64-TiC composites were built to validate the PF results since the deposition parameters were designed based on the simulation results. Gas atomized commercially pure spherical Ti powders and Ti6Al4V powders from AP&C®, and

irregularly shaped TiC particles (45 – 150 μm) from Atlantic Equipment Engineers®, were used to premix the Ti-40vol.%TiC precursors and Ti6Al4V-TiC with 1 vol.%, 5 vol.%, 10 vol.% and 15 vol.% TiC. The mixture was blended on a roller mill at 90 rpm for 12 hours. A 3.5-mm thick hot rolled Ti64 plate was used as the substrate whose surface was cleaned and degreased with ethanol prior to usage. Single-track beads and multi-layer bulk parts were built with an Optomec LENS® 750 system, which uses a 500 W fiber laser with a wavelength of 1064 nm and a focused beam diameter of approximately 660 μm . Argon gas was used to deliver the powder and to maintain an inert atmosphere in the working chamber. Since Ti and its alloys are reactive in absorbing interstitial elements [236], the oxygen level in the chamber was controlled below 10 ppm. The DED parameters for Ti-40vol.%TiC samples were designed via preliminary tests and summarized in Table 2.5. These parameters are used in the DED model.

Table 2.5. Direct energy deposition parameters for the Ti-40vol.%TiC composite.

Parameters	Value	Unit
Laser power	260	W
Laser scan speed	15	mm/s
Powder feed rate	3.5	g/min
Track spacing	304.8	μm

According to the PF results (to be presented in Section), the resolidified dendritic TiC_x can be eliminated if the content of free C atoms in the liquid is low. Therefore, the deposition conditions for Ti6Al4V-TiC composites are designed to control the melting degree of mixed TiC particles. In this work, most melting (M) and least melting (L) conditions were used to indicate two extreme melting degrees. The LENS® 750 system is designed to feed powders with a size range of 45 – 150 μm . Therefore, 90 – 150 μm TiC particulates were used for the least melting control of embedded TiC, while < 45 μm TiC particles were used for the most melting control of TiC. The small particles have a larger surface area, and easier to melt than larger particles. The laser deposition parameters for melting control of TiC particles to obtain a dense and desirable microstructure are summarized in Table 2.6.

To characterize the microstructure, the specimens were cross-sectioned, mounted in bakelite and polished with SiC sandpapers up to 1200 mesh, followed by vibratory polishing in colloidal silica for 24 hours. To observe the morphology of resolidified TiC_x , the polished parts were not

etched, which are observed using an optical microscope (Nikon Eclipse LV150) as well as a scanning electron microscope (SEM, Quanta 3D FEG). The composition examination was performed via the energy dispersive X-ray spectroscopy (EDX) that was attached to the SEM.

Table 2.6. Summarized DED deposition conditions for Ti6Al4V and Ti6Al4V-TiC composites with different TiC contents.

Sample No.	Premixed TiC (vol.%)	TiC size (μm)	Melting degree	Laser power (W)	Powder feed rate (g/min)	Laser scan speed (mm/s)	Layer thickness (μm)
1	0	-	-	300	1.5	15	254
2	1	90 – 150	least	290	1.8	15	254
3	1	<45	most	375	1.2	15	254
4	5	90 – 150	least	265	1.8	15	254
5	5	<45	most	350	1.3	15	254
6	10	90 – 150	least	230	1.8	15	254
7	15	90 – 150	least	200	2,0	15	228

2.3 Results and Discussion

2.3.1 Experimental Results of Resolidified dendritic TiC_x in Ti-40vol.%TiC

Figure 2.3 shows SEM and EDX results of the DED manufactured Ti-40 vol.%TiC composite. The EDX mapping reveals a high concentration of C in the dendritic phase, indicating that the dendrites are resolidified TiC_x . As premixed TiC particulates are the only source of C, melting and dissolution must have occurred to the TiC particles under the current DED condition. When the molten pool cools down, the free C atoms react with matrix Ti atoms and form dendritic TiC_x grains, precipitating out from the Ti matrix [12, 54, 62]. As illustrated in Figure 2.3(a), the resolidified dendritic TiC_x nuclei are formed randomly and grow with different crystallographic orientations. The dendrites do not solidify simultaneously. Some nuclei are newly formed while some are well developed with ternary rebranching. The continuous growth of dendrites eventually influences the growth of each other and leads to coordinated growth orientations and grain sizes. Although the high cooling rate in the DED process could lead to non-equilibrium α' martensite [12, 71, 237, 238], the authors' previous study revealed that the adding of TiC led to the formation of α -Ti instead of α' martensite [12]. The detection of aluminum elements in the matrix must diffuse from the Ti6Al4V substrate due to the dilute effect.

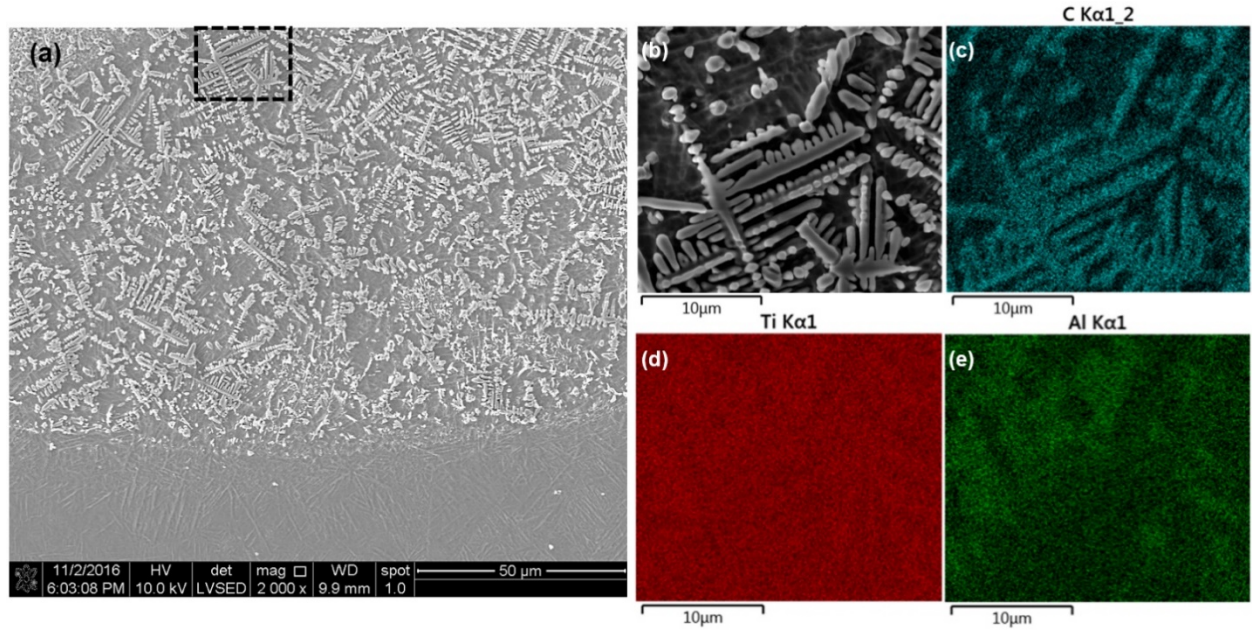


Figure 2.3. (a) SEM and (b-e) EDX mapping results of the DED-deposited Ti-40 vol.%TiC composite.

2.3.2 Phase-field Modeling of Isothermal Solidification of Dendritic TiC_x

Figure 2.4(a) and (c) show the grain index field and the concentration field of isothermal solidification of TiC_x at 2800 K predicted by the PF model, respectively. The isothermal solidification was first performed to verify the PF-thermodynamics model for TiC_x solidification. In total, nine dendrites are formed and grow at different crystallographic orientations. The earlier solidified grains block the growth of the later formed nuclei, and the secondary and ternary branches display an asymmetric morphology. Although the simulation was carried out at a constant temperature, the predicted solidification pattern of the resolidified TiC_x dendrites is quite comparable to the experimental observation in Figure 2.3.

The simulation reveals that when the dendrite tips of two grains grow close to each other, the growth direction of one grain deviates from its initial orientation. These phenomena are known as competitive growth, particularly common in the directional solidification. For example, Viardin et al. [239] revealed that the growth direction inclines to align with the temperature gradient. The competitive growth causes stagnancy or elimination of some grains depending on the angle differences in adjacent grain boundary trajectories. Tourret and Karma [240] further found that the selection of the trajectory is stochastic since the initial branching is induced by the thermal noise around the dendrite tip. However, the temperature gradient and pulling speed are still responsible

for the following growth of grains. In the current study, the competition for solute is demonstrated to be another reason for the competitive growth since the isothermal solidification is free from the temperature gradient or pulling speed.

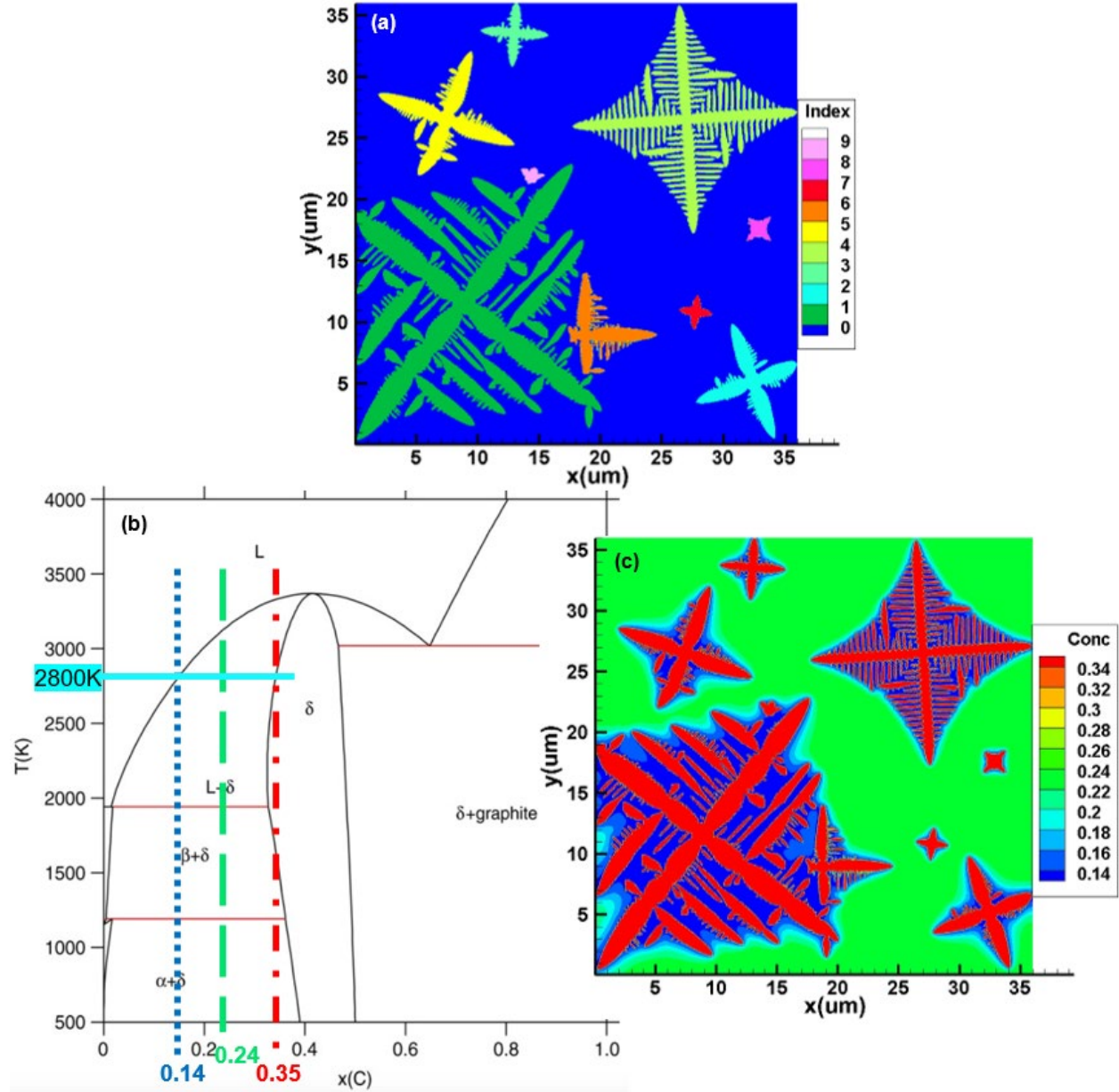


Figure 2.4. Phase-field simulation results for isothermal solidification of TiC_x at 2800 K: (a) the grain index field and (c) the concentration field of carbon, which is validated by (b) the equilibrium concentrations in the Ti-C phase diagram [81].

The predicted concentration field of carbon (Figure 2.4(c)) is validated against the equilibrium concentrations in Ti-C phase diagram (Figure 2.4(b)). As shown in Figure 2.4(c), the

concentration is indicated by different colors. The initial molar concentration of C in the Ti-C liquid is 0.24 (Figure 2.4(c), light green color), which is equal to the calculated value using the image processing procedure (Figure 2.2). The predicted equilibrium C concentration in the solid dendrite (Figure 2.2(c), red color) is approximately 0.35. When C diffuses from the Ti-C liquid to TiC_x , a liquid zone with only about 0.14 carbon (Figure 2.4(c), dark blue color) is formed around the dendrite, and C decreases from the initial concentration over the liquid/solid interface. In the Ti-C phase diagram (Figure 2.4(b)), at 2800 K, the equilibrium molar fractions of carbon on liquid and solid sides are about 0.14 and 0.35, respectively. The predicted concentration of carbon matches the Ti-C phase diagram in excellent agreement, which verifies the accuracy of the PF-thermodynamics model of TiC_x developed in this work.

2.3.3 DED Model Validation and Temperature Field Extraction

Temperature isotherms for the β -transus temperature of the Ti6Al4V substrate (1269 K) and the liquidus temperature of the composite (1943 K) were extracted and superimposed on the cross-section image of single-track Ti-40vol.%TiC to provide a visual comparison with molten pool and heat affected zone boundaries, respectively. The simulation results against the experimental data are shown in Figure 2.5 where the yellow (upper), red (middle) and green (lower) lines indicate the free surface, molten pool and heat affected zone boundaries, respectively.

The free surface and heat affected zone boundary are captured in good agreement with the experimental result. Unfortunately, the prediction error associated with the molten pool boundary deviates from the experimental data by approximately 80 μm in width and 50 μm in depth. Since the rules of mixtures and assumptions made in the simulation of the DED process will inevitably involve errors, the prediction is hence expected to deviate to some extent. As the predicted profiles are representative of the experimental data, the temperature field produced by the DED model can be utilized as inputs to the PF model.

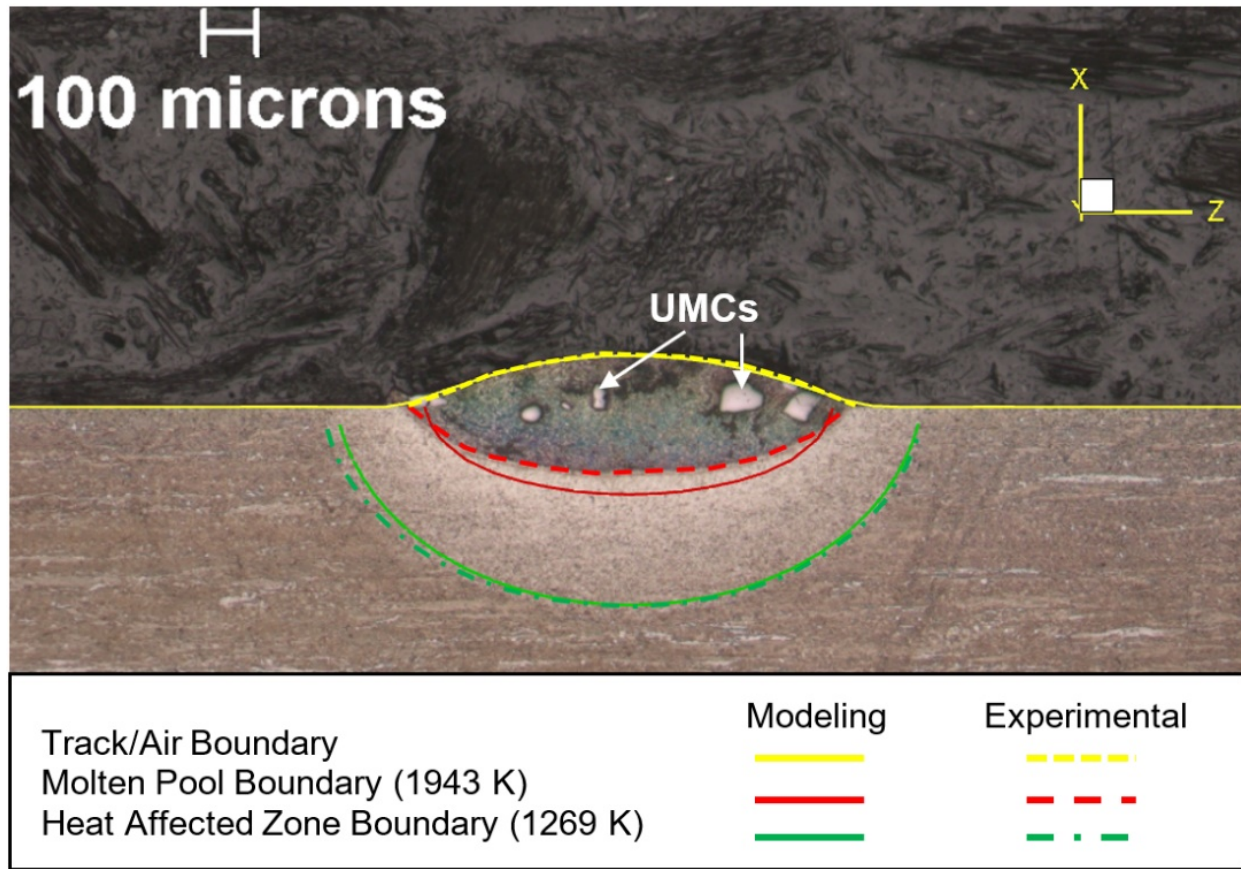


Figure 2.5. The predicted free surface, molten pool boundary and heat affected zone boundary obtained from the DED model for single-track Ti-40vol.%TiC as compared to the experimental data. UMCs indicate unmelted TiC particles.

Temperature contours of the DED manufactured single-track Ti-40vol.%TiC are presented in Figure 2.6(a) and (b). To provide clarity of the molten pool region in each of the subfigures, temperatures in excess of liquidus temperature are displayed as white. Figure 2.6(c) shows the extracted temporal temperature fields at different locations along the arrow in Figure 2.6(b). In total, seven locations were analyzed with an equivalent time interval passing the laser beam center. An average cooling rate as high as 10^4 K/s is produced and decreases from its maximum near the free surface to the bottom of the molten pool. The peak temperature also decreases from top to bottom zones in the molten pool, indicating an increased undercooling.

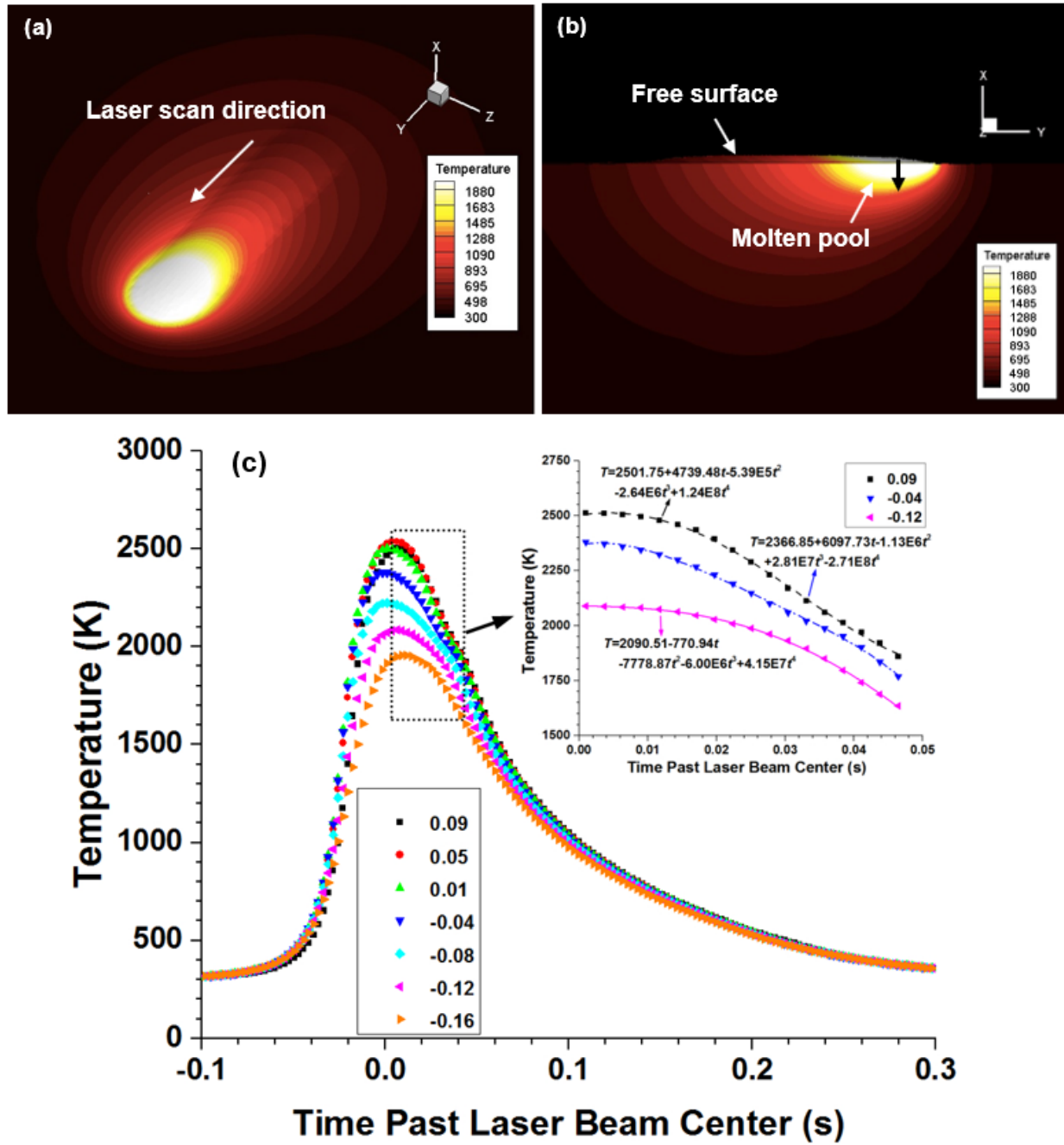


Figure 2.6. Temperature contours of the DED-deposited single-track Ti-40vol.%TiC: (a) top view, (b) side view and (c) temperature profiles extracted at various locations (in mm) along the arrow in (b).

The maximum temperature in the molten pool is about 2550 K and appears at $X = 0.05$ mm instead of the very top surface ($X = 0.09$ mm), which is believed to be caused by the convection effect induced by the argon flow on the free surface. Since the maximum temperature in the molten

pool is much lower than the melting temperature of TiC, the melting of TiC particles is believed to be caused by the laser-particle interaction and occurs before the particles are blown into the molten pool. In addition, the high-temperature diffusion of C from UMC particles to the liquid should also result in the dissolution of the embedded UMC particles [229]. However, dissolution should play a less dominant role than melting due to the high cooling rate in the molten pool.

Three representative temperature fields produced at $X = 0.09$ mm, -0.04 mm and -0.12 mm are selected for the PF model to study the solidification of TiC_x dendrites at the top, middle and bottom regions in the molten pool. Since the current work studies the solidification process of TiC_x , only the cooling stage above the liquidus temperature (1943 K) should be considered. In order to produce an accurate curve fit, the temperature range is expanded to include more value points and a fourth-order function is utilized to fit the temperature curves, as shown in Figure 2.6(c).

2.3.4 Phase-field Modeling Coupled with Temperature Field

Influences of three temperature fields produced at the top, middle and bottom zones in the molten pool (Figure 2.6(c)) on the morphology of resolidified TiC_x dendrites and on the distribution of C are exhibited in Figure 2.7(a) to (c). To save calculation cost, the simulation was stopped when the results are representative of experimental results. In total, the simulation was continued for 0.007 s, but the simulated morphology of dendrites agrees well with the experimental observation in Figure 2.3. The dendrites solidify at various orientations. Since nuclei are formed at different time moments, the dendrites grow into different sizes. Asymmetric and competitive secondary branches are also produced, which reflect the realistic microstructure morphology (Figure 2.3).

The three images in Figure 2.7 reveal an increased growth rate from top to bottom zones in the molten pool. Since the simulation lasts 0.007 s, Figure 2.7 mainly evidences the crucial role of undercooling in the determination of the microstructure evolution. Figure 2.7(d) plots out the average growth rate of dendrite tips as a function of undercooling within 0.007 s for the three different zones. As is clearly illustrated, the average growth rate is almost proportional to the undercooling. When the undercooling is small (Figure 2.7(a)), dendrites grow slowly, and the liquid/solid interface is very stable. As the undercooling increases (Figure 2.7(a) to (c)), dendrites grow at a higher growth rate with a longer primary trunk and better developed secondary branches. Similar observations were also revealed in Refs. [107, 241].

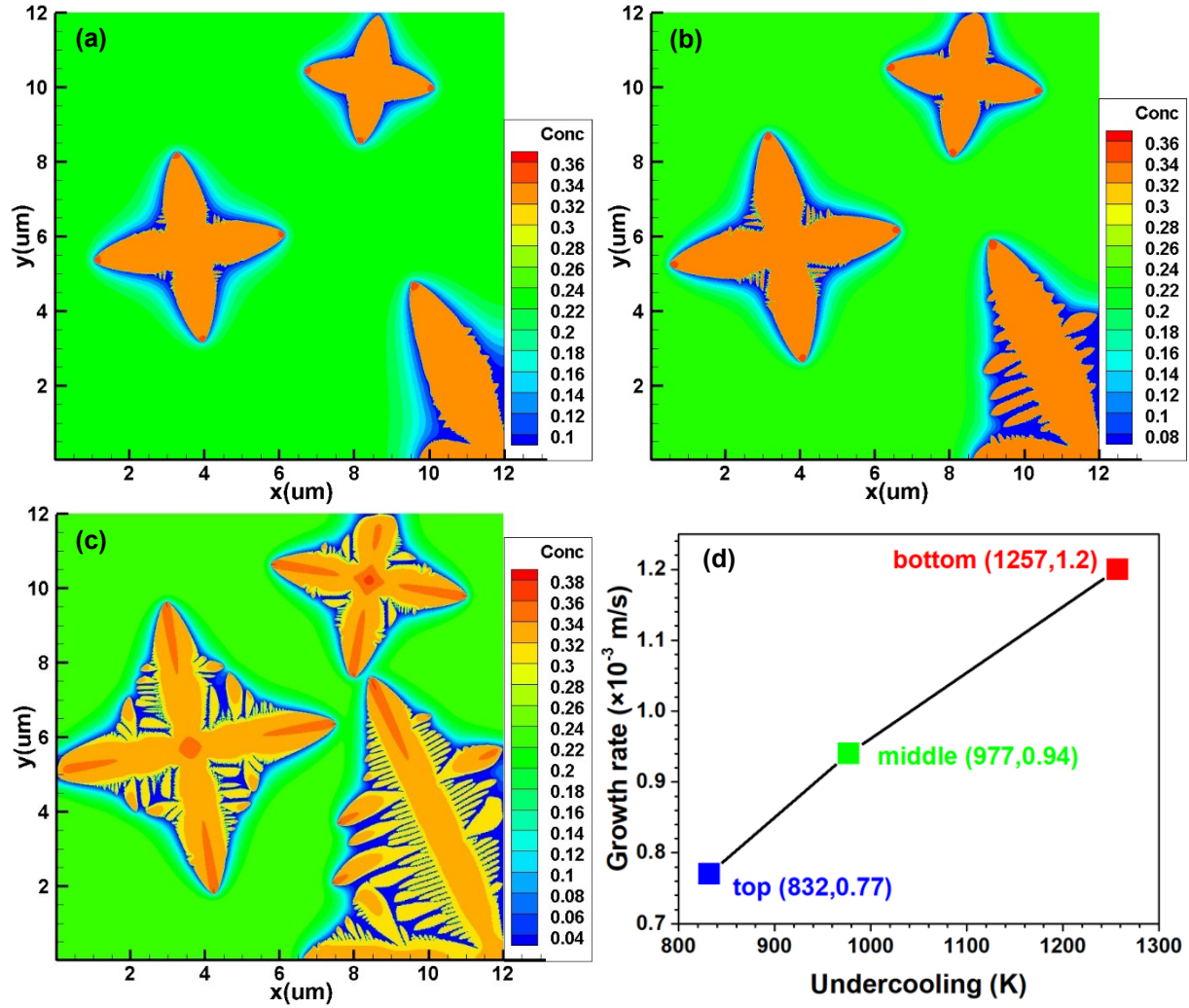


Figure 2.7. The influence of temperature profiles produced at (a) top, (b) middle and (c) bottom zone on the morphology evolution of resolidified TiC_x dendrites. The simulation lasts for 0.007 s. (d) The average growth rate of dendrite tips versus undercooling within 0.007 s for three different zones.

The underlying reason behind the growth rate associated with the undercooling is that the large undercooling can amplify the noise at the grain boundary, and the surface energy can not effectively restrain the amplification of the noise, leading to an unstable interface. It is commonly accepted that the side-branching is caused by the thermal noise at the dendrite surface. With the thermal noise amplified by larger undercooling, side branches are extruded from the primary dendrite and then grow competitively [242]. The overgrown side branches may become new primary dendrites, making the final morphology of the dendrites highly dependent on the side

branches. With the increasing speed of growth, the dendrite arms become slender than those formed under smaller undercooling [243].

When the cooling stage is considered, the distribution of C is no longer uniform. The C is more concentrated at dendrite tips, resulting in microsegregation. As can be seen from Figure 2.7(a) to Figure 2.7(c), microsegregation becomes more prominent at decreased temperatures. This phenomenon indicates a decreased solubility of C in TiC_x with a decrease in temperature, which forces the solidified TiC_x dendrite to constantly eject C from the central zone of the primary trunk to dendrite tips during its continuous growth. This prediction matches the Ti-C phase diagram (Figure 2.4(b)), where the temperature-dependent concentration of C in TiC_x exhibits a decreased solubility along the solidus line as the temperature decreases.

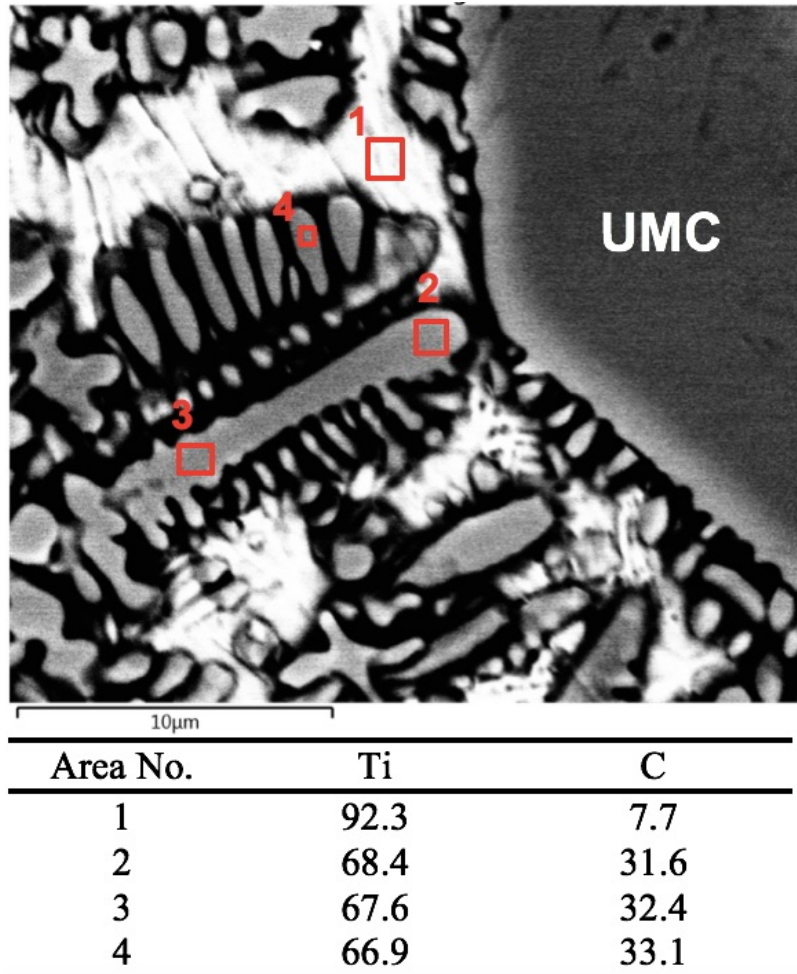


Figure 2.8. EDX area detection reveals the distribution of Ti and C (at.%) in the resolidified TiC_x dendrite and α -Ti matrix. UMC indicates unmelted TiC particle.

In order to validate the C distribution over the resolidified TiC_x dendrite, EDX area detection was performed, as shown in Figure 2.8. Before the EDX test, the sample surface was degreased with ethanol to eliminate the C contamination. It needs to be pointed out that EDX is a semi-quantitative technique and is not accurate for detecting light elements like C. Additionally, it has an approximately 2 at.% error in the reported element content. Therefore, EDX results are employed to give a qualitative validation of the PF simulation. As shown in Figure 2.8, the detected average concentration of C in the resolidified TiC_x (spots 2 – 4) is about 32 at.%, which matches the PF prediction (Figure 2.7) with an acceptable deviation. In addition, the microsegregation leads to a small fluctuation in the C concentration at different zones in the resolidified TiC_x dendrite. As the C in the liquid was consumed by TiC_x , it is reasonable to expect a low C concentration in the α -Ti matrix (spot 1).

The temperature field plotted out in Figure 2.6(c) shows that it takes about 0.05 s for the temperature in the molten pool to drop below the solidus temperature. Within this period of time, the dendrites are expected to be fully developed based on the simulation time scale in Figure 2.7. Indeed, the microstructure characterization presented in Figure 2.3(a) really confirms this expectation, where the fully developed resolidified TiC_x dendrites finally grow close to each other and form a network, covering the surface of α -Ti matrix. Since it is so easy for the resolidified TiC_x dendrites to form in the DED process, the most effective way to control the formation of dendritic TiC_x would be the decrease of C concentration in the molten pool. Without enough C supporting, the growth of dendritic TiC_x must be inhibited.

2.3.5 Validation of Simulation Results

Figure 2.9 illustrates the formation mechanism and morphology evolution of primary dendritic TiC_x (PDC) in $\text{Ti6Al4V-10vol.\%TiC}$ composites. When the laser power is 230 W, only PSC, EGC and ESC are observed, while several short PDC grains are produced for 250 W. As the laser power further increased to 300 W, more and larger PDC grains are produced. Actually, the increased laser power leads to increased laser energy as other parameters are kept constant, and the melting degree of the embedded TiC hence increases. This result reveals the direct relationship between the formation of PDC and the melting degree of embedded TiC particles that the formation of PDC can really be controlled. It is believed that as the melting degree of the embedded

TiC increased, more carbon dissolved in the liquid. When the carbon content reached a certain amount, the dendritic TiC_x begins to form and attached to PSC as nuclei. The primary carbides consumed the carbon, and hence the eutectic carbide content decreased (Figure 2.9(c)).

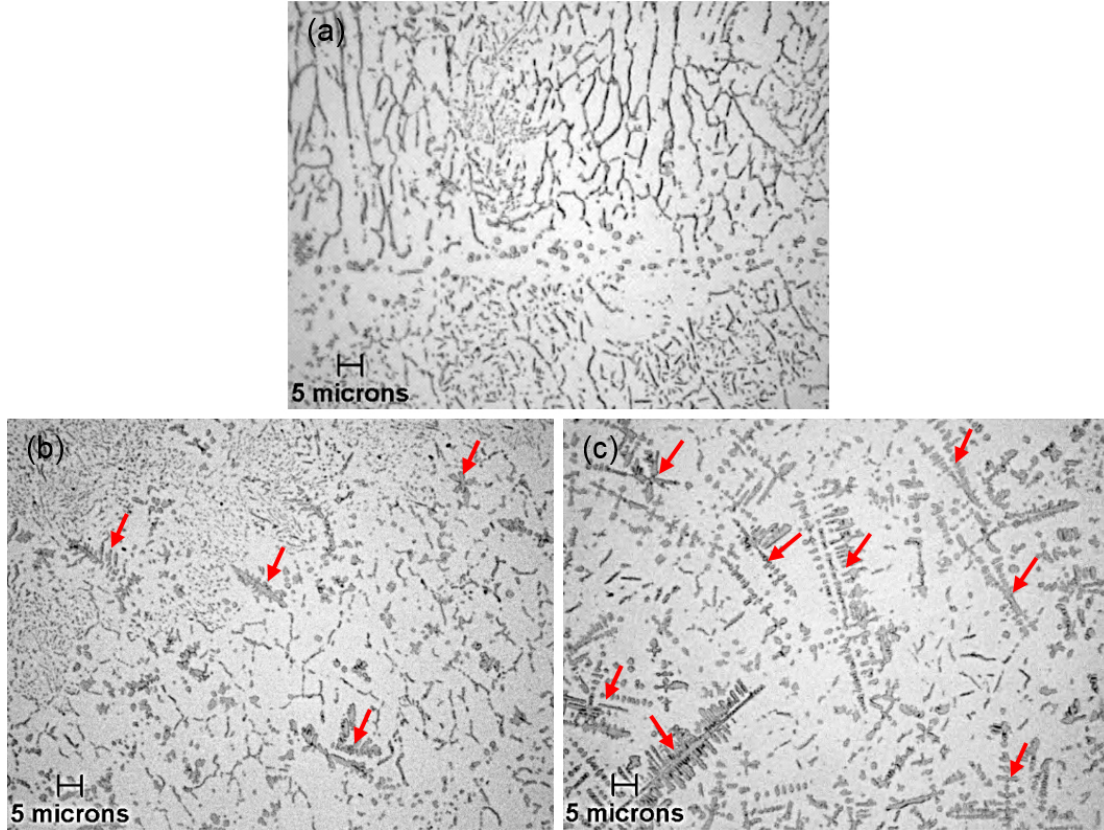


Figure 2.9. The formation and morphology evolution of dendritic TiC in Ti6Al4V-10vol.%TiC composites built with a 15 mm/s laser scan speed, a 254 μm layer height and the same TiC particle size but different laser powers: (a) 230 W, (b) 250 W, and (c) 300 W. Dendritic TiC grains are indicated by arrows.

In addition to the laser energy density, the embedded TiC content also affects the melting degree. According to the microstructural analysis, 5 vol.% TiC or less will not produce PDC even when the embedded TiC particles are almost completely melted, as will be shown later. To avoid the formation of dendritic TiC_x , the DED parameters must be carefully selected for more than 5 vol.% TiC. Therefore, the most melting control condition was only performed on embedded 1 vol.% and 5 vol.%TiC. For brevity, hereafter we define the most melting conditions for 1 and 5 vol.% TiC as 1M and 5M, and the least melting conditions for 1, 5, 10 and 15 vol.% TiC as 1L, 5L, 10L, and 15L.

For the least melting control, the lowest energy density condition was tested by increasing the powder feed rate so as to increase the layer height for set laser power and laser scan speed. However, two kinds of defects are easy to form in this process and should be avoided (Figure 2.10). If the laser power is not high enough for the preset layer thickness, a lack-of-fusion defect will be produced, resulting in premature failure of the composites [244-246]. This lack-of-fusion defect exhibits an irregular-shaped void and is primarily formed in the inter-pass overlap (Figure 2.10(a)).

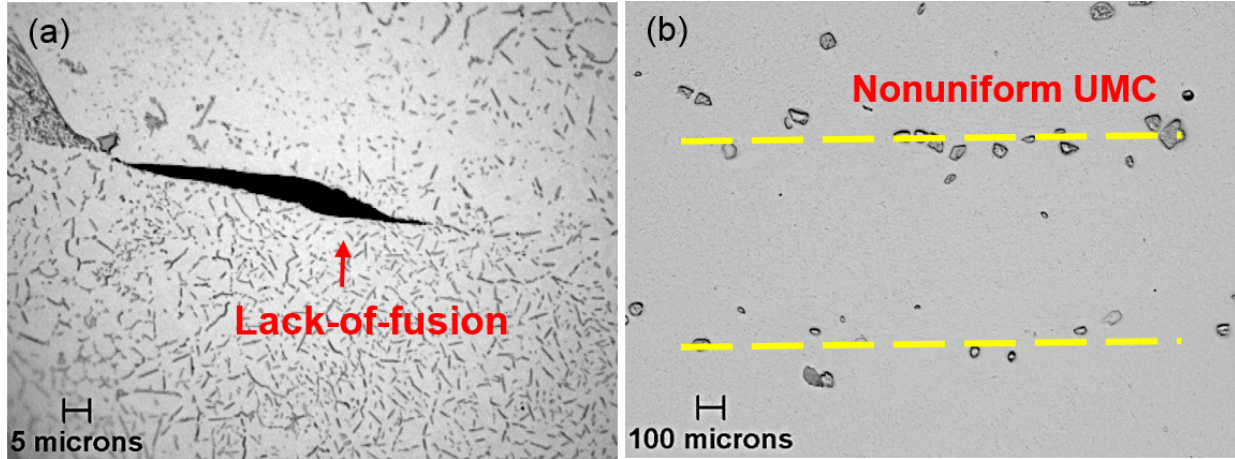


Figure 2.10. Potential defects in the least melting control of DED-deposited Ti6Al4V-TiC composites: (a) lack-of-fusion, and (b) inhomogeneous distribution of unmelted TiC particulates.

On the contrary, a high energy density will produce a deep molten pool, leading to high layer thickness. The vigorous Marangoni flow and buoyancy force in the molten pool will push the UMC particles to the edge zones of the molten pool [247, 248]. The nonuniform distribution of the UMCs (Figure 2.10(b)) will cause anisotropy in the mechanical properties. Finally, the defect-free condition with the lowest energy input was selected as the optimized deposition condition for the least melting control. For different embedded TiC contents, the optimized laser deposition conditions are different (Table 2.6). The microstructures of the UMC and resolidified TiC are illustrated in Figure 2.11. As can be seen, the deposition conditions produce a dense and defect-free structure where no PDC grains are formed and the UMC particles are uniformly distributed in the Ti6Al4V matrix for all compositions.

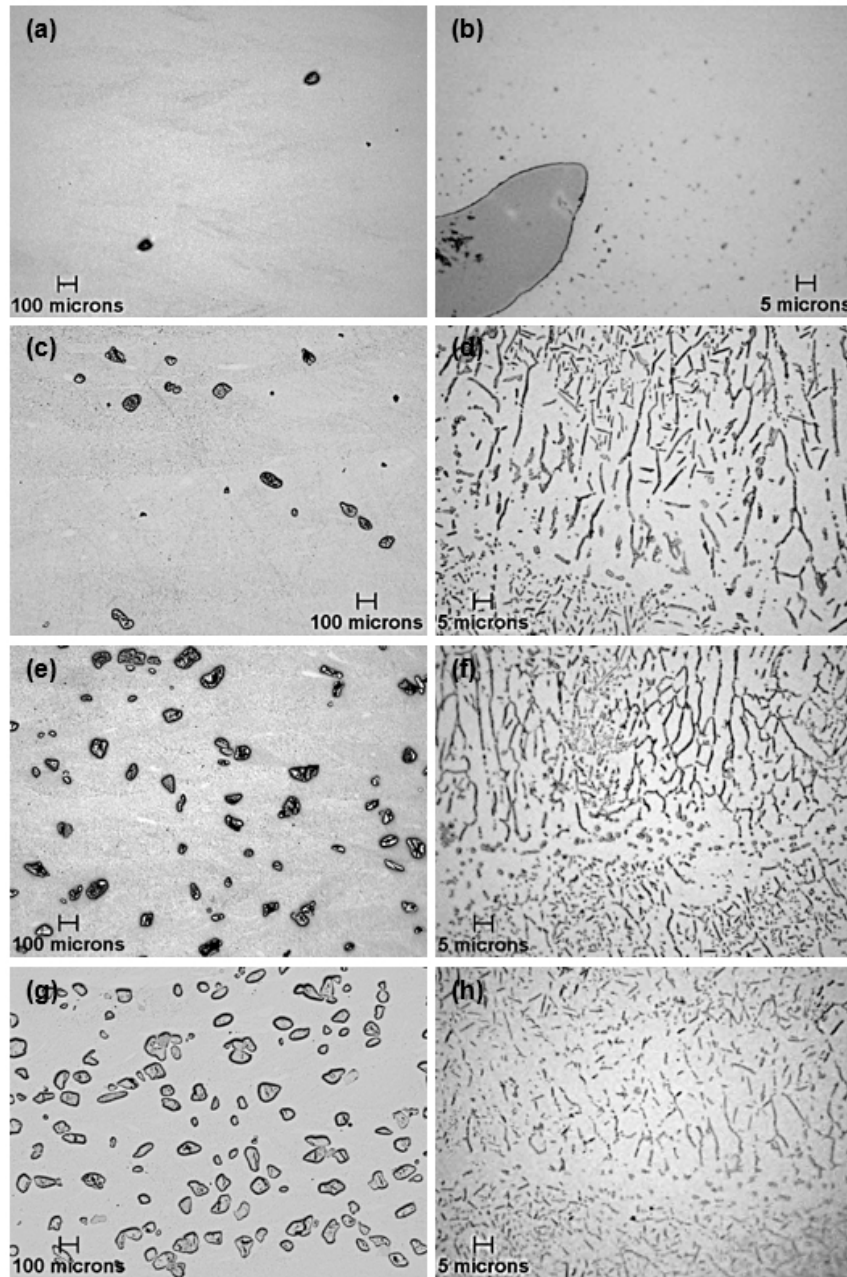


Figure 2.11. Microstructures of unmelted TiC particles and resolidified carbides in DED-deposited Ti6Al4V-TiC composites with the least melting control of TiC reinforcements: (a, b) 1 vol.% TiC; (c, d) 5 vol.% TiC; (e, f) 10 vol.% TiC; (g, h) 15 vol.% TiC.

Figure 2.12 shows the microstructures of the resolidified TiC with the most melting control of reinforced TiC in Ti6Al4V-TiC MMCs. No PDC was detected even though the embedded TiC particles were almost completely melted. The resolidified TiC in 5M displays a needle-shaped or spherical-shaped eutectic morphology (Figure 2.12(b)), but for 1M, no obvious resolidified carbides

are observed (Figure 2.12(a)). This indicates that the melted TiC completely dissolves into the Ti6Al4V matrix. According to Figure 2.11 and Figure 2.12, the formation of dendritic TiC_x can definitely be controlled as long as the concentration of carbon atoms in the liquid is controlled to a low level, which successfully verifies the PF simulation results.

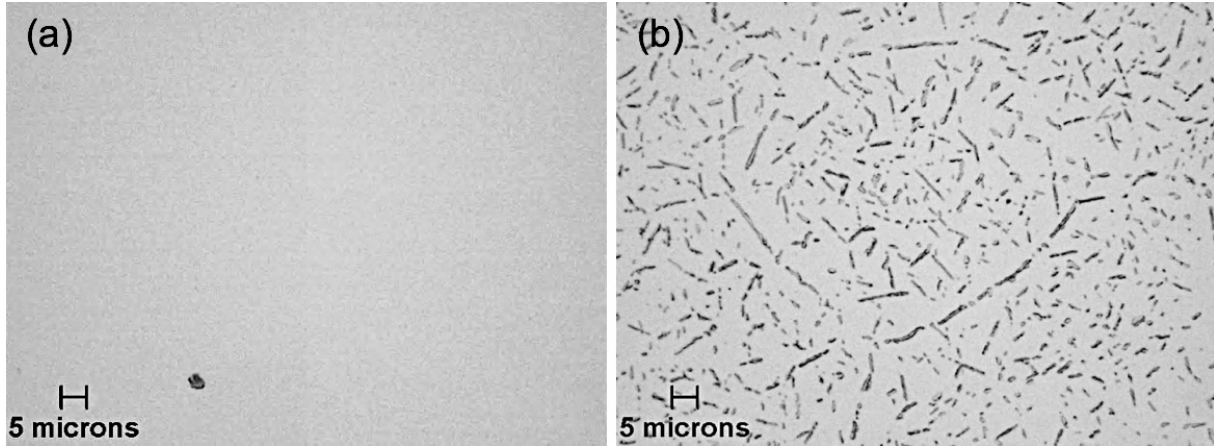


Figure 2.12. Microstructures of Ti6Al4V-TiC with the most melting control of TiC: (a) 1 vol.% TiC; (b) 5 vol.% TiC.

2.4 Summary

In this chapter, an improved binary PF model that was coupled with the thermodynamically-consistent database of the Ti-C system was developed to simulate the formation mechanism of resolidified dendritic TiC_x in Ti (Ti6Al4V)-TiC composites. In this improved PF model, a grain index was introduced to track the crystallographic orientation of each grain to reflect the polycrystalline growth pattern of TiC_x dendrites. The thermodynamic database of ordered TiC_x is established using a two-sublattice model. Since the modification avoids the using of multiple phase variables, the calculation efficiency will be dramatically improved. With the temporal and spatial temperature fields within the molten pool calculated by the DED model, the thermodynamic consistent PF model predicted the solidification process of TiC_x polycrystals in different zones in the molten pool. The free surface, molten pool, and heat affected zone of single track Ti-40vol.%TiC predicted by the DDD model were representative of the experimental result, which indicated the feasibility of the DED model to predict the thermal behavior of a composite material.

The accuracy of the PF model was verified by the equilibrium concentrations indicated in the Ti-C phase diagram via the isothermal solidification. The predicted dendritic morphology and distribution of carbon matched experimental observation. Melting of TiC particles occurred due to

the laser-particle interaction before the particles were blown into the molten pool since the maximum temperature in the molten pool was below the melting temperature of TiC. The overlapped solute field around different dendrites was responsible for competitive growth. As the temperature in the molten pool decreases, microsegregation occurred to the distribution of carbon over the dendrite because of the decreased solubility at lower temperatures. The increased undercooling from the top to bottom of the molten pool led to an increased growth rate. Due to the easy formation and fast growth feature of resolidified dendritic TiC_x , to control the carbon concentration in the Ti-C liquid via reducing the melting degree of premixed TiC particles would be the most effective way to control the formation and growth of dendritic TiC_x .

To verify the PF results, DED conditions that controlled the melting degree of embedded TiC particles were designed to test the formation of dendritic resolidified TiC_x . It turned out that the melting degree of the embedded TiC was determined by the added TiC content and the input laser energy density. The laser energy density would not result in dendritic carbides if the volume fraction of the mixed TiC particles is no more than 5 vol.%. It was difficult to avoid the formation of dendritic carbides when the premixed TiC is larger than 15 vol.%. By proper controlling the input laser energy density, the Ti6Al4V-TiC composites with 5 – 15 vol.% TiC were free from dendritic carbides. The experimental results successfully proved that as long as the concentration of carbon atoms in the liquid is controlled to a low level, the formation of dendritic TiC_x can be controlled, which is consistent with the PF simulation results.

3. DIRECTED ENERGY DEPOSITION OF TERNARY Ti6Al4V AND MICROSTRUCTURE MODELING

In this chapter, a complete and systematic modeling study of the solidification, grain structure evolution, and phase transformation in the DED-built ternary Ti6Al4V alloy via the establish of an integrated multi-physics and multi-scale simulation framework by combining a 3D macro-scale DED model, a 3D macro-scale CA model, a 2D multi-phase and multi-component micro-scale PF model, an integrated 2D meso-scale CA-PF model, as well as a 2D phase prediction model.

3.1 Experimental Procedure

Ti6Al4V powders (Grade 5, 44 – 149 μm) from Puris® were used as the raw materials, and a hot rolled Ti6Al4V plate (3.5 mm thick) was used as the substrate and was thoroughly cleaned before usage. Single, two, and three-track Ti6Al4V depositions were built in the argon-filled chamber of the Optomec LENS® 750 system, which is equipped with a 500 W fiber laser. The beam diameter is about 660 μm . In order to avoid oxidation, the oxygen level in the chamber was controlled below 10 ppm [249]. The laser power, scan speed, powder feed rate and track spacing are 330 W, 15 mm/s, 2 g/min and 304.8 μm , respectively. All of these parameters were used as inputs for the DED modeling.

Since the deposited tracks are used to verify the simulation results, the experimental condition must be equal to the simulation condition. To acquire the initial temperature of approximately 300 K prior to performing the deposition for each track, a time interval of 15 minutes was added before depositing the following track, which allowed complete cooling of the substrate. In addition, after depositing one track, the laser head was moved back with a lateral distance by 304.8 μm to the initial position for preparing the next track. The sketch of the DED process for depositing Ti6Al4V tracks is illustrated in Figure 3.1.

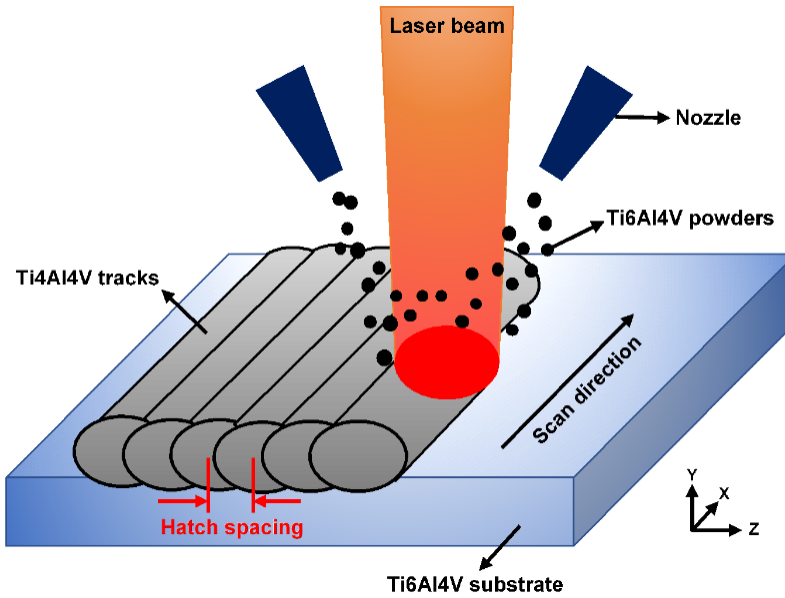


Figure 3.1. Sketch of the DED process for depositing the Ti6Al4V tracks and the 3D DED Modeling.

For microstructure characterization, the tracks were cross-sectioned, ground using #240 – #1200 SiC papers followed by the vibratory polishing in colloidal silica for 24 hours, and etched with the Kroll's etchant (ASTM 192) to reveal the microstructure. The track was about 30 mm long, from which six cross-sections were bladed. The microstructure was observed using an optical microscope (Nikon Eclipse LV150) and a scanning electron microscope (JEOL-6400). The microhardness test was performed on the cross-sections of the three-track depositions with a load of 200 g and a dwell time of 13 s using a LECO KM 247AT tester. A distance of 100 μm was set between adjacent indentations.

3.2 Model Description

The integrated simulation framework includes a 3D DED model, a 3D CA model and a 2D phase prediction model. The DED model was used to calculate the spatial and temporal temperature fields and heating/cooling rates in the deposited tracks. After achieving the pseudo-steady-state, such thermal information in 3D was extracted and input to the 3D CA model to predict the solidification process and competitive growth of β grains within the entire molten pool. The thermal information was then applied to the phase prediction model to capture the solid-state phase transformation of $\beta \rightarrow \alpha/\alpha'$. With the combination of three predictive models, a complete

prediction for solidification and phase transformation in the DED-built Ti6Al4V depositions was carried out. A detailed phase diagram of Ti6Al4V with a flow chart of three models is illustrated in Figure 3.2. It should be noted that the grid size of the 3D CA model ($5 \times 5 \times 5 \mu\text{m}^3$) and 2D phase prediction model ($5 \times 5 \mu\text{m}^2$) is smaller than the DED model ($50 \times 33 \times 50 \mu\text{m}^3$), and thus a linear interpolation was used to map the temperature field from the DED model onto the domains of the other two models.

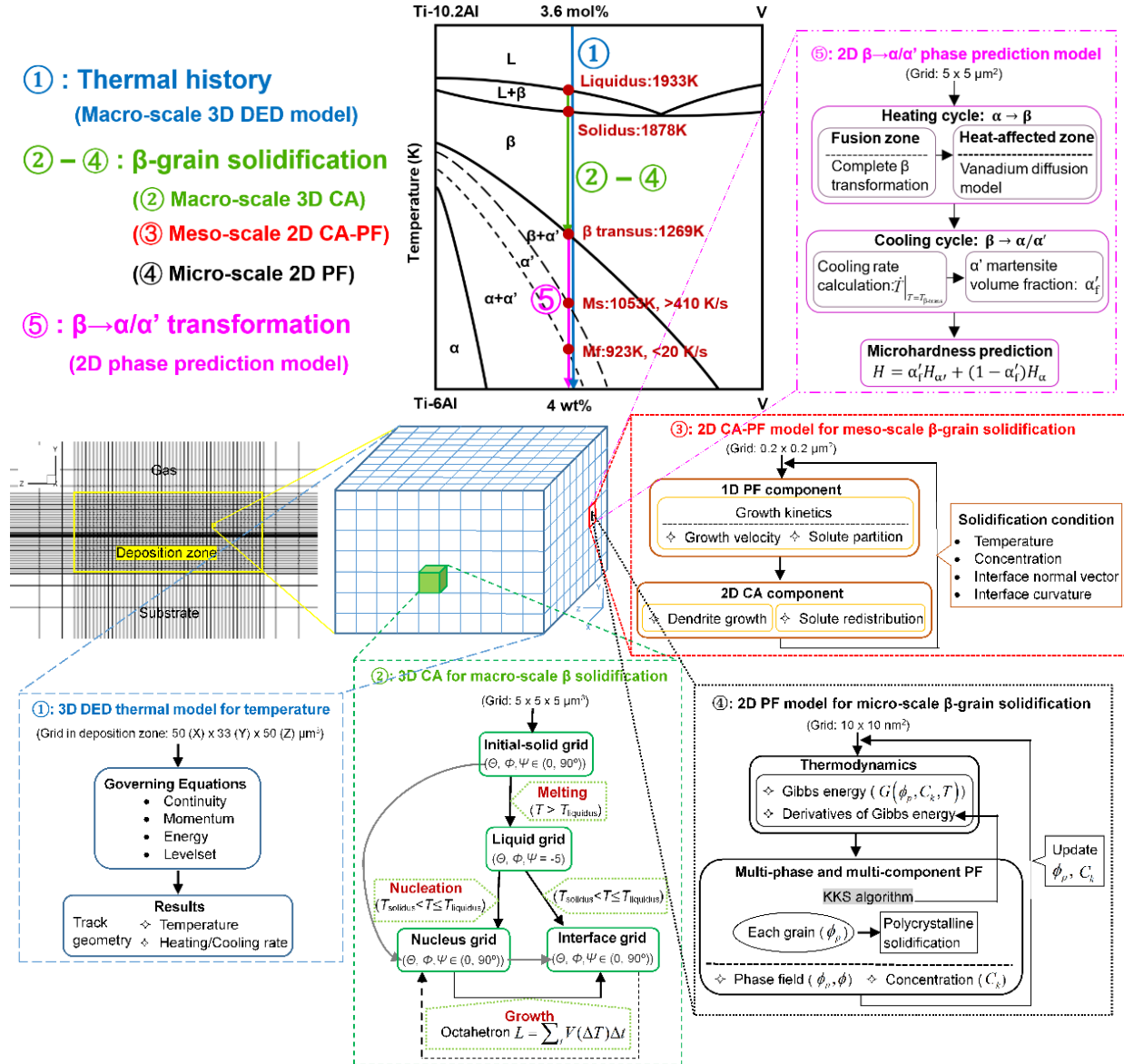


Figure 3.2. Phase diagram of Ti6Al4V and an integrated flow chart of three models. Ms and Mf indicate the martensite start and finish temperatures, respectively.

3.2.1 3D Macro-scale DED Model for Thermal History in DED-built Ti6Al4V

In this section, the experimentally-validated DED model is applied to simulate the multi-track DED process of Ti6Al4V alloy. In order to avoid repetition, please refer to Ref. [67, 68, 207] for the detailed descriptions of the DED model. Table 3.1 provides the thermal and physical properties used for Ti6Al4V throughout the deposition modeling. The solid thermal conductivity was obtained via a linear curve fit of the property data from [231] and [250]. Using the levelset technique for free surface tracking, a gas with the same density as the substrate material was utilized to maintain numerical stability, though remaining properties were set to those of argon gas, which resembled the environment in which the experimentation was performed. The convective heat transfer coefficient at the free surface was modeled as $100 \text{ W}/(\text{m}^2 \cdot \text{K})$, which was estimated based on the flow rate from the gas-assisted nozzle impinging on the surface. During the melting and solidification process, material shrinkage would occur. However, the shrinkage of Ti6Al4V was not considered in the current study because the density of Ti6Al4V changes due to the temperature range within this study is approximately 10% [251], which was deemed not a significant impact given the temperature change.

Table 3.1. Material properties of Ti6Al4V for the DED model.

Property	Units	Solid phase	Liquid phase
Density	kg/m^3	4506 [231]	4506 [231]
Specific heat	$\text{J}/(\text{kg} \cdot \text{K})$	560 [232]	560 [232]
Thermal conductivity	$\text{W}/(\text{m} \cdot \text{K})$	$0.01327T + 2.770$ [252]	$0.0183T - 6.66$ [252]
Liquid viscosity	$\text{kg}/(\text{m} \cdot \text{s})$	-	3.2×10^{-3} [253]
Thermal expansion coefficient	$1/\text{K}$	8.9×10^{-6} [232]	-
Absorptivity	-	0.34 [254]	-
Emissivity	-	0.25 [254]	-
Latent heat of fusion	J/kg	3.65×10^5 [232]	-
Solidus temperature	K	1878 [231, 250, 252]	
Liquidus temperature	K	1933 [231, 250, 252]	-
Surface tension	N/m	-	1.65 [253]
Surface tension temperature coefficient	$\text{N}/(\text{m} \cdot \text{K})$	-	-2.4×10^{-4} [253]
Convective heat transfer coefficient	$\text{W}/(\text{m}^2 \cdot \text{K})$	100	-

To carry out the simulation, a 3D domain consisting of a upper region of $12.0 \text{ (X)} \times 3.0 \text{ (Y)} \times 12.0 \text{ (Z)} \text{ mm}^3$ for the gas and a bottom region of $12.0 \text{ (X)} \times 5.0 \text{ (Y)} \times 12.0 \text{ (Z)} \text{ mm}^3$ for the

Ti6Al4V substrate was created and discretized into a uniform mesh ($50 (X) \times 33 (Y) \times 50 (Z) \mu\text{m}^3$) in the deposition zone ($7.2 (X) \times 1.0 (Y) \times 3.3 (Z) \text{mm}^3$) and a non-uniform mesh elsewhere. The size of the deposition zone was predetermined based on the microstructure images, which covers the whole deposition and some of the substrate and gas regions, as depicted by the solid box in the top left inset in Figure 3.2. A dual-time stepping algorithm, where a physical time step of 1.0×10^{-5} seconds included 25 pseudo-time steps, was used to solve the governing equations. The simulation was continued for 0.16 seconds for each track to obtain the pseudo-steady-state conditions, with no change of the molten pool or track geometry with regard to the moving of the laser beam.

It has been experimentally proved that the geometry and temperature field of three parallel tracks are representative of multi-track depositions [255]; therefore, a three-track deposition was used as inputs in the current work. In order to save computation cost, the initial temperature was reset to 300 K when simulating the following tracks; and the laser was positioned back to parallel the starting point of the previous track. After reaching the pseudo-steady-state, the temperature field was extracted, based on which the heating/cooling rates along the laser scan direction could be calculated using the chain rule below:

$$\frac{dT}{dt} = \frac{dT}{d\vec{x}} \frac{d\vec{x}}{dt} \Big|_{\text{laser-scan}} \quad (3.1)$$

where T is the temperature and $\vec{x}$ is the spatial vector along the laser scan direction.

3.2.2 3D Macro-scale CA Modeling of Ti6Al4V Solidification

To apply the 3D CA model, a 3D domain was created with uniform $5 \times 5 \times 5 \mu\text{m}^3$ cubic grids. Each grid carried three variables: phase state (φ , initial-solid, liquid, nucleus, and interface), crystallographic orientation (consisting of three Euler angles Θ , Φ , and Ψ), and temperature (T , calculated by the DED model). At the beginning of the simulation, all the grids in the domain had the initial-solid state, indicating the state of the substrate. A random angle value between 0° and 90° was assigned to each of the three Euler angles for every CA grid because the experimental observation reveals an almost random crystallographic orientation in the substrate. The solid grids with the same crystallographic orientation were combined to form a grain. As the laser approaches a grid, if the temperature of a grid exceeds the melting temperature ($T_m = T_{\text{liquidus}}$), its phase state will be changed to liquid. Its crystallographic orientation is erased correspondently, and its three

Euler angles are changed to the value of -5 in order to be distinguished from the solid phase. The liquid grid can be changed into solid if the grid becomes the nucleus or interface grids.

CA model predicts solidification in two stages: nucleation and growth. Nucleation is a function of undercooling and occurs on the fusion line (molten pool boundary) or within the molten pool [104, 105, 256]. Wang et al. [257] experimentally proved that heterogeneous nucleation on partially melted powder particles inside the molten pool produced equiaxed grains while the epitaxial growth from the molten pool bottom resulted in columnar grains, which was critically related to the mass deposition rate at a fixed laser energy density. In order to achieve a very dense structure, the selected laser deposition condition used in this paper resulted in producing only elongated columnar β grains of Ti6Al4V [4]; therefore, the current work only simulated the epitaxial growth of β grains onto the fusion line and the nucleation within the molten pool was not considered. Consequently, when the laser beam traveled away, and the temperature of the liquid grids on the fusion line dropped below T_{liquidus} , some of them were randomly selected as nuclei [55, 195]. These nuclei grids first inherited the crystallographic orientations from their closest solid parent grids. When they “grow” to touch the liquid neighboring grids, those liquid grids are captured as interface grids, inheriting the grid variables from the capturing grid.

The growth of an interface grid in the CA model is simulated by a cellular automata-like rule, where each interface grid is assumed to develop with an envelope using the de-centered square algorithm [195]. In the 3D space, this envelope is a regular octahedron, whose diagonal is well aligned with its crystallographic orientation. The half-diagonal of the envelope is defined as:

$$L = \sum_i V(\Delta T) \Delta t \quad (3.2)$$

where Δt is the time step (5×10^{-5} s), and $V(\Delta T)$ is the grain growth velocity that depends on the undercooling ΔT and is approximated with polynomial expressions [55, 104, 105, 256]. In this work, the following polynomial was adopted from Ref. [105]:

$$V(\Delta T) = 2.03 \times 10^{-4} (\Delta T)^2 + 0.544 \times 10^{-4} (\Delta T)^3 \quad (3.3)$$

where $\Delta T = T_m - T$, T_m is the liquidus temperature of Ti6Al4V and T is the actual temperature of an undercooled liquid grid.

Given a period of time, the envelope will grow out of this interface grid and its diagonal tip will touch the neighboring grids. If the touched grid is a liquid grid, it is captured as a new interface

grid and the capturing interface grid's state is then changed to the nucleus. The envelope of this new captured interface grid is centered at the diagonal tip of the capturing envelope and grows with its own growth velocity. Solidification proceeds with continuous transformation of liquid grids to interface grids and further to nucleus grids. Since a grain is represented by a certain crystallographic orientation, and shape and distribution of solidified grains can hence be predicted.

3.2.3 2D Micro-scale PF modeling of Ti6Al4V Solidification

3.2.3.1 Multi-component and Multi-phase PF Modeling of β -grain Solidification

Microstructure evolves by minimizing the free energy of the entire system. No matter how complex the system is, the microstructure evolution can be captured by tracking two types of order parameters in PF models: non-conserved order parameter (ϕ) for structural phases and conserved order parameter (C) for chemical compositions. The composition is usually calculated using a molar fraction for PF models. For a system with N phases and M components, the solute number is $M - 1$. In the entire domain, the two order parameters should satisfy the following constraints at every time moment for a given position in the calculation domain:

$$\text{Phase-field parameter: } \sum_{p=1}^N \phi_p = 1 \text{ and } \phi_p = 1, \phi_{p \neq q} = 0 \quad (3.4)$$

$$\text{Chemical parameter: } \sum_{k=1}^M C_k = 1 \quad (3.5)$$

This multi-phase and multi-component PF model can also be utilized to study multigrain growth [76, 233], where each grain is assigned with a different ϕ_p . A total of $N - 1$ grains grow from the parent phase that is described by ϕ_N . For the competitive growth of β grains during the solidification of Ti6Al4V, $\phi_p (p = 1, 2, \dots, N - 1)$ describes $(N - 1)$ β grains while ϕ_N indicates the parent liquid phase. For any point in the domain, Eq. (3.4) is always satisfied. If multiple ϕ_p exist for a given point in the domain, only the dominant ϕ_p that has the largest value will be retained and all others will be erased.

If neglecting impurity and trace components, there are three dominant components Ti, Al and V in the Ti6Al4V system, and thus $M = 3$. Due to the high mass fraction of Ti (90 wt%), Ti

will be treated as the solvent while Al and V are solutes that require two chemical parameters C_k ($k = \text{Al}, \text{V}$) to track the composition evolution for Al and V. In this section, the general multi-phase and multi-component PF model is derived for the specific application to the polycrystalline growth of β grains during the rapid solidification of Ti6Al4V.

For a system with N -phase and M -component, the total molar Gibbs free energy can be expressed by involving the abovementioned order parameters as [258]:

$$G(\phi_p, C_k, T) = \int_V \left[G_m(\phi_p, C_k, T) + \sum_{p=1}^N \sum_{q>p}^N \frac{\varepsilon_{pq}^2}{2} \nabla \phi_p \nabla \phi_q \right] dV, \quad k = 1, 2, \dots, M-1 \quad (3.6)$$

where G is the total Gibbs free energy of the system, G_m is the local molar free energy density, T is temperature, ε_{pq} is the gradient energy coefficient. The subscript m is the abbreviation of molar.

For multi-grain solidification of β phase in Ti6Al4V system, the total molar Gibbs free energy for the Ti-Al-V system can be written as:

$$G(\phi_p, C_k, T) = \int_V \left[G_m(\phi_p, C_k, T) + \sum_{p=1}^N \sum_{q>p}^N \frac{\varepsilon_{pq}^2}{2} \nabla \phi_p \nabla \phi_q \right] dV, \quad k = \text{Al}, \text{V} \quad (3.7)$$

where T is the temperature in the molten pool of DED-built Ti6Al4V depositions, and is calculated by the DED model.

The molar free energy density $G_m(\phi_p, C_k, T)$ is defined as:

$$G_m(\phi_p, C_k, T) = \frac{1}{V_m} \left\{ \sum_{p=1}^{N-1} h(\phi_p) G_m^\beta(C_{\text{Al}}^\beta, C_{\text{V}}^\beta, T) + \left[1 - \sum_{p=1}^{N-1} h(\phi_p) \right] G_m^L(C_{\text{Al}}^L, C_{\text{V}}^L, T) \right\} + \sum_{p=1}^N \sum_{q>p}^N \omega_{pq} \phi_p^2 \phi_q^2 \quad (3.8)$$

where V_m is the molar volume. The monotonous polynomial $h(\phi_p)$ has the expression of

$h(\phi_p) = \phi_p^3(6\phi_p^2 - 15\phi_p + 10)$ and satisfies $\sum_{p=1}^N h(\phi_p) = 1$, which is used to link the free energies of

different phases or grains. ω_{pq} is the height of the double-well potential that describes the free energy jump at the boundaries of different phases or grains. $G_m^\beta(C_{\text{Al}}^\beta, C_{\text{V}}^\beta, T)$ and $G_m^L(C_{\text{Al}}^L, C_{\text{V}}^L, T)$ are the free energies of β phase and liquid phase of Ti6Al4V, respectively, which are generated based on the thermodynamic database of Ti-Al-V system, and will be further elucidated in Section

3.2.3.2. C_k^β and C_k^L are the local equilibrium compositions of the β (solid) and liquid sides at the β /liquid interface. To calculate C_k^β and C_k^L ($k = \text{Al}, \text{V}$), the Kim, Kim and Suzuki (KKS) model is adopted [225], which defines the phase interface with the same chemical potential μ_k but different compositions as:

$$C_k = \sum_{p=1}^{N-1} h(\phi_p) C_k^\beta + \left[1 - \sum_{p=1}^{N-1} h(\phi_p) \right] C_k^L, k = \text{Al}, \text{V} \quad (3.9)$$

$$\mu_k = \frac{\partial G_m^\beta(C_{\text{Al}}^\beta, C_{\text{V}}^\beta, T)}{C_k^\beta} = \frac{\partial G_m^L(C_{\text{Al}}^L, C_{\text{V}}^L, T)}{C_k^L}, k = \text{Al}, \text{V} \quad (3.10)$$

The governing equations for phase-field and concentration variables are formulated as:

$$\frac{\partial \phi_p}{\partial t} = - \sum_{p \neq q}^N L_{pq} \left(\frac{\delta G}{\delta \phi_p} - \frac{\delta G}{\delta \phi_q} \right) \quad (3.11)$$

$$\frac{\partial C_k}{\partial t} = \nabla \cdot \sum_{k,l=\text{Al},\text{V}} M_{kl} \nabla \frac{\delta G}{\delta C_l} \quad (3.12)$$

where L_{pq} and M_{kl} are the phase field and solute diffusion mobility, respectively. L_{pq} can be determined at a vanishing kinetic coefficient [259].

The derivative terms in Eq. (3.11) and Eq. (3.12) can be calculated as:

$$\frac{\delta G}{\delta \phi_p} = \sum_{p \neq q}^N \left(-\frac{\varepsilon_{pq}^2}{2} \nabla^2 \phi_q + 2\omega_{pq} \phi_p \phi_q^2 \right) + \frac{1}{V_m} \left\{ h'(\phi_p) (G_m^\beta - G_m^L) + \sum_{r=1}^{N-1} h(\phi_r) \sum_{k=\text{Al},\text{V}} \frac{\partial G_m^\beta}{\partial C_k^\beta} \frac{\partial C_k^\beta}{\partial \phi_p} + \left[1 - \sum_{r=1}^{N-1} h(\phi_r) \right] \sum_{k=\text{Al},\text{V}} \frac{\partial G_m^L}{\partial C_k^L} \frac{\partial C_k^L}{\partial \phi_p} \right\} \quad (3.13)$$

$$= \sum_{p \neq q}^N \left(-\frac{\varepsilon_{pq}^2}{2} \nabla^2 \phi_q + 2\omega_{pq} \phi_p \phi_q^2 \right) + \frac{1}{V_m} \left\{ h'(\phi_p) (G_m^\beta - G_m^L) + \sum_{k=\text{Al},\text{V}} \mu_k \left\{ \sum_{r=1}^{N-1} h(\phi_r) \frac{\partial C_k^\beta}{\partial \phi_p} + \left[1 - \sum_{r=1}^{N-1} h(\phi_r) \right] \frac{\partial C_k^L}{\partial \phi_p} \right\} \right\}$$

$$\begin{aligned} \frac{\delta G}{\delta C_l} &= \frac{\delta G_m}{\delta C_l} = \frac{1}{V_m} \left\{ \sum_{p=1}^{N-1} h(\phi_p) \sum_{k=\text{Al},\text{V}} \frac{\partial G_m^\beta}{\partial C_k^\beta} \frac{\partial C_k^\beta}{\partial C_l} + \left[1 - \sum_{p=1}^{N-1} h(\phi_p) \right] \sum_{k=\text{Al},\text{V}} \frac{\partial G_m^L}{\partial C_k^L} \frac{\partial C_k^L}{\partial C_l} \right\} \\ &= \frac{1}{V_m} \left\{ \sum_{k=\text{Al},\text{V}} \mu_k \left\{ \sum_{p=1}^{N-1} h(\phi_p) \frac{\partial C_k^\beta}{\partial C_l} + \left[1 - \sum_{p=1}^{N-1} h(\phi_p) \right] \frac{\partial C_k^L}{\partial C_l} \right\} \right\}, l = \text{Al}, \text{V} \end{aligned} \quad (3.14)$$

In order to get the expressions for $\frac{\partial C_k^\beta}{\partial \phi_p}$, $\frac{\partial C_k^L}{\partial \phi_p}$ in Eq. (3.13) and $\frac{\partial C_k^\beta}{\partial C_l}$, $\frac{\partial C_k^L}{\partial C_l}$ in Eq.

(3.14), partial differentiation is performed on Eq. (3.9), and the following equations are obtained:

$$h'(\phi_p)(C_k^\beta - C_k^L) + \sum_{r=1}^{N-1} h(\phi_r) \frac{\partial C_k^\beta}{\partial \phi_p} + \left(1 - \sum_{r=1}^{N-1} h(\phi_r)\right) \frac{\partial C_k^L}{\partial \phi_p} = 0, k = \text{Al, V} \quad (3.15)$$

$$\sum_{p=1}^{N-1} h(\phi_p) \frac{\partial C_k^\beta}{\partial C_l} + \left[1 - \sum_{p=1}^{N-1} h(\phi_p)\right] \frac{\partial C_k^L}{\partial C_l} = \begin{cases} 1, k = l \\ 0, k \neq l \end{cases}, k = \text{Al, V}; l = \text{Al, V} \quad (3.16)$$

Substituting Eq. (3.15) and Eq. (3.16) into Eq. (3.13) and Eq. (3.14), and then into Eq. (3.12),

$\frac{\delta G}{\delta \phi_p}$ and $\frac{\partial C_k}{\partial t}$ are updated as:

$$\frac{\delta G}{\delta \phi_p} = \sum_{p \neq q}^N \left(-\frac{\varepsilon_{pq}^2}{2} \nabla^2 \phi_q + 2\omega_{pq} \phi_p \phi_q^2 \right) + \frac{h'(\phi_p)}{V_m} \left[(G_m^\beta - G_m^L) - \sum_{k=\text{Al, V}} \mu_k (C_k^\beta - C_k^L) \right] \quad (3.17)$$

$$\frac{\partial C_k}{\partial t} = \nabla \cdot \sum_{k,l=\text{Al, V}} M_{kl} \nabla \frac{\delta G}{\delta C_l} = \frac{1}{V_m} \nabla \cdot \sum_{k,l=\text{Al, V}} M_{kl} \nabla \mu_l \quad (3.18)$$

When the interfacial free energy anisotropy is considered, ε_{pq} in Eq. (3.17) has the same expression as ε in Eq. 2.18.

The concentration diffusion coefficient M_{kl} in Eq. (3.18) is determined by the diffusion matrix as below [259]:

$$D_{kl} = \sum_{k,l=\text{Al, V}} M_{kl} \frac{\partial^2 G_m}{\partial C_k \partial C_l} \quad (3.19)$$

The diffusion matrix for Ti-Al-V system can be expressed as:

$$\mathbf{D} = \begin{pmatrix} D_{\text{Al, Al}} & D_{\text{Al, V}} \\ D_{\text{V, Al}} & D_{\text{V, V}} \end{pmatrix} \quad (3.20)$$

If all the off-diagonal components in the diffusion matrix are zero, the solute diffusion is considered independently, and the concentration evolution of each solute can be calculated similarly to binary alloys. In a real system with multiple solutes, however, the solute diffusion actually affects each other, and the cross-diffusion between solutes indicated by the off-diagonal diffusion parameters should be considered. D_{kl} in the diffusion matrix (Eq. (3.20)) is calculated based on the fraction-weighted average of D_{kl}^β and D_{kl}^L as:

$$D_{kl} = \left\{ \sum_{p=1}^{N-1} h(\phi_p) D_{kl}^\beta + \left[1 - \sum_{p=1}^{N-1} h(\phi_p)\right] D_{kl}^L \right\}, k = \text{Al, V}; l = \text{Al, V} \quad (3.21)$$

It is worth mentioning that rapid solidification is prone to causing solute trapping [230, 231], which is known as the phenomenon that solute atoms are trapped in the solid phase due to the lack of time to diffuse back to liquid, which results in a concentration profile deviating from the equilibrium solidification [226-228]. This solute trapping phenomenon becomes more serious with the increase of the numerical interface width. In order to alleviate solute trapping, an anti-trapping current is always added to the concentration equation to make the concentration distribution to be independent of the length scale for the numerical interface with, as shown in Eq. (3.22) [231]:

$$\frac{\partial C_k}{\partial t} = \nabla \cdot \left(\sum_{k,l=Al,V} M_{kl} \nabla \frac{\delta G}{\delta C_l} - j_k \right) \quad (3.22)$$

The anti-trapping term j_k for each solute has the following expression:

$$j_k = -a_k C_\infty^k (1 - K_{eq}^k) W e^{u^k} \sum_{p=1}^N \frac{\partial \phi_p}{\partial t} \frac{\nabla \phi_p}{|\nabla \phi_p|}, k = Al, V \quad (3.23)$$

where a_k is the parameter to control the magnitude of the anti-trapping current, C_∞^k is the far-field solute concentration, K_{eq}^k is the equilibrium partition coefficient between the solid and liquid for the solute k , and has the expression of $K_{eq}^k = C_{eq}^{S^k} / C_{eq}^{L^k}$. u^k is a dimensionless parameter [231].

In terms of a multi-component system, the K_{eq}^k value for each solute can be obtained by its binary phase diagram by treating other components to be the solvent. As for the ternary Ti6Al4V system, the solvent is Ti. For 6 wt% Al and 4 wt% V, the initial molar fraction for aluminum and vanadium is $C_{Al}^0 = 0.102$ and $C_V^0 = 0.036$, respectively. The binary phase diagrams of Ti-Al and Ti-V are presented in Figure 3.3(a) and (b), respectively. As is clearly shown in these two phase diagrams, both the solid (β) and liquid curves for the Al composition less than 22 at.% and for V less than 40 at.% overlap each other, indicating an equal equilibrium composition $C_{eq}^{S^k}$ and $C_{eq}^{L^k}$; therefore, both $K_{eq}^{Al} = C_{eq}^{S^{Al}} / C_{eq}^{L^{Al}}$ and $K_{eq}^V = C_{eq}^{S^V} / C_{eq}^{L^V}$ are equal to 1, resulting in j_{Al} and j_V to be 0. This implies that there is no requirement to consider the anti-trapping phenomenon for Ti6Al4V solidification. This finding indicates that the predicted concentration distributions of Al and V during rapid solidification are physical concentrations with regards to the solidification condition and thermal history only.

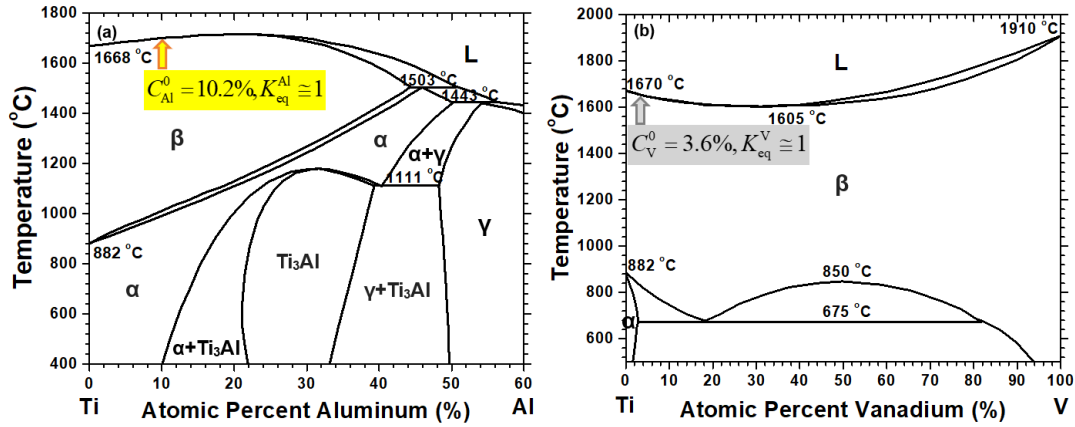


Figure 3.3. Phase diagram of (a) Ti-Al [260] and (b) Ti-V binary alloy systems [261].

Table 3.2. Simulation parameters for phase-field modeling of Ti6Al4V solidification.

Parameters	Symbol	Value	Unit
Mesh size	$\Delta x, \Delta y$	1×10^{-8}	m
Time step	Δt	3×10^{-9}	s
Interface width	2λ	$8 \Delta x$	m
Anisotropy strength	δ	0.2	-
Preferential growth direction	θ_p^0	0	radian
Symmetric mode number	k	4	-
Phase-field mobility	L_{pq}	6.2×10^{-5}	$\text{m}^4/\text{s} \cdot \text{J}$
Interface energy	σ	0.093	J/m^2
Molar volume	V_m	1.06×10^{-5}	m^3/mol
Interface parameter	α	2.2	-

To conduct the PF modeling, an explicit finite difference method was utilized to discretize the governing equations. Zero flux boundary conditions were applied. Modeling of nucleation was not considered in this work but can be found in Ref. [234]. Instead, rectangular seeds with various sizes were randomly placed at the bottom of the simulation domain. Programming was done using parallel computing MPI of 51 processors to carry out the computation. Computational parameters and the independent and cross-diffusion mobility data for performing the PF modeling of Ti6Al4V solidification are summarized in Table 3.2 – Table 3.4. It should be noted that diffusion coefficients should be slightly concentration and temperature-dependent [262]. Due to the lack of available data for the diffusion coefficients in the liquid phase, some assumption was made to estimate the cross-diffusion coefficients in the liquid phase (Table 3.4).

Table 3.3. Impurity diffusion coefficients for TiAlV alloy.

Parameter	Liquid, m ² /s	β-BCC A2, m ² /s [262]
Impurity diffusion coefficient of Al in Ti	1.0×10 ⁻¹¹	1.3×10 ⁻⁷ exp(-150000/RT)
Impurity diffusion coefficient of V in Ti	1.0×10 ⁻¹¹	4.3×10 ⁻⁷ exp(-165000/RT)

Table 3.4. Approximated cross-diffusion mobility data for TiAlV alloy.

Parameter	Liquid, m ² /s	β-BCC A2, m ² /s [262]
D_{AlAl}^{Ti}	5.0×10 ⁻¹²	7.4×10 ⁻¹³
D_{AlV}^{Ti}	1.0×10 ⁻¹²	1.2×10 ⁻¹³
D_{VAl}^{Ti}	1.0×10 ⁻¹²	1.7×10 ⁻¹³
D_{VV}^{Ti}	5.0×10 ⁻¹²	4.1×10 ⁻¹³

Note: The cross-diffusion mobility data for the solid β phase are for the composition of Ti6.4Al4.5V, which is close to Ti6Al4V.

3.2.3.2 Thermodynamic and Kinetic Data of Ti-Al-V System

Above about 1473 K [263], the β phase displays a disordered BCC structure, which is known as BCC_A1. When the temperature drops below this threshold, the disordered BCC_A1 is changed to ordered BCC_A2. The current work focuses on the solidification of β phase, where the temperature is no less than the solidus temperature 1878 K; therefore, only the disordered BCC_A1 phase is studied. In this way, the standard solution model is used to formulate the molar Gibbs energy for both the β phase and liquid phase:

$$G_o^\varphi = X_{Ti} {}^\circ G_{Ti}^\varphi + X_{Al} {}^\circ G_{Al}^\varphi + X_V {}^\circ G_V^\varphi \quad (3.24)$$

$$G_{mix}^{ideal} = RT(X_{Ti} \ln X_{Ti} + X_{Al} \ln X_{Al} + X_V \ln X_V) \quad (3.25)$$

$$\begin{aligned} G_{mix}^{ex} = & X_{Ti} X_{Al} [L_{TiAl,0} + L_{TiAl,1}(X_{Ti} - X_{Al})^1 + L_{TiAl,2}(X_{Ti} - X_{Al})^2] \\ & + X_{Al} X_V [L_{AlV,0} + L_{AlV,1}(X_{Al} - X_V)^1 + L_{AlV,2}(X_{Al} - X_V)^2] \\ & + X_{Ti} X_V [L_{TiV,0} + L_{TiV,1}(X_{Ti} - X_V)^1 + L_{TiV,2}(X_{Ti} - X_V)^2] + X_{Ti} X_{Al} X_V L^{ter} \end{aligned} \quad (3.26)$$

where the expression of G_{mix}^{ex} in Eq. (3.26) is derived by taking Ti as the solvent while Al and V are solutes. φ indicates the liquid phase (L) or β phase (BCC_A2). ${}^\circ G_{Ti}^L$, ${}^\circ G_{Al}^L$, ${}^\circ G_V^L$, ${}^\circ G_{Ti}^{BCC_A2}$,

${}^\circ G_{Al}^{BCC_A2}$, ${}^\circ G_V^{BCC_A2}$ are the Gibbs energies of each component in liquid or BCC_A2 phase in their

standard states, and can be found in the Scientific Group Thermodata Europe (SGTE) element database [235]. The values for interaction parameters are summarized in Table 3.5.

Table 3.5. Interaction parameters of Ti-Al-V system. The values are from Ref. [264].

Parameter	Liquid (J/mol) (298.15 K < T < 6000 K)	BCC_A2 (disordered β) (298.15 K < T < 6000 K)
$L_{\text{TiAl},0}$	$-118048+41.972T$	$-132903+39.961T$
$L_{\text{TiAl},1}$	$23613-19.704T$	-4890
$L_{\text{TiAl},2}$	$34757-13.844T$	400
$L_{\text{TiV},0}$	-487.022551	$9782.97194-2.1414765T$
$L_{\text{TiV},1}$	2730.75528	827.027631
$L_{\text{TiV},2}$	0	0
$L_{\text{AlV},0}$	$-78539.7392+10.0693642T$	$-79105.7344+0.654036617T$
$L_{\text{AlV},1}$	17593.7037	6644.63293
$L_{\text{AlV},2}$	0	0
L^{ter} [263]	0	0

3.2.4 2D Meso-scale CA-PF Modeling of Ti6Al4V Solidification

The integrated CA-PF model is established to reveal the grain details on the sub-grain level. This integrated model consists of two components: the CA component tracks the evolution of the dendritic grain morphology and calculates the solute redistribution $C_{e,k}$; while the PF component calculates the local growth kinetics for the CA component including the instantaneous growth velocity $V(t_i)$ at the solidification front and the equilibrium solute partition on the solid side C_k^β and liquid side C_k^L at the solid/liquid interface. The main theory of the integrated CA-PF model is presented in this section while a thorough description can be found in Ref. [200].

3.2.4.1 2D CA Component

A 2D domain with square cells ($0.2 \mu\text{m} \times 0.2 \mu\text{m}$) is created for the CA component, which still simulates the solidification using the cellular automata-rule described in Section 3.2.2. The

major difference between this 2D CA model and the 3D CA model is that the 2D CA model calculates the solid fraction for every CA interface cell and the associated concentration redistribution in every CA time step. Therefore, each 2D CA cell carries variables of phase state (nuclei, liquid, interface, re-solid), concentration $C_{e,k}$ and temperature T . For the CA interface cells, extra variables of interface normal direction n , interface curvature κ and crystallographic orientation θ are also defined. Since the dendrite tip has a positive curvature in the 2D domain, each CA interface cell is assumed as a circular with a distinctive curvature. The entire interface is composed of these consecutive circulars. The algorithm to calculate n can be found in Raghavan's work [265] while that of Martorano et al's work [266] was used to calculate κ . A random crystallographic orientation of $0^\circ - 90^\circ$ is assigned to the nuclei cells on the fusion line.

The interface cell will become re-solid when its solid fraction f_s reaches 1. f_s is calculated using Eq. (3.27):

$$f_s = \frac{L}{\Delta x(|\sin \theta| + \cos \theta)} \quad (3.27)$$

where Δx is the mesh size of the 2D CA domain, L is the half diagonal length of the 2D de-centered square envelope. L is also calculated with Eq. (3.2); however, the growth velocity $V(t_n)$ is a function of both temperature and solute concentration in the 2D CA component and is provided by the PF component.

The solute redistribution including the solute partition at the interface and solute diffusion in bulk solid and liquid phases is calculated with Eq. (3.28):

$$\frac{\partial C_{e,k}}{\partial t} = \nabla \cdot (D_{e,k} \nabla C_{e,k}) + \frac{\partial f_s}{\partial t} (C_k^L - C_k^\beta), (k = Al, V) \quad (3.28)$$

where C_k^L and C_k^β are the liquid and solid solutes at the interface, which are calculated by PF modeling via Eqs. (3.9) and (3.10). $C_{e,k}$ and $D_{e,k}$ are the equivalent composition and diffusion coefficients, and are defined using Eq. (3.29):

$$\text{For liquid and interface cells: } C_{e,k} = C_{L,k}, D_{e,k} = D_{L,k} \quad (3.29a)$$

$$\text{For solid cells: } C_{e,k} = C_{\beta,k}, D_{e,k} = D_{\beta,k} \quad (3.29b)$$

For interface cells, $C_{L,k}$ is the concentration in the liquid portion while for the solid portion, the concentration $C_{\beta,k}$ is updated using the equation below:

$$C_{\beta,k} = \frac{\sum_i \Delta f_s(t_n) C_k^\beta(t_n)}{\sum_i \Delta f_s(t_n)} \quad (3.30)$$

where $\Delta f_s(t_n)$ is the solid fraction increment at time t_n . The calculated $C_{\beta,k}$ will be assigned to the cell once its stage changes from interface to re-solid.

3.2.4.2 1D PF Component

The PF component is used to provide the CA component with instantaneous growth kinetics based on the local solidification conditions (temperature T , solute concentrations in liquid $C_i(x)$, interface normal direction n , interface curvature κ). The growth of a dendrite tip is primarily dominated by the local composition diffusion in the normal direction of the liquid/solid interface; therefore, using a 1D PF model to calculate the growth kinetics at the solidification front is a reasonable approximation. For dendrites growing on the 2D domain, they have positive curvature. The 1D PF model is hence more accurate to derive in polar coordinates. In addition, modeling of single-grain growth is sufficient for calculating growth kinetics. The details for calculating the competitive polycrystalline β -grain growth in the 2D Cartesian coordinate system have been exhaustively described in Section 3.2.3. The derived 1D PF model for single-grain growth in polar coordinates is presented below:

$$\frac{1}{L_\phi} \frac{\partial \phi}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} \left(\varepsilon^2 r \frac{\partial \phi}{\partial t} \right) - \frac{\partial G_m}{\partial \phi} \quad (3.31)$$

$$\frac{\partial C_k}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} \left(r \sum_{k,l=A1,V} \left(D_{kl} \frac{\partial C_l}{\partial r} \right) \right) + \frac{1}{r} \frac{\partial}{\partial r} \left(r \sum_{k,l=A1,V} \left(M_{kl} \frac{\partial^2 G_m}{\partial C_j \partial \phi} \right) \frac{\partial \phi}{\partial r} \right) \quad (3.32)$$

where r is the local radius for a circular interface. ϕ is the phase field parameter and is equal to 1 or 0 for the solid (β) and liquid phase while $0 < \phi < 1$ for the liquid/solid interface.

For single-grain growth, the molar free energy density $G_m(\phi, C_k, T)$ is simplified as:

$$G_m(\phi, C_k, T) = \frac{1}{V_m} \left\{ h(\phi) G_m^\beta(C_{Al}^\beta, C_V^\beta, T) + [1 - h(\phi)] G_m^L(C_{Al}^L, C_V^L, T) \right\} + \omega g(\phi) \quad (3.33)$$

where $g(\phi) = \phi^2(1-\phi)^2$ is the double well function. All other parameters can be found in Section 3.2.3.

The solute concentrations in liquid $C_k(x)$ are inputs for the PF component to calculate the growth kinetics. The concentration profile $C_k(x)$ is along the normal direction of the liquid/solid interface and is expressed as:

$$C_k(x) = C_{\infty,k} + [C_k^L - C_{\infty,k}] \exp[-A_k x], k = \text{Al, V} \quad (3.34)$$

where x is the distance from the interface to the liquid, C_k^L is the liquid concentration at the interface from the last step while $C_{\infty,k}$ is the liquid concentration at infinity. A_k is a variable to describe the steepness of the concentration profile. To calculate A_k , a normal vector is generated for a CA interface cell, and a number of points are selected along the vector. The concentration value of each point is interpolated based on the concentration values of the four closest CA cells. Details can be found in Ref. [200]. The concentration profile is then re-mapped onto the PF domain using Eq. (3.34). The mid-point of the PF interface ($\phi = 0.5$) is positioned at $r = 1/\kappa$ in the polar coordinate system.

It should be noted that while calculating the growth kinetics the temperature of the PF domain is assumed constant since the PF mesh size and time step are much smaller than the CA component. Once the PF calculation has become converged, the instantaneous growth velocity is calculated by dividing the growth of dendrite tip with the time duration. The obtained equilibrium solute partition C_k^L and C_k^β will also be given back to the CA component to update dendrite growth and concentration redistribution. It can be seen that the PF model should be called to calculate the growth kinetics for every CA interface cell at every CA time step. To save calculation cost, some sample solidification conditions are pre-selected to calculate a growth kinetic database. The database should cover a large number of sample solidification conditions to produce a reasonable interpolation for the real growth kinetics for an actual solidification condition.

3.2.5 Phase Prediction Model for $\beta \rightarrow \alpha/\alpha'$ Transformation

To simulate the solid-state phase transformation of $\beta \rightarrow \alpha/\alpha'$ during the DED process for Ti6Al4V, a diffusion/diffusionless kinetic model that was first developed by Ashby and Easterling [114] to study the solid-state phase transformation and hardness evolution for carbon steels was considered. The model was then adapted by Hahn et al. [126] to study the phase transformation and assess the hardness change during the laser surface hardening of Ti6Al4V. In a recent publication dealing with laser welding of Ti6Al4V [110], the efficacy of this kinetic model was successfully demonstrated for addressing the phase and hardness evolution in FZ and HAZ regions in response to different welding conditions. For brevity, only the core theory and formulations are presented in this paper and readers are suggested to refer to the abovementioned publications for more details.

It is well known that the prior β grains formed during the Ti6Al4V solidification will further experience solid-state $\beta \rightarrow \alpha/\alpha'$ phase transformation when the temperature drops below $T_{\beta\text{-trans}}$. This transformation is determined by temperature and cooling rate. Elmer et al. [267] used in-situ time-resolved x-ray diffraction to track the phase transformation during gas tungsten arc welding of Ti6Al4V and uncovered that the diffusionless martensitic transformation began below M_s and occupied the entire FZ. In the HAZ, $\beta \rightarrow \alpha$ transformation was initiated at $T_{\beta\text{-trans}}$, and after approximately 5–10% of the β transformed to α , $\beta \rightarrow \alpha'$ took place and was terminated below M_s [267]. Table 3.6 summarizes the resultant phases after $\beta \rightarrow \alpha/\alpha'$ phase transformation as a function of cooling rate according to the continuous cooling transformation (CCT) phase diagram [112]. The formation of α' has two preconditions: the temperature lower than M_s and cooling rate higher than 410 K/s. It should be noted that the M_s temperature may vary depending on the initial microstructure and composition homogeneity [268, 269]. In this work, the M_s temperature was selected as 1053 K [41] (Figure 3.2). To simulate the solid-phase $\beta \rightarrow \alpha/\alpha'$ transformation in FZ and HAZ during the DED process for Ti6Al4V, the predicted thermal history including the temporal and spatial temperature profiles and heating/cooling rates, which were predicted by the DED model, were incorporated to the kinetic phase prediction model.

Table 3.6. $\beta \rightarrow \alpha/\alpha'$ transformation as a function of the cooling rate in Ti6Al4V [112].

Cooling rate, K/s	> 410	410 – 20	20 – 1.5	< 1.5
Resultant phases	α' martensite	α and α'	α	α and retained β

In order to accurately quantify α and α' phases in the final microstructure, the volume percentage of prior β phase before $\beta \rightarrow \alpha/\alpha'$ transformation must be calculated first. During the DED process, the FZ undergoes a melting and resolidification cycle, resulting in a complete β phase upon solidification of the molten pool; therefore, the volume fraction of prior β phase in FZ is 1. In the HAZ, the peak temperature (T_p) for every grid is between $T_{\beta\text{-trans}}$ and T_{liquidus} , so the initial α phase in the Ti6Al4V substrate will be subjected to the transformation to β . The $\alpha \rightarrow \beta$ transformation is a diffusion-controlled process, which requires significant superheating and/or enough time for completion [267]. Since vanadium is a β -stabilizer while α is stabilized by aluminum, the diffusion of vanadium out of the initial β phase into the α phase drives the transformation of α . The volume fraction of the total β phase, β_n , including the initial β and the newly formed β for a grid in the FZ and HAZ domain is calculated using Eq. (3.35) [110]:

$$\beta_n = \begin{cases} 1, & \text{in FZ } (T_p > T_{\text{liquidus}}) \\ 1 - (1 - \beta_i) \cdot \exp\left\{-\frac{12\beta_i^{2/3}}{\pi^{1/2}g} \ln\left[\frac{V_c - V_\alpha}{2(V_\beta - V_\alpha)}\right] (Dt)^{1/2}\right\}, & \text{in HAZ } (T_{\beta\text{-trans}} < T_p < T_{\text{liquidus}}) \end{cases} \quad (3.35)$$

where β_i is the volume percentage of the initial β phase in the Ti6Al4V substrate, g is the average diameter of initial β grains. V_α and V_β are the measured average vanadium content in the initial α phase and β phase while V_c is the critical vanadium content for transformation. The value of V_α , V_β and V_c can be found in Ref. [126]. D is the diffusion of vanadium in β phase and t is time. $(Dt)^{1/2}$ indicates the diffusion distance. For a non-isothermal cycle, Dt has the following expression [110, 126]:

$$Dt = \int_{t_1}^{t_2} D_0 \exp\left(-\frac{Q}{RT(t)}\right) dt \quad (3.36)$$

where D_0 is the diffusion coefficient of vanadium in β phase ($1.6 \times 10^{-8} \text{ cm}^2/\text{s}$), Q is the activation energy (123.9 kJ/mol), R is the gas constant (8.314 J/(mol·K)). $T(t)$ is the temporal and spatial temperature profile simulated by the DED model. t_1 and t_2 are time moments. In the HAZ domain, every grid will experience two time moments when the temperature equals $T_{\beta\text{-trans}}$ during a heating/cooling cycle. If t_1 and t_2 are selected at these two moments separately, the maximum (final) volume fraction of β phase before $\beta \rightarrow \alpha/\alpha'$ transformation for any grid in the HAZ domain can be obtained.

When the temperature further drops below $T_{\beta\text{-trans}}$, $\beta \rightarrow \alpha/\alpha'$ transformation takes place. A complete α' transformation occurs at the cooling rate higher than 410 K/s passing below M_s while a mixture of α and α' will be formed if the cooling rate is between 410 K/s and 20 K/s (Table 3.6). The massive α was reported to have a similar formation mechanism, composition, and crystal structure to α' martensite such that it was always treated as the same phase as α' [111-113]. In this work, the nucleation of α grain boundary and α platelets is not considered, and these two α morphologies are not distinguished. The formed volume fraction of α' is calculated as:

$$\alpha'_f = \beta_n \cdot \alpha'_{fi} \quad (3.37)$$

where α'_{fi} is the intermediate partial phase transformation variable accounting for the volume fraction of the formed α' , which is simplified with the linear expression $\alpha'_{fi} = (\dot{T} - 20)/390$ [110], according to the CCT phase diagram [112]. $\dot{T}$ is the local cooling rate calculated at $T_{\beta\text{-trans}}$ for simplicity and is calculated using Eq. (3.1). For the local cooling rate that is higher than 410 K/s or lower than 20 K/s, α'_{fi} equals 1 or 0, respectively. Since the cooling rate in FZ is in the order of 10^4 K/s, the FZ is expected to be composed of full α' martensite while the HAZ consists of a mixture of α and α' after the solid-state phase transformation. This model is on the assumption that the cooling curves between $T_{\beta\text{-trans}}$ and M_s are approximately linear and hence will produce errors when the assumption does not hold true. However, as shown in Figure 3.5(d), the cooling curves in the DED process used in this study are approximately linear, indicating an approximately constant cooling rate for a given location in the deposition when the temperature drops below

$T_{\beta\text{-trans}}$. It should be noted that a tiny amount of β , estimated to be less than 5 vol % based on the average value from microstructure characterization of typical regions in the HAZ, will be retained to the room temperature in the HAZ if the cooling rate at $T_{\beta\text{-trans}}$ is lower than 1.5 K/s [112]. Jadhav et al. [270] studied the effect of volume fraction of α and transformed β on the high cycle fatigue properties of bimodal Ti6Al4V alloy, and the indicated hardness of β is about 39 HRC while that of α is about 30 HRC via linear interpolation of the contribution of α and β phases to the overall hardness based on rules of mixtures. If considering 5 vol% retained β in the final microstructure, the relative error of the predicted hardness is approximately in the range of 0.57% (only $\alpha' + \beta$ in the final microstructure) – 1.5% (only $\alpha + \beta$ in the final microstructure); therefore, the effect of β phase on the hardness assessment is neglected in order to simplify the calculation. Consequently, the final phase in FZ and HAZ is assumed to be α' , α or a mixture of both. The microhardness for every grid in the domain is thus accessed based on the rules of mixtures:

$$H = \alpha'_f H_{\alpha'} + (1 - \alpha'_f) H_{\alpha} \quad (3.38)$$

where H_{α} and $H_{\alpha'}$ are the hardness of the α phase (300 HV or 30 HRC) and α' phase (427 HV or 44 HRC, a measured value with 100% α') [126].

3.3 Results and Discussion

3.3.1 DED Modeling of Ti6Al4V Tracks and Validation

Figure 3.4 illustrates the predicted free surface and temperature distributions for the DED built single, two and three tracks. The free surface was acquired by plotting the zero levelset isocontour, which indicates the interface between the gas and metal. In Figure 3.4(d), the 3D view of temperature distributions along the scan direction (XY plane) and on the central cross-section (YZ plane) are shown. In order to depict the molten pool, temperatures above T_{liquidus} (1933 K) were plotted red. As is clearly shown in Figure 3.4, when depositing subsequent tracks, part of the previous track and the top zone of the substrate will be melted. With proper hatch spacing between tracks, a smooth layer surface is obtained.

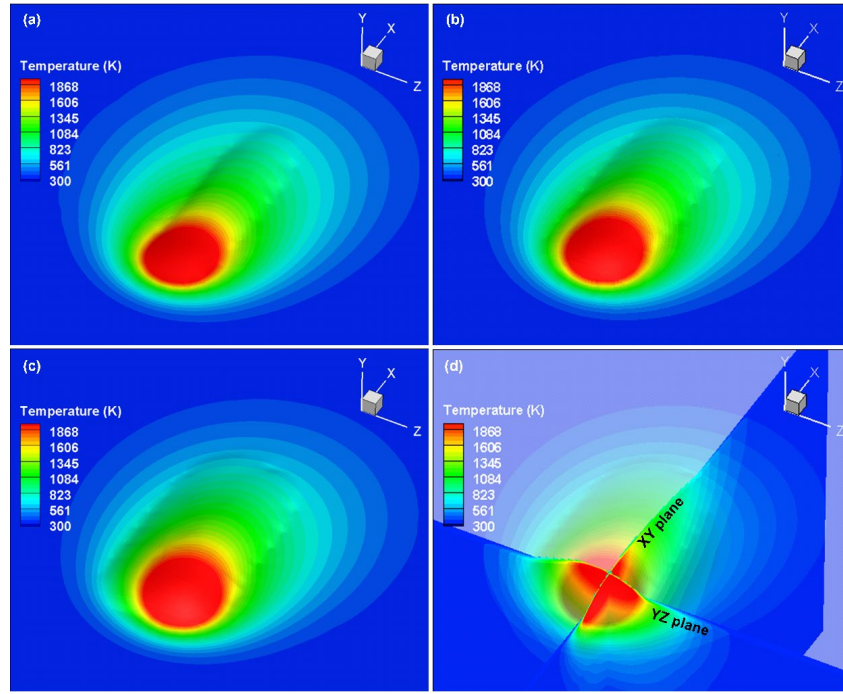


Figure 3.4. Top views of predicted free surface indicated by the levelset value of zero and temperature distributions for the DED-deposited (a) single-track, (b) two-track, (c) three-track Ti6Al4V deposits. (d) A 3D view of temperature distributions on different planes.

Figure 3.5 illustrates the predicted temperature field for the DED-built single-track Ti6Al4V and the schematic view of the track's cross-section and horizontal-section. The inset of Figure 3.5(a) shows the extracted temperature field used as inputs for the 3D CA modeling of grain distribution, which only covers half of the molten pool located at $Z \geq 0$ (rectangular frame). The results for two and three tracks are not shown due to their similarity to the single track case. The track's free surface is the zero levelset isocontour, which indicates the interface between gas and metal. To depict the molten pool a maximum temperature of T_{liquidus} are plotted, where T_{liquidus} equals the isotherm of the FZ boundary. In the extracted temperature domain, the predicted temperature distribution is plotted with a peak temperature of 2682 K in the molten pool. On the central XY plane, a total of six temperature curves are extracted at different locations along the Y-axis with an equivalent time interval passing the laser beam center, as displayed in Figure 3.5(d). Since the extracted temperature field is quasi-steady-state, the plotted temperature profiles remain unchanged at each incremental movement of the laser beam. The simulation is defined in a 3D

Cartesian coordinate, as shown in Figure 3.5(b) for the cross-section and in Figure 3.5(c) for the horizontal-section.

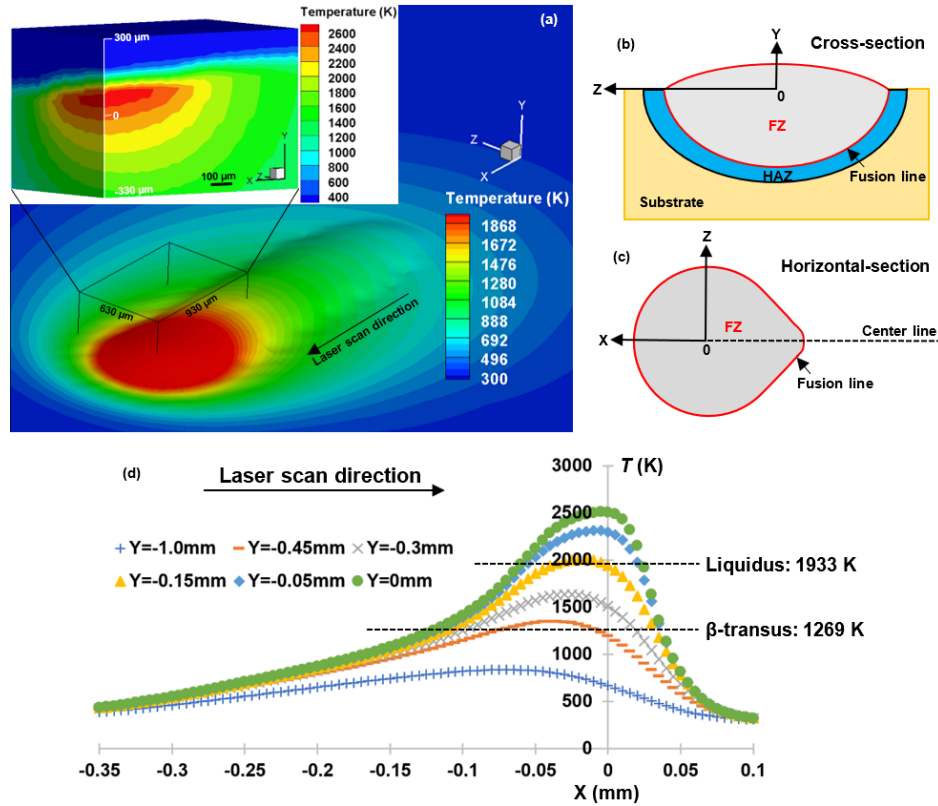


Figure 3.5. (a) The predicted temperature field of the DED-built single-track Ti6Al4V and the extracted temperature field for 3D CA modeling as well as (d) the extracted temperature curves at different locations along the Y-axis on the central XY plane. The schematic view of the track's (b) cross-section and (c) horizontal-section.

In order to validate the DED model, the predicted free surface and temperature field on the central cross-section of single to three-track depositions are used to provide a visual comparison with the experimental results. Figure 3.6 depicts the predicted free surface and extracted isotherms for the FZ boundary (T_{liquidus}) and HAZ boundary ($T_{\beta\text{-trans}}$) that are superimposed on the experimental microstructure for each of the experiments: one, two, and three track depositions, where the solid lines are simulation results while the dashed lines are experimental observations. As clearly shown in Figure 3.6, the free surface, FZ boundary and HAZ boundary, especially the FZ boundary, are well predicted by the DED model; however, the error associated with the prediction increases with the increase of track numbers. Throughout the prediction of the deposition process, the depth of the HAZ is accurately captured by the model, though the width deviates from the experimental

data by up to 120 μm for the three-track case. The geometry of the free surface for single and two-tracks is predicted in good agreement with experimental results, although the error increases to nearly 50 μm for the third track.

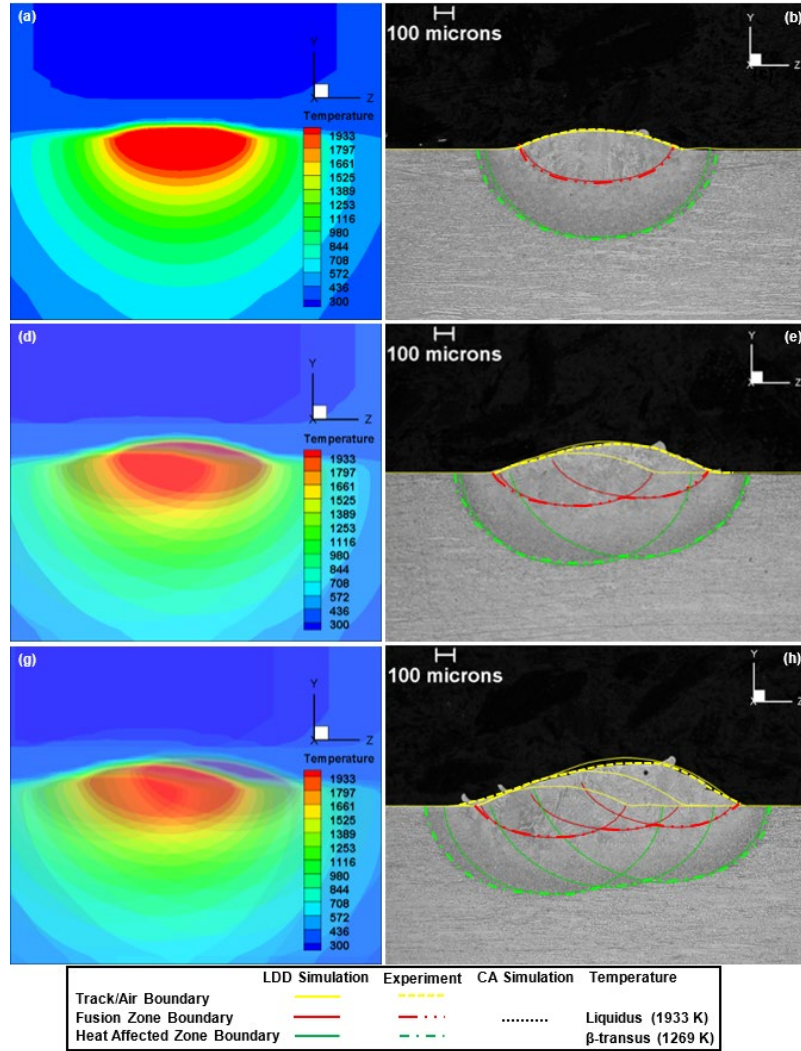


Figure 3.6. Cross-section views of predicted free surface, fusion zone (FZ) and heat affected zone (HAZ) boundaries compared with experimental observations for (a, b) single-track, (c, d) two-track, (e, f) three-track Ti6Al4V deposits built by the DED process.

It should be noted that the cross-section shape may not be consistent throughout a long track due to the factors such as the adhesion of partially melted particles to the track surface, the contamination on the substrate surface and the sudden instability of the argon flow; therefore, an estimated error within 5% is expected for the experimental profile. Given this error, the predicted geometry and temperature fields are representative of the experimental data, and can hence be

utilized in phase prediction modeling. From previous literature, the track geometry of a third parallel track on a substrate is known to be representative of that from any additional tracks [271]. The temperature field and free surface profiles will not change significantly for subsequent tracks and can, therefore, be extracted as inputs to predict the material phases of any multi-track deposition process.

The temperature fields and heating/cooling rates along the laser scan direction (XY plane) are depicted in Figure 3.7. The extracted temperature contours and heating/cooling rates at different locations in the deposition are also presented in Figure 3.7(c) and (d), respectively. The heating/cooling rate for a given location is obtained using Eq. (3.1). Since the pseudo-steady-state temperature field is extracted, the plotted temperature profile and heating/cooling rates shown in Figure 3.7 remains unchanged at each incremental movement of the laser beam. In total, six locations along the Y-axis are analyzed with an equivalent time interval passing the laser beam center. The predicted peak temperature at $Y=0$ is about 2511 K. The peak heating rate at the molten pool front and the cooling rate at the back of the molten pool is about 6.9×10^4 K/s and 2.4×10^4 K/s, respectively. Both the maximum temperature and heating/cooling rates decrease with the position downwards to the bottom of the molten pool. Since the current work focuses on the solidification of β phase, only the thermal information in the molten pool is considered.

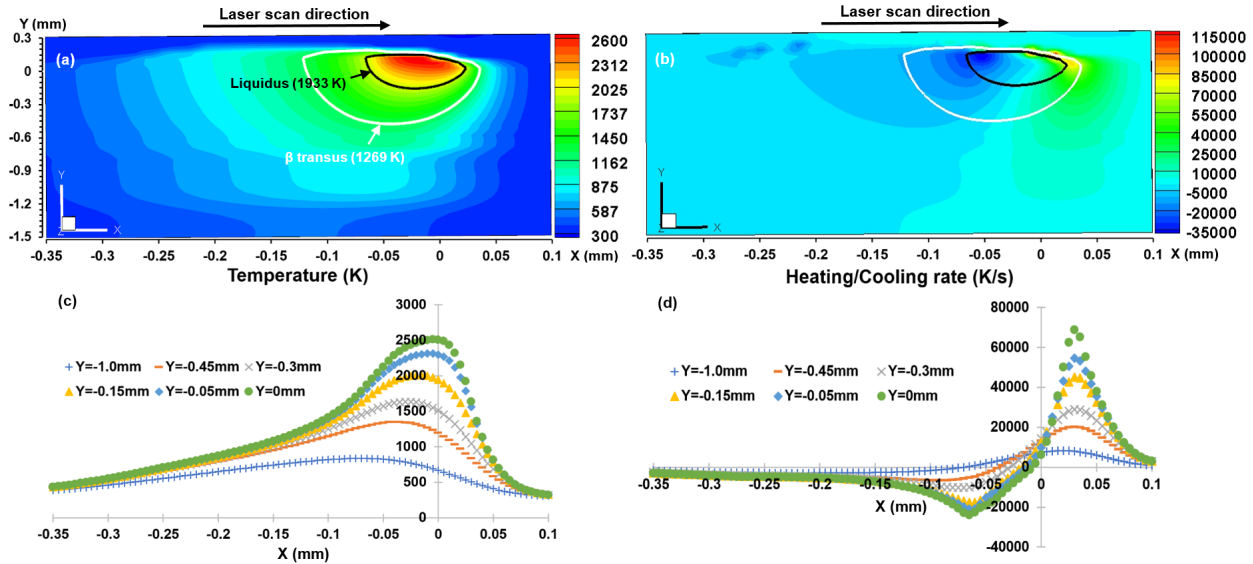


Figure 3.7. (a) Temperature fields and (b) heating/cooling fields on the central XY plane along the laser scan direction. (c) The extracted temperature profiles and (d) heating/cooling curves at different locations along the Y-axis predicted by the DED model for the DED-built single-track Ti6Al4V.

3.3.2 3D Macro-scale CA Modeling of Ti6Al4V Solidification

Incorporated with the extracted temperature field shown in the inset of Figure 3.5(a), Figure 3.8 exhibits the 3D CA modeling of the competitive growth and distribution of β grains upon solidification of the molten pool as the laser beam travels along the positive X direction for single-track Ti6Al4V. The simulated β -grain morphology on the horizontal-section of $Y=0$ is verified with the microstructure result shown in Figure 3.8(d). The third Euler angle (gamma, Ψ) is plotted with different colors to illustrate the grain morphology since a grain has a specific crystallographic orientation and is indicated by a certain gamma value. In this work, the grains predicted by the 3D CA modeling are all marked out by the gamma angles.

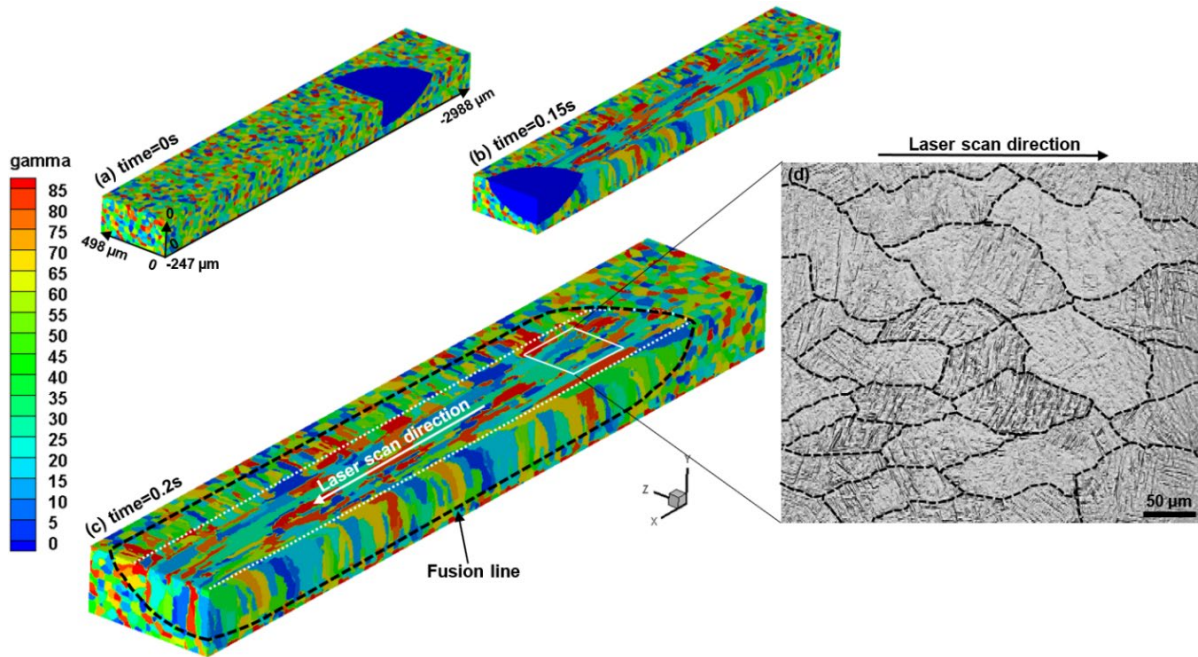


Figure 3.8. (a-c) Simulated 3D view of competitive growth and distribution of β grains upon solidification of the single-track Ti6Al4V molten pool as laser scans along the positive X direction. The growth pattern of β grains on the horizontal-section of $Y=0$ is validated with (d) the microstructure result.

At the beginning of the simulation, the substrate is occupied by the equiaxial grains that have a uniform grain size and various orientations. After the cross-section is passed by the laser beam, the resolidified microstructure in the FZ mainly features elongated β grains of columnar shape, which grow epitaxially from the partially melted grains on the fusion line that is marked out by the black dashed lines in Figure 3.8(c). As the solidification gets close to the central zone of the molten pool, the growth front of the columnar β grains on cross-section and longitudinal-section

(XY plane) tilts towards the laser scan direction. In the central zone of the molten pool, the growth front of β grains completely rotates to align with the laser scan direction, as shown on the horizontal-section of $Y=0$, which is well validated by the microstructure result (Figure 3.8(d)). While approaching the central zone of the molten pool, the solidification front of β grains begins to tilt and eventually rotates by 90° to align with the laser scan direction. This feature has been successfully validated by the microstructure characterization shown in Figure 3.8(d).

The growth pattern of β grains is governed by the thermal history of the DED process. For an AM-deposited track, the shape of its molten pool resembles a “bowl”, and the isotherms are parallel to the “bowl” surface, as illustrated by the inset in Figure 3.6. Consequently, the temperature gradient is perpendicular to the isotherms downwards to the unmelted substrate, and β grains, in turn, nucleate from the fusion line and epitaxially grow upwards to the center of the molten pool. Since the laser keeps moving instead of interacting with the substrate motionlessly, the back zone of the molten pool becomes another path of heat dissipation other than the vertical conduction downwards to the “bowl” surface. When the solidification gets close to the central zone of the molten pool, the temperature gradient turns rapidly to be almost opposite to the laser scan direction. As a result, the pool tail becomes the fusion line for the central zone of the molten pool, and β grains hence rotate their normal direction of the solidification front at the pool tail to be well aligned with the laser scan direction, as illustrated in the region enclosed by the white dashed line in Figure 3.8(c).

Figure 3.9(a-c) display the solidification process of β grains on the end cross-section at different time moments. Since only the left half of the temperature field is extracted (inset in Figure 3.5), the predicted β -grain distribution covers the left half of the cross-section and is compared with the right half of the experimental observation (Figure 3.9(d)). The growth pattern and morphology of β grains are qualitatively captured by the simulation results. However, the average grain size for the simulated results is shorter by approximately 25% than the experimental characterization despite comparable width. The simulation results clearly show that β grains grow epitaxially by inheriting the crystallographic orientations from the partially melted grains on the fusion line. While all the columnar grains advance towards the center of the molten pool, almost no grains can stretch across the entire cross-section. This is because the fierce competitive growth is likely to cause the disappearance of some subordinate grains since their crystallographic

orientations deviate from the maximum temperature gradient. Some new grains will also form attaching to the solidified β grains and grow with their own growth rates.

In addition to the elongated columnar grains, some smaller grains of equiaxial shape are also observed while approaching the central zone of the molten pool (Figure 3.9(c)). The possible reason is that the normal direction of the growth front, although is aligned with the maximum temperature gradient, may not be perfectly parallel to the extracted cross-section plane. At some points, some elongated grains are intercepted by this cross-section and only their truncated surfaces are displayed, exhibiting a smaller aspect ratio. Particularly for the central zone of FZ, the grains completely rotate by 90° to align with the scan direction (Figure 3.8). When looking through the cross-section, the short axes of the elongated grains will be captured and exhibit equiaxed morphology. This feature has been well predicted by the experimental microstructure characterizing the elongated grains along the laser scan direction (Figure 3.8(d)), which indicates the good prediction of the β -grain solidification by the 3D CA modeling in the DED-built Ti6Al4V depositions.

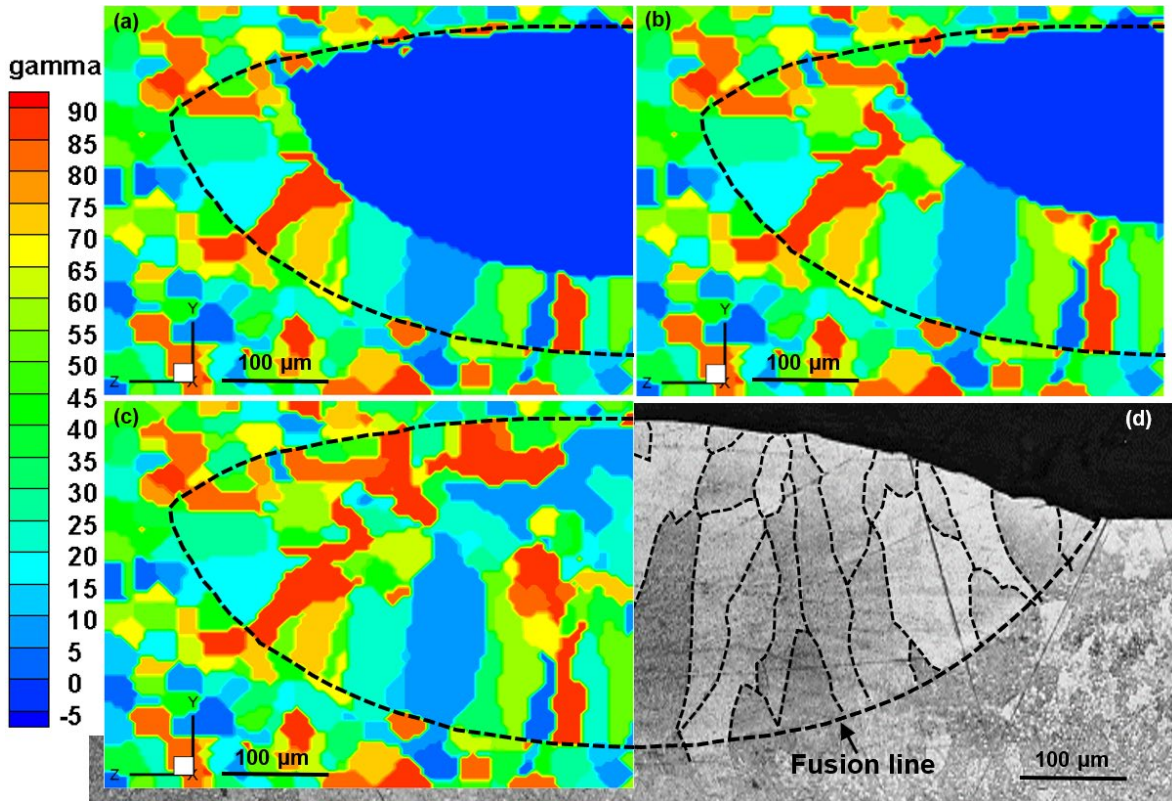


Figure 3.9. The predicted β -grain solidification on the cross-section of $X=0$ for the single-track Ti6Al4V at (a) 0.02 s, (b) 0.025 s, (c) 0.0325 s as validated against (d) the microstructural characterization.

In Figure 3.10, the cross-sections of (a) two-track and (b) three-track Ti6Al4V depositions are used to compare the simulation results against the experimental data. The predicted free surface and extracted isotherms for the FZ boundary and HAZ boundary (solid lines) are superimposed on the experimental microstructure, which exhibits a good agreement with the experimental observation (dashed lines). Figure 3.10(c) and (d) show the predicted β -grain distribution within the FZ on the multi-track cross-sections of $X=0$. Compared with the single-track results shown in Figure 3.9, the grain structure prediction for multi-track depositions has larger errors. Some of the clear grain boundaries of the real β grains are illustrated by the dotted lines in Figure 3.10(a) and (b), whose average size is larger by approximately 30% in width and 40% in length than the predicted β grains shown in Figure 3.10(c) and (d). Another big difference is observed in the overlapping zone, where the experimental microstructure characterizes the epitaxial growth of β grains stretching across multiple tracks while the simulation results exhibit a discontinuous growth passing the FZ boundaries. In addition, more equiaxial grains are revealed in FZ's central zone by the simulation results than the experimental data. These shortcomings should be further considered in future research.

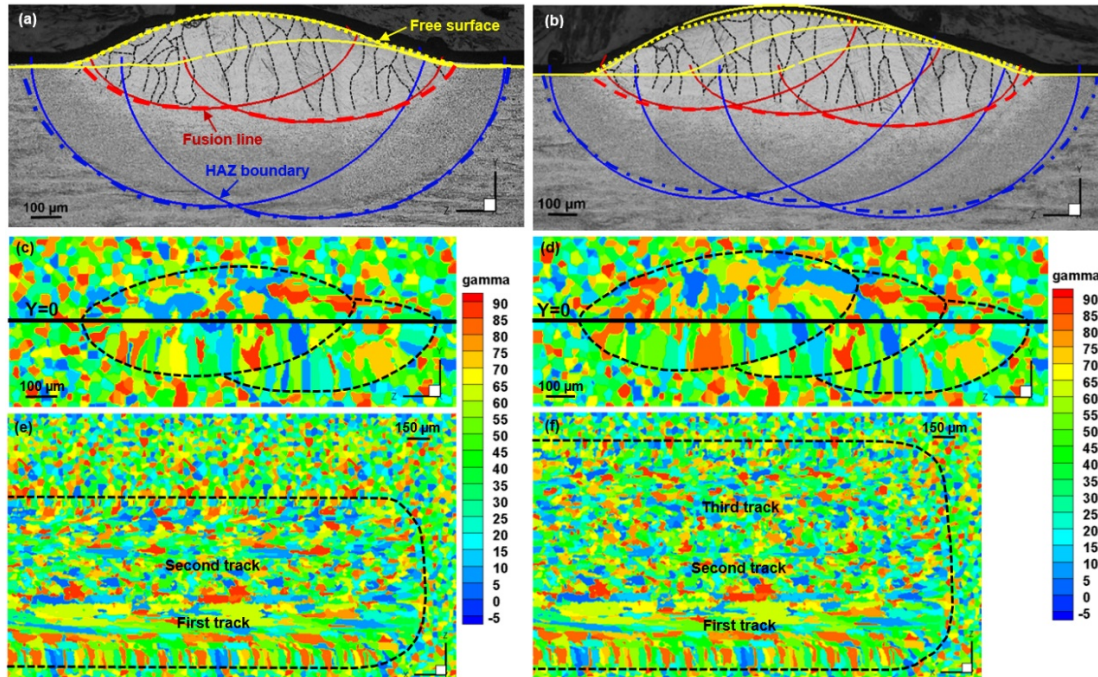


Figure 3.10. Predicted free surface, fusion zone boundary and heat-affected zone boundary (solid lines) vs experimental data (dashed lines) on the cross-section of (a) two-track and (b) three-track Ti6Al4V depositions. Simulated β -grain distributions within the fusion zone on the (c,d) cross-sections of $X=0$ and (e,f) horizontal-sections of $Y=0$ positioning at the solid lines in (c) and (d) for the (c,e) two-track deposition and (d,f) three-track deposition.

The predicted β -grain distribution within the FZ on the horizontal-section of $Y=0$ (upper surface of the substrate, illustrated in Figure 3.5(b)) for two-track and three-track Ti6Al4V depositions are shown in Figure 3.10(e) and (f). For the single-track case, Figure 3.8(c) depicts the microstructure thoroughly. The region near the fusion line of the first-track is still dominated by the elongated grains of columnar shape; however, the grain morphology is fairly different from each track in the central zone. This difference is associated with the location of the displayed horizontal-section. According to the cross-section views shown in Figure 3.10(a) and (b), the molten pool of the second track and third track rotates about 20° and 40° in the anticlockwise direction and hence becomes shallower in the substrate due to the overlapping of adjacent tracks. When extracting the upper surface of the substrate, this extracted horizontal-section gets closer to the molten pool bottom from the first track to the third track. Since β grains mainly epitaxially grow from the molten pool bottom and then rotate their solidification front to align with the scan direction in the central zone of the molten pool, the extracted horizontal-section is expected to reveal large columnar grains for the first track. When getting closer to the molten pool bottom, the extracted horizontal-section will intercept the short axis of β grains, revealing more equiaxial grains with smaller aspect ratios.

3.3.3 2D Micro-scale PF Modeling of Ti6Al4V Solidification

As the 2D PF domain is only $2.0 (X) \times 1.6 (Y) \mu\text{m}^2$, which is much smaller than the molten pool size, the temperature in the PF simulation domain can be considered to be constant at each time step. To study the microstructure evolution at different locations in the molten pool, the simulated temporal and spatial temperature profiles are coupled as inputs. The authors' previous work revealed that these temperature profiles can be simplified as constant temperatures with different undercoolings since the temperature changes little during the short simulation period [13]. Therefore, the temperature profiles at different locations in the molten pool are simplified with various corresponding undercoolings.

Figure 3.11 exhibits the solidification process of β grains under the undercooling of 55 K. At the beginning of solidification (0.00012 s), a couple of nuclei with various sizes and shapes are formed at the bottom of the domain. As time elapses to 0.0006 s, nuclei grow larger and touch each other. The continuous growth of some predominant grains eventually blocks the growth of

some subordinate grains at 0.006 s. This competitive growth is quite common in directional solidification. The grains, whose crystallographic orientations at the solidification front are aligned with the maximum temperature gradient direction, are likely to survive from the competitive growth. As the solidification process presented in Figure 3.11 is performed with a constant undercooling of 55 K, there is no temperature gradient at the solidification front. Therefore, the stagnancy of some grains results mainly from the nucleation location and nuclei sizes.

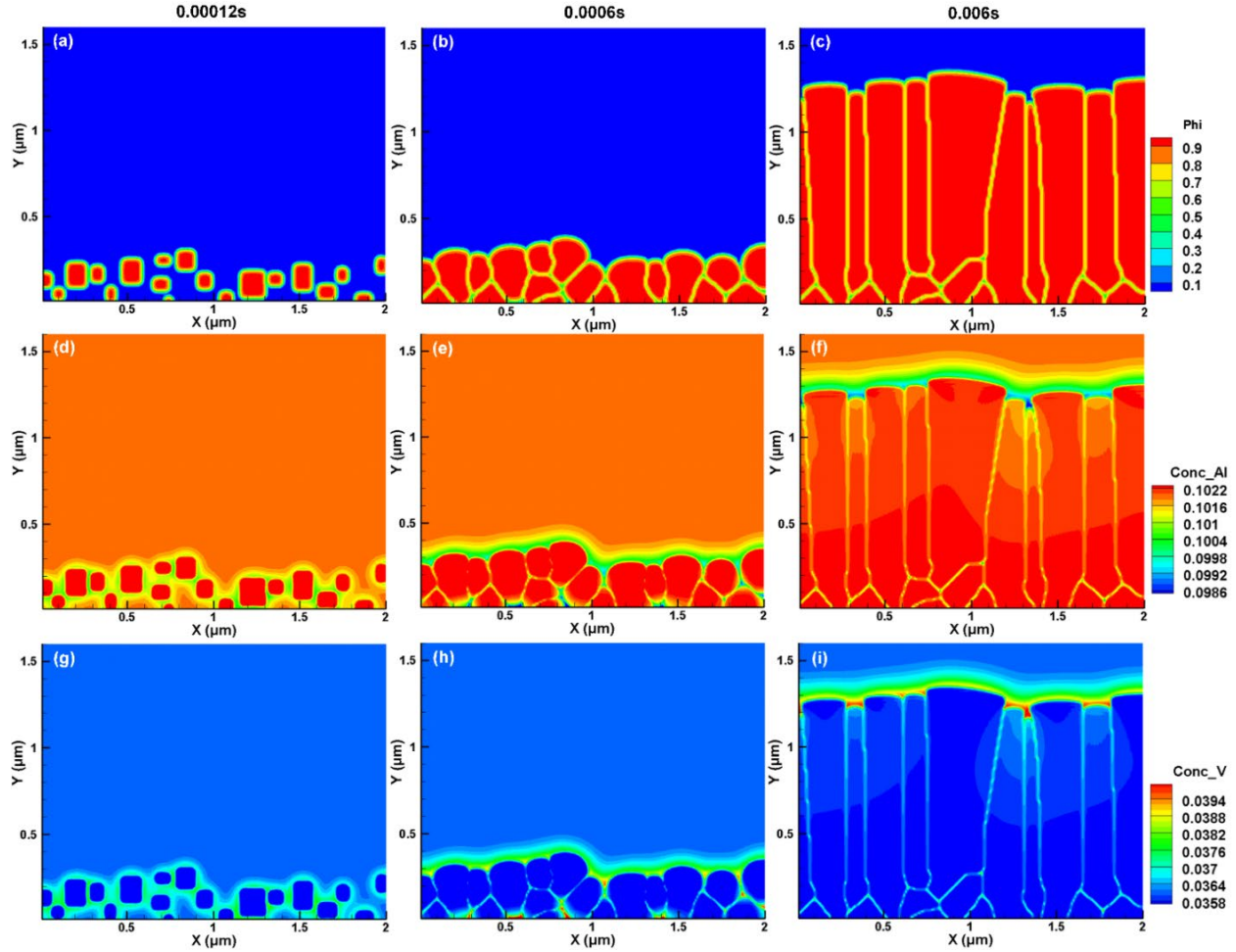


Figure 3.11. Solidification of β grains under the undercooling of 55 K.

The solutal evolution for Al and V during β -grain solidification is plotted in Figure 3.11(d-f) and (g-i), respectively. It is readily seen that the predicted solid β phase has a slightly higher Al concentration and lower V concentration than the liquid phase, which is actually consistent with the Ti-Al and Ti-V phase diagrams. As clearly shown in Figure 3.3, the phase diagram of Ti-Al

reveals positive slopes in the solidus and liquidus curves for the Al concentration less than 22 at.%, indicating a little higher equilibrium concentration of Al in the solid phase than in the liquid phase. The case for V with a concentration lower than 40 at.% is opposite, and therefore, the V concentration in the solid is expected to be a little lower than in the liquid.

Since the β phase has higher Al but lower V percentages, Al and V atoms will diffuse into and out of the β phase, respectively, leaving a boundary region with lower Al but higher V in the solidification front. As some dominant grains grow faster, they will first absorb Al atoms from and expel V atoms to the surroundings. Without sufficient concentrations for the slower-growth grains, the concentration distribution throughout these subordinate grains is non-uniform, and their growth will be blocked eventually (Figure 3.11(f) and (i)). In spite of the tiny difference in the concentrations between liquid and solid phases, both local K_{eq}^{Al} and K_{eq}^V are approximately equal to 1, which also matches the phase diagram of Ti-Al and Ti-V (Figure 3.3) well. The underlying reason for the similar concentrations in solid and liquid phases is associated with the high diffusion mobility of Al and V in the solid β phase. As the predicted concentration distributions are highly consistent with the phase diagrams, the accuracy of the thermodynamically-consistent PF model developed in this study is successfully verified. Since PF modeling is performed on a much smaller domain, it can reveal more details in local microstructure and concentration evolutions.

Influences of different undercoolings from the top to bottom in the molten pool on the morphology and growth kinetics of solidified β grains are displayed in Figure 3.12. The simulation is continued for 0.006 s. The growth kinetics is calculated at the solidification front with $\phi_p = 0.5$. As is clearly illustrated in Figure 3.12(d), the undercooling displays an almost linear relationship in increasing the growth kinetics. At a smaller undercooling (Figure 3.12(a)), the grain boundary is wider and has a higher ϕ_p value. A similar influence of undercooling on growth kinetics is also revealed in Refs. [13, 107]. The leading contribution from a large undercooling is its enhanced driving force in the solidification front.

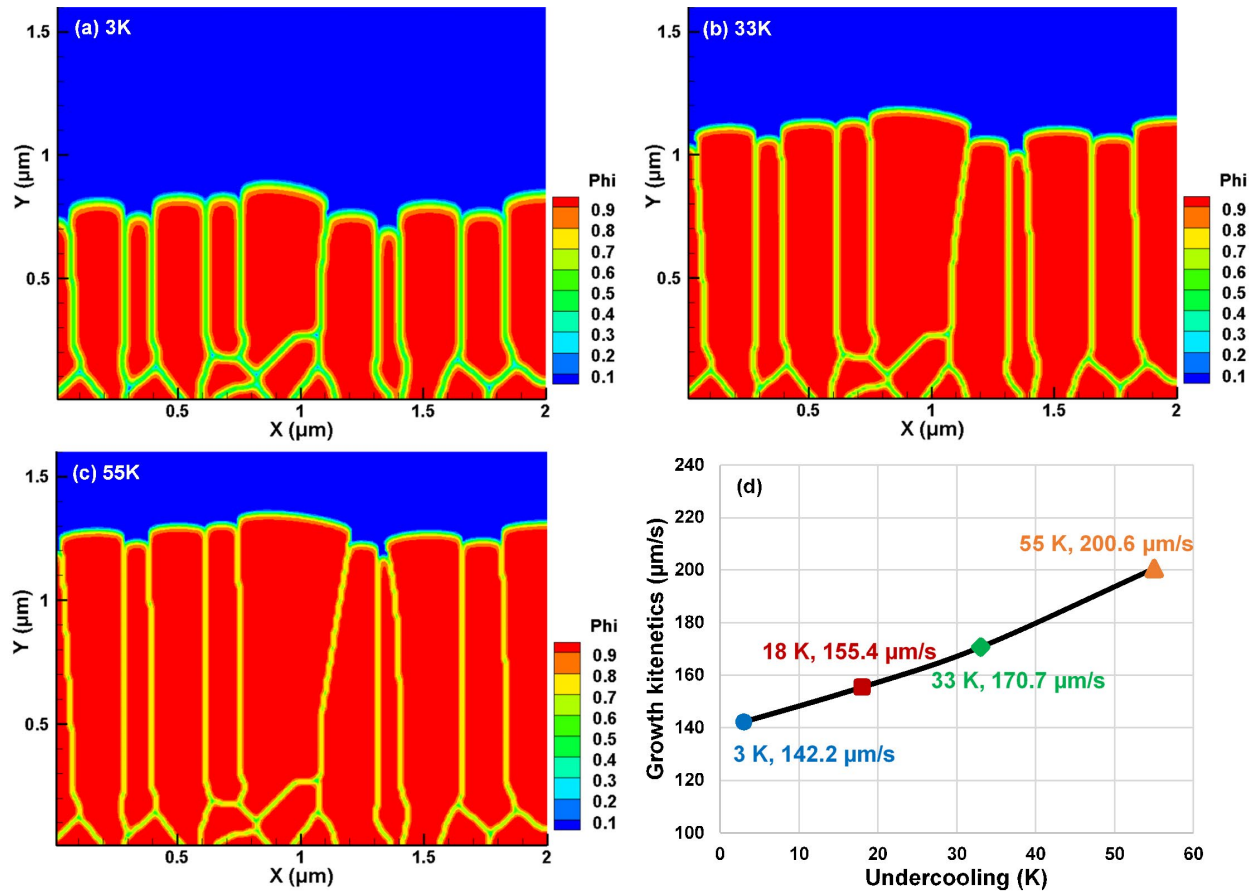


Figure 3.12. Influence of undercooling on β grain morphology and growth kinetics.

The influence of cooling rate on the microstructure morphology of the solidified β grains is depicted in Figure 3.13, where the peak cooling rates of 2.4×10^4 K/s at the top (Figure 3.13(a)) and of 1.76×10^4 K/s at the bottom (Figure 3.13(b)) in the molten pool are incorporated. The simulation lasted for 0.006 s for both conditions. Comparing Figure 3.13(a) and (b), it is apparent that the cooling rate throughout the entire molten pool has little effect on the solidification rate. The simulated competitive growth patterns of β grains are validated against the SEM micrographs for single-track (Figure 3.13(c)) and multilayer (Figure 3.13(d)) depositions. In the fusion zone of single-track deposition (Figure 3.13(c)), the prior β grains nucleate on the fusion line and competitively grow towards the central zone of the molten pool. The growth direction in the solidification front is opposite to the maximum temperature gradient direction [257, 272].

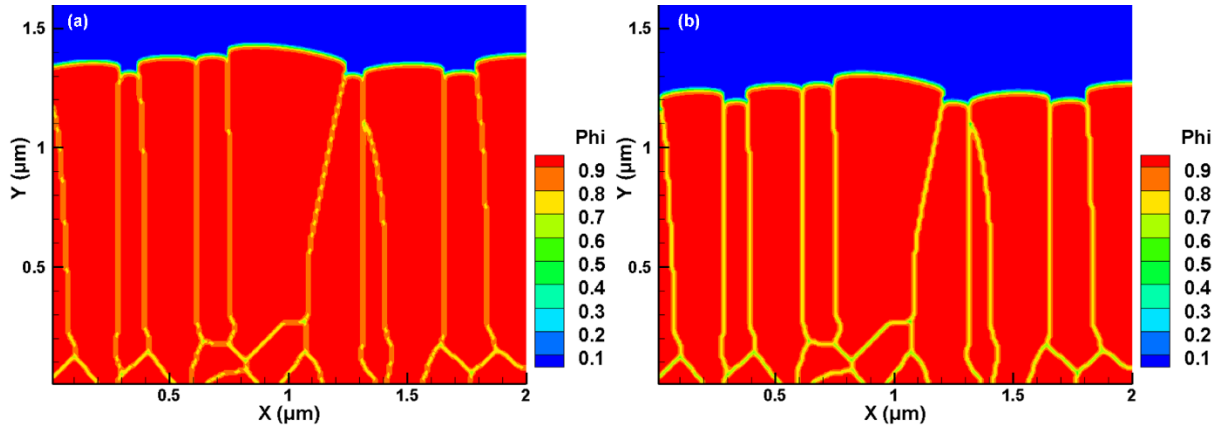


Figure 3.13. Influence of cooling rates of (a) 2.4×10^4 K/s and (b) 1.76×10^4 K/s on the microstructure morphology of solidified β grains.

When comparing the PF simulation results with experimental observation shown in Figure 3.8(d), Figure 3.9(d), and Figure 3.10(a, b), it is apparent that the grain morphology and solidification pattern of β grains during the solidification of Ti6Al4V in the DED process are well captured by the PF simulation; however, it should be noted that the PF simulation can only be carried out on a small domain due to its high computation cost, which is much smaller than the macro-scale molten pool and bulk multilayer part. The predicted grain size thus cannot be quantitatively compared with the experimental results due to the small simulation domain. The current PF simulation, therefore, only uncovers the local growth pattern and concentration evolutions of Ti6Al4V solidification. As a result, the influence of the large temperature gradient for a real system, e.g. the temperature gradient within the entire molten pool, on the grain morphology cannot be well captured by PF modeling.

As the PF modeling coupled with independent diffusion of Al and V was successfully validated, the cross-diffusion between Al and V is considered and shown in Figure 3.14. Taking advantage of the multigrain pattern, a smaller domain with fewer grains is utilized to perform the simulation. As can be seen in Figure 3.14(b) and (c), both $D_{Al,V}$ and $D_{V,Al}$ have positive values, indicating that the solutes Al and V have repulsive diffusional interaction [262, 273], which confirms the predicted concentration distributions of Al and V in this work. As shown in Figure 3.11, the solid β phase has a higher Al concentration but a lower V concentration than the liquid

phase. It is, therefore, reasonable to conclude that Al and V atoms diffuse along opposite paths during the solidification of β phase and hence would block the diffusion of each other.

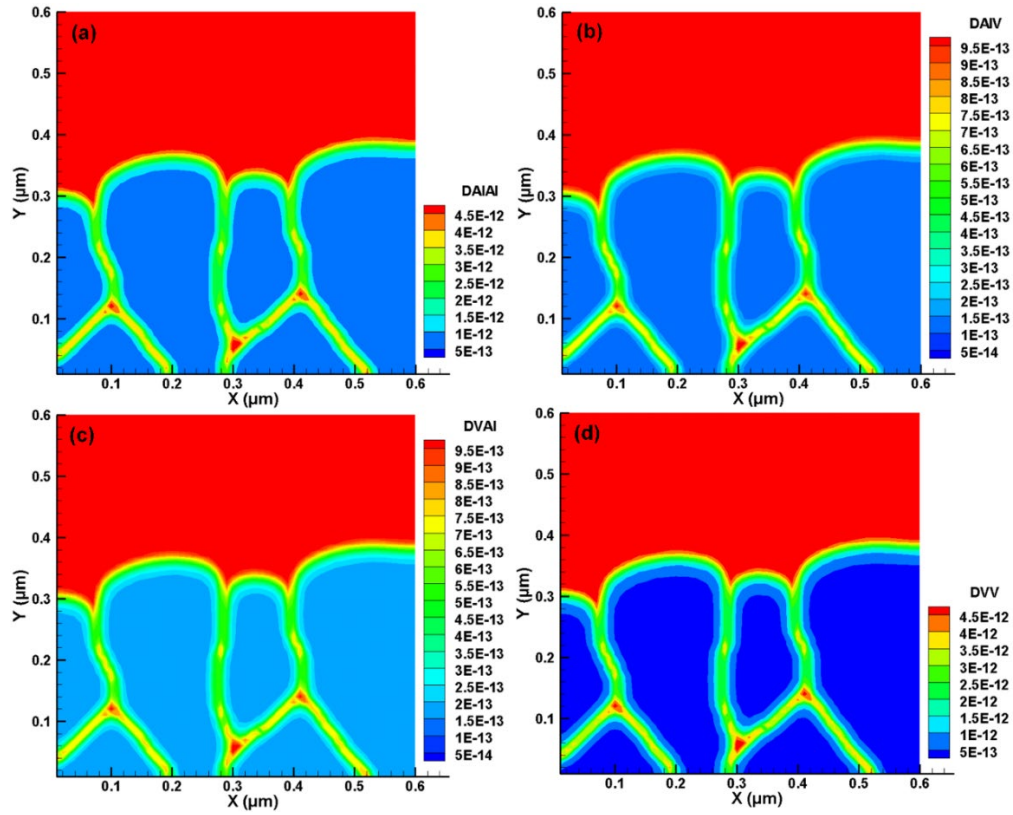


Figure 3.14. Cross-diffusion mobility profiles for β grain growth during the solidification of DED-built Ti6Al4V under the undercooling of 3 K for 0.0015 s: (a) $D_{Al,Al}$, (b) $D_{Al,V}$, (c) $D_{V,Al}$, (d) $D_{V,V}$.

The influence of different undercoolings on the composition distribution for Al and V in the Y direction across the grains located at $X = 0.9 \mu\text{m}$ in Figure 3.13 is illustrated in Figure 3.15(a) and (b), respectively. The solidification was continued for 0.003 s. The concentration distribution after considering the cross-diffusion between solutes for the case of 55 K undercooling was also carried out to provide a direct comparison. Due to a similar distribution pattern, the concentration evolution associated with the cross-diffusion for other undercooling cases are not shown. Figure 3.15 reveals the concentrations in four different regions from $Y = 0$ to $Y = 1.4 \mu\text{m}$: solid (β), solid/solid grain boundary, solid/liquid interface, and liquid. For the Al concentration distribution (Figure 3.15(a)), the undercooling has little effect on its concentration in both solid β phase and liquid, while the increased undercooling produces a lower peak Al concentration at the solid/liquid interface. This is because the rapid growth of β grains induced by the higher undercooling absorbs

more Al atoms from liquid, leaving a lower Al concentration in the solidification front. In terms of the solid/solid grain boundary (first peak), the larger undercooling leads to a slightly higher concentration, but the difference is not significant. The increased undercooling also maintains a consistent distribution pattern for V concentration (Figure 3.15(b)). Opposite to the Al case, the increased undercooling increases the peak concentration at the solid/liquid interface. In addition, the increased undercooling also increases the V concentration in the solid β phase, indicating a higher solubility of V in the solid β phase with the decrease of temperature, which matches the phase diagram (Figure 3.3(b)) well.

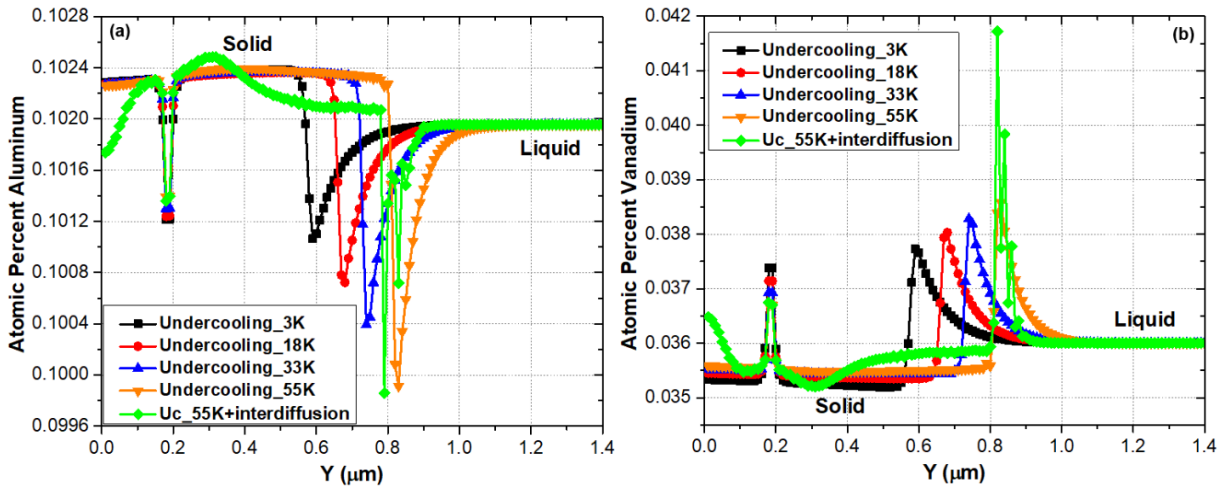


Figure 3.15. Concentration distributions of (a) Al and (b) V across the grain at $X=0.9 \mu\text{m}$ in Figure 3.13 after solidification for 0.003 s under different undercoolings. The concentration evolution after incorporating the cross-diffusion mobility data from Table 3.5 is displayed for the 55 K undercooling.

After considering the cross-diffusion between solutes, the concentration distributions of Al and V in the liquid phase are altered little but those in solid are no longer uniform such that the Al concentration first increases from 0.10175 to the peak value of about 0.10255, and then decreases to about 0.1021 when approaching the solid/liquid interface. On the contrary, the V concentration first drops from 0.0365 to the peak of 0.0352 and then rises back to about 0.036 near the solid/liquid interface. The concentrations of Al and V fluctuate significantly at the solid/liquid interface. Compared with the independent-diffusion case, the coupling of cross-diffusion data decreases the local $K_{\text{eq}}^{\text{Al}}$ from 1.0033 to 1.0011 while increases the local K_{eq}^{V} from 0.9878 to 0.998, which is more close to the equilibrium condition as illustrated in the phase diagrams of Ti-Al and Ti-V (Figure 3.3).

3.3.4 2D Meso-scale CA-PF of Ti6Al4V Solidification

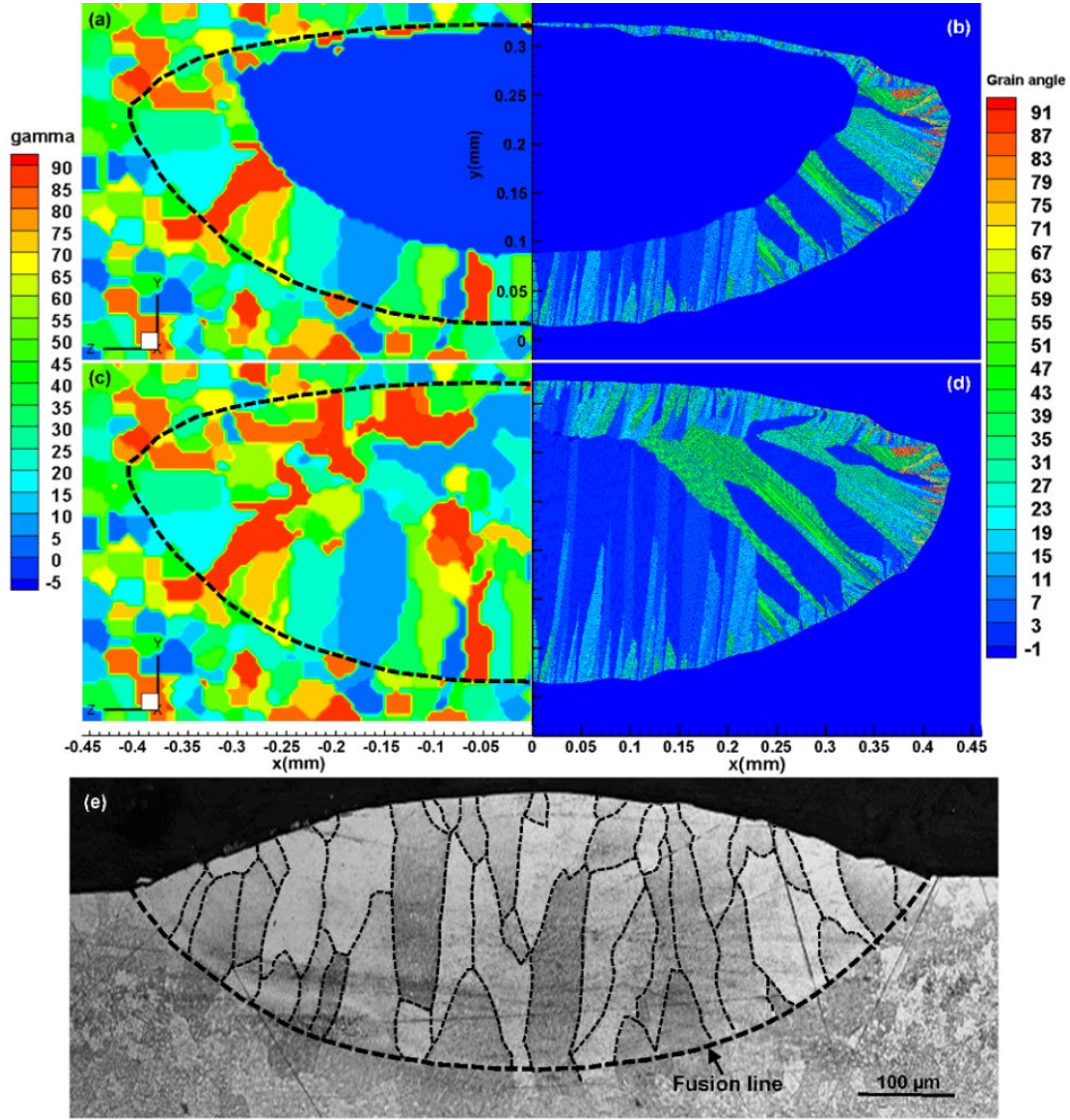


Figure 3.16. (a, c) 3D CA and (b, d) 2D CA-PF results of as-solidified β -grain structure on the cross-section of $X=0$ for the single-track Ti6Al4V as validated against (e) the microstructural characterization.

When comparing the simulation and experimental results, it is readily observed that the growth pattern and texture of β grains are qualitatively well captured by both CA and CA-PF modeling, where the predicted as-solidified microstructure mainly features elongated β grains of columnar shape. The 3D CA modeling predicts the grain texture well but fails to capture the sub-grain morphology. The integrated 2D CA-PF modeling successfully addresses this shortcoming by revealing more details within a grain, as depicted in Figure 3.17. It can be seen from Figure 3.17

that the β grains have a dendritic morphology on the sub-grain level, which should be attributed to the large supercooling within the molten pool [193]. The dendritic feature was also reported in recently published papers [106-108]. However, it should be pointed out that the solidification of Ti6Al4V is a high-temperature process that occurs beyond the solidus temperature of Ti6Al4V (1878 K [274]), and thus is difficult to be experimentally observed based on the current techniques. The simulation results, therefore, provide some insights on the grain morphology but lack of sufficient validation.

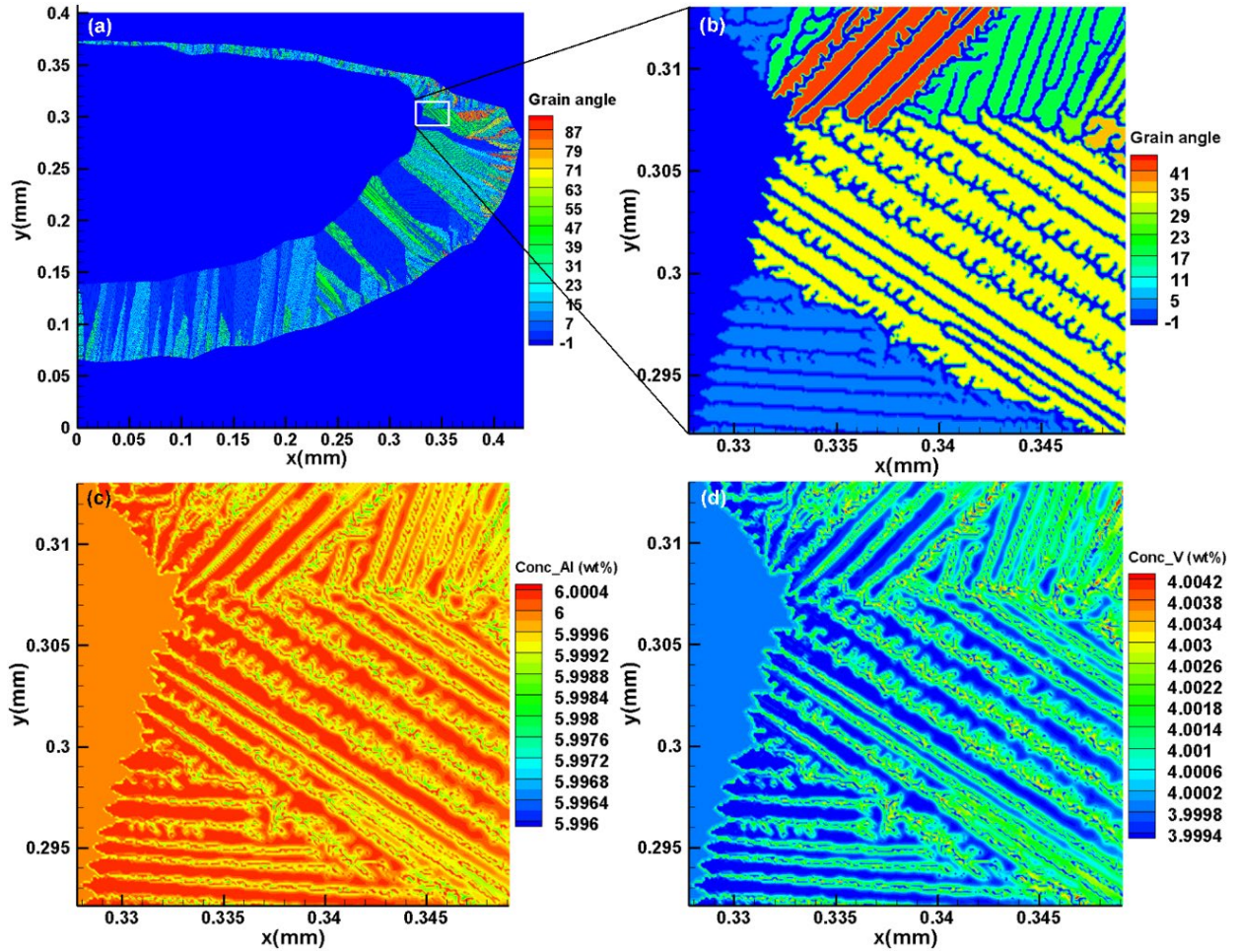


Figure 3.17. (a) 2D CA-PF modeling of as-solidified β -grain microstructure reveals (b) dendritic grain morphology, (c) solute Al concentration, and (d) solute V concentration.

In addition to capturing the details of grain structure, the integrated CA-PF model is also able to predict the concentration evolution of each solute. Figure 3.17(c) and (d) exhibit the predicted solutal concentration distribution of Al and V, respectively. The dendrite trunk has a

slightly higher Al but lower V concentration than the liquid phase, leaving the dendrite interface and solid/liquid interface with a lower Al and higher V. Similar to the 2D PF modeling results, the predicted concentration distribution of solutal Al and V agrees well with the phase diagram of Ti-Al and Ti-V (Figure 3.3). It should be noted that the β phase solidification in Ti6Al4V alloy is a high-temperature transformation process and the as-solidified β phase is an intermediate phase. The as-solidified β phase cannot be retained to room temperature as it will deform into α/α' phases when the temperature drops below the β -transus temperature [4, 41, 112]. To the authors' best knowledge, there is no available technique that could measure the solute evolution during a high-temperature transformation process. Consequently, the validation of Al and V concentrations in the as-solidified β phase in Ti6Al4V is beyond the feasibility of experimental methods. Simulation, on the other hand, may provide some insights via numerical technique.

The predicted as-solidified β -grain structure for a three-track cross-section validated against the experimental result is exhibited in Figure 3.18. In the experimental microstructure (Figure 3.18(c)), the β grains are illustrated by the black dashed lines. The predicted free surface (solid yellow lines) and extracted isotherms for the FZ boundary (solid red lines) and HAZ boundary (solid blue lines) are superimposed on the experimental microstructure, which exhibits good agreement with the experimental observation (dashed lines), indicating that the macro-scale DED model produces representative prediction of temperature profiles. Similar to the single-track case shown in Figure 3.16, elongated β grains still dominate the FZ. Both 3D CA and 2D CA-PF modeling clearly show the epitaxial growth of β grains initiating from the fusion line of each track.

Similar to the single-track case, an intense competitive growth occurring at the initial stage of solidification is observed, particularly for the CA-PF simulation result (Figure 3.18(b)). Initially, grains with different crystallographic orientations nucleate on the fusion line. In the following growth cycle, grains with favorable growth direction more parallel to the maximum temperature gradient win this competitive growth, which causes the stagnant growth to non-preferred grains. With a lot of small grains retained near the fusion line, the average grain size predicted by the 2D CA-PF modeling is smaller than the experimental result. Different from the CA-PF modeling, the 3D CA modeling also predicts some equiaxial grains in the central zone of FZ (Figure 3.16(c) and Figure 3.18(a)), and there is a high possibility for these equiaxial grains to be the intercepts of

elongated grains formed along the scan direction (Figure 3.8(c)). Unfortunately, the capture of these equiaxial grains is beyond of capability of 2D modeling.

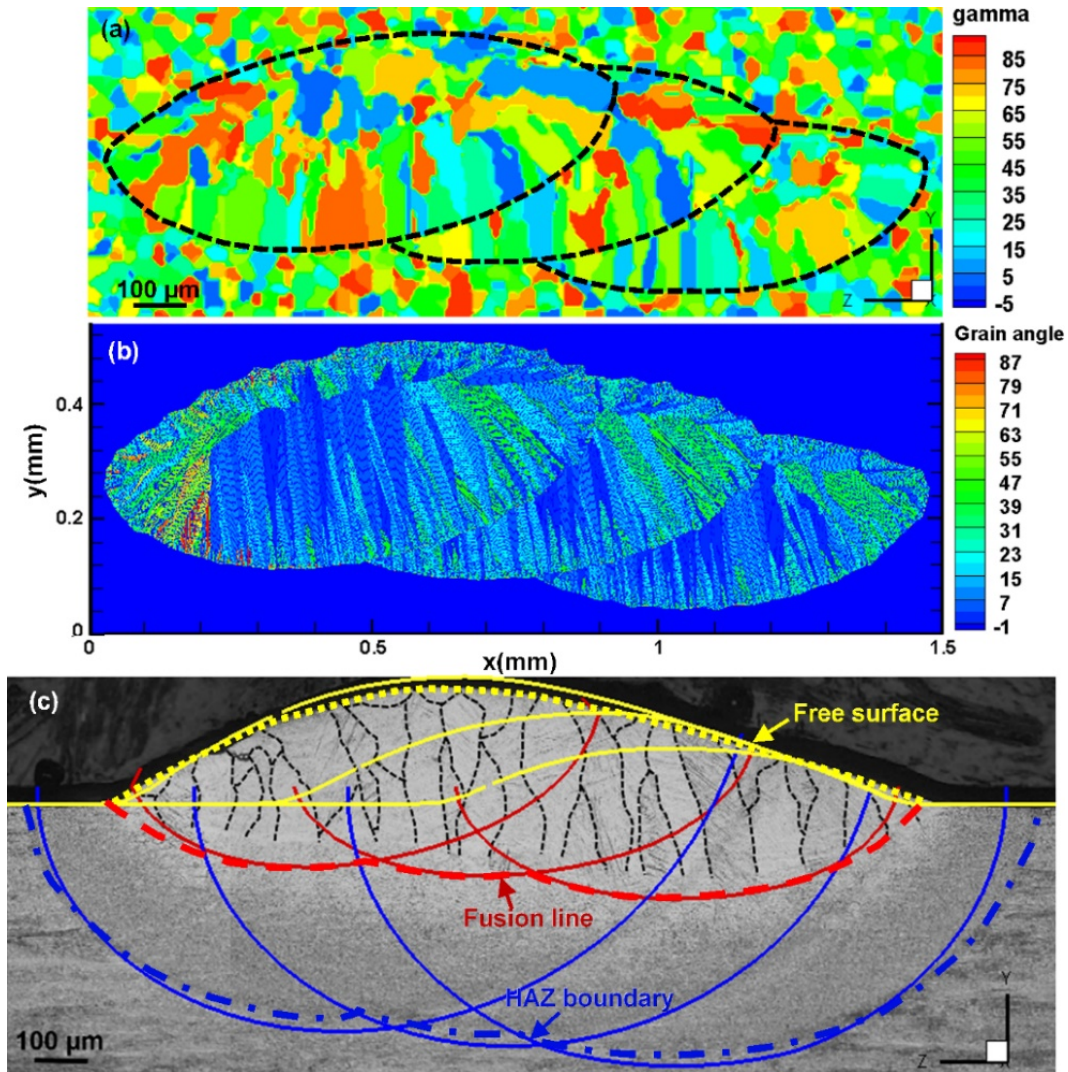


Figure 3.18. (a) 3D CA modeling and (b) 2D CA-PF modeling of β -grain distribution on a cross-section of three-track Ti6Al4V deposition as compared with (c) microstructural result. The extracted free surface, fusion zone boundary (fusion line) and heat-affected zone boundary (solid lines) from the predicted temperature profile vs experimental data (dashed lines) are superimposed on the three-track deposition.

In conjunction with the densely packed grains at the molten pool boundary, a band of small equiaxial grains is also formed at the molten pool surface of the three-track deposition. Compared with the experimental observation that reveals only a few individual grains of equiaxial shape (Figure 3.18(c)), both 3D CA (Figure 3.18(a)) and 2D CA-PF (Figure 3.18(b)) modeling present a qualitative prediction in the grain number and grain morphology. A larger deviation is readily

observed in the 2D CA-PF simulation than the 3D CA modeling. These shortcomings should be attributed to the inherent limitations of 2D models. Bailey et al. [205] performed a comparative assessment of dendrite morphology via 2D and 3D PF models in a recently published paper and reported that the 3D simulation is much more accurate than 2D simulation in predicting grain morphology, solutal concentration, and growth velocity since the temperature gradient and solute diffusion are 3D. The differences between 2D and 3D results are more significant if the extracted plane is away from the temperature gradient. For β -grain solidification during the DED process of Ti6Al4V, the solidification front of β grains rotates to align with the temperature gradient in the central zone of the molten pool due to the movement of laser beam [195]. This feature is well captured by 3D CA modeling but is not revealed by 2D models. Therefore, the 3D CA-PF model is in high demand.

Table 3.7 summarizes the physical simulation time of the 3D CA, 2D CA-PF, 2D PF modeling. It is clear that the CA model is most efficient among the three predictive tools. Although PF models can capture local grain structure and composition evolution more accurately, the expensive calculation cost makes it not applicable to a large domain. With the increase of components and phases, the calculation cost would always increase exponentially. However, PF models can be used to provide accurate local information for the CA-PF modeling, which incorporates the advantages of both CA and PF models and alleviates their disadvantages accordingly. As given in Table 3.7, the 2D CA-PF modeling improves the calculation efficiency by more than 5 orders of magnitude as compared with 2D PF modeling. Compared with the grain structure predicted by the 3D CA modeling shown in Figure 3.9, Figure 3.10, Figure 3.16(a, c) and Figure 3.18(a), and composition simulation performed by 2D PF modeling in Figure 3.11, CA-PF modeling also provides a reasonable prediction for microstructure and composition evolution.

Table 3.7. The physical simulation time for 3D CA, 2D CA-PF, and 2D PF modeling

Models	3D CA	2D CA-PF	2D PF
Grid size	$5 \times 5 \times 5 \mu\text{m}^3$	$0.2 \times 0.2 \mu\text{m}^2$	$10 \times 10 \text{ nm}^2$
Domain size	$3 \times 0.6 \times 1.7 \text{ mm}^3$	$0.548 \times 1.508 \text{ mm}^2$	$2 \times 1.6 \mu\text{m}^2$
Processor number	20	50	51
Physical simulation time	0.85 hour	36.8 hour	17.5 hour

3.3.5 Phase and Microhardness Prediction Against Experimental Data

Using the phase prediction model, the microhardness of the Ti6Al4V depositions was calculated according to the predicted α' martensite content. Figure 3.19(a) presents the predicted microhardness distribution of the three-track Ti6Al4V deposition. The microhardness distribution map is compared to the optical micrograph (Figure 3.19(b)), on which the typical regions were selected for microstructural analysis, as shown in Figure 3.20. The shape of FZ identified by the maximum microhardness in Figure 3.19(a) matches the FZ geometry illustrated in Figure 3.19(b).

In DED processing of multi-track Ti6Al4V, the peak temperature appears in the FZ and decreases from the FZ to HAZ. According to the Ti6Al4V phase diagram [112, 275], as the temperature in the molten pool approaches the solidus temperature, prior β grains begin to form [257]. As the temperature further decreases to M_s temperature, β phase will be transformed to a non-equilibrium α' martensitic phase due to the high cooling rate experienced in the DED process [42, 112, 275]. The microhardness predicted in the FZ (uniformly 427 HV) indicates a complete formation of α' martensite, and is in agreement with microstructure observations (Figure 3.20(d-f)), based on the needle-shaped α' phase observed.

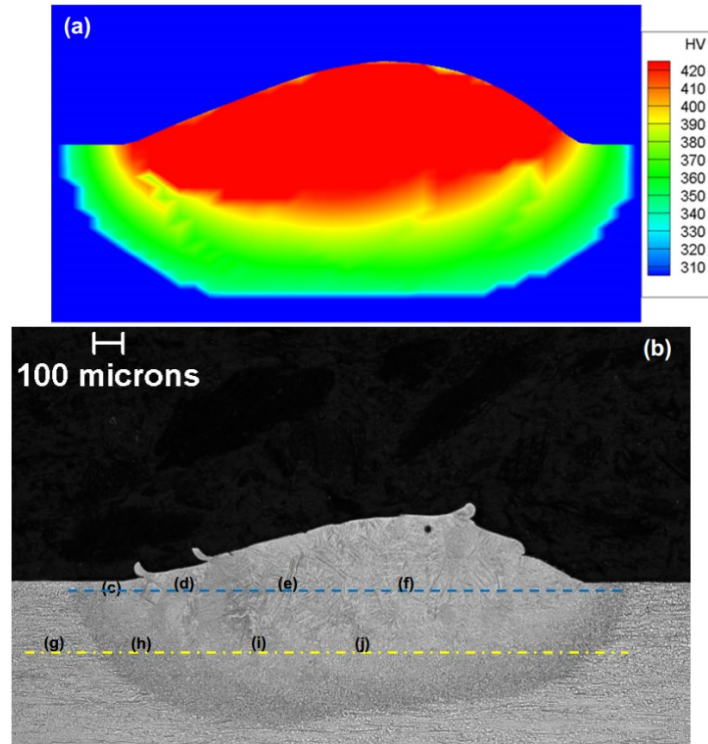


Figure 3.19. (a) Microhardness distribution map of DED-deposited three-track Ti6Al4V predicted by phase prediction model in comparison to (b) the optical view of the track geometry.

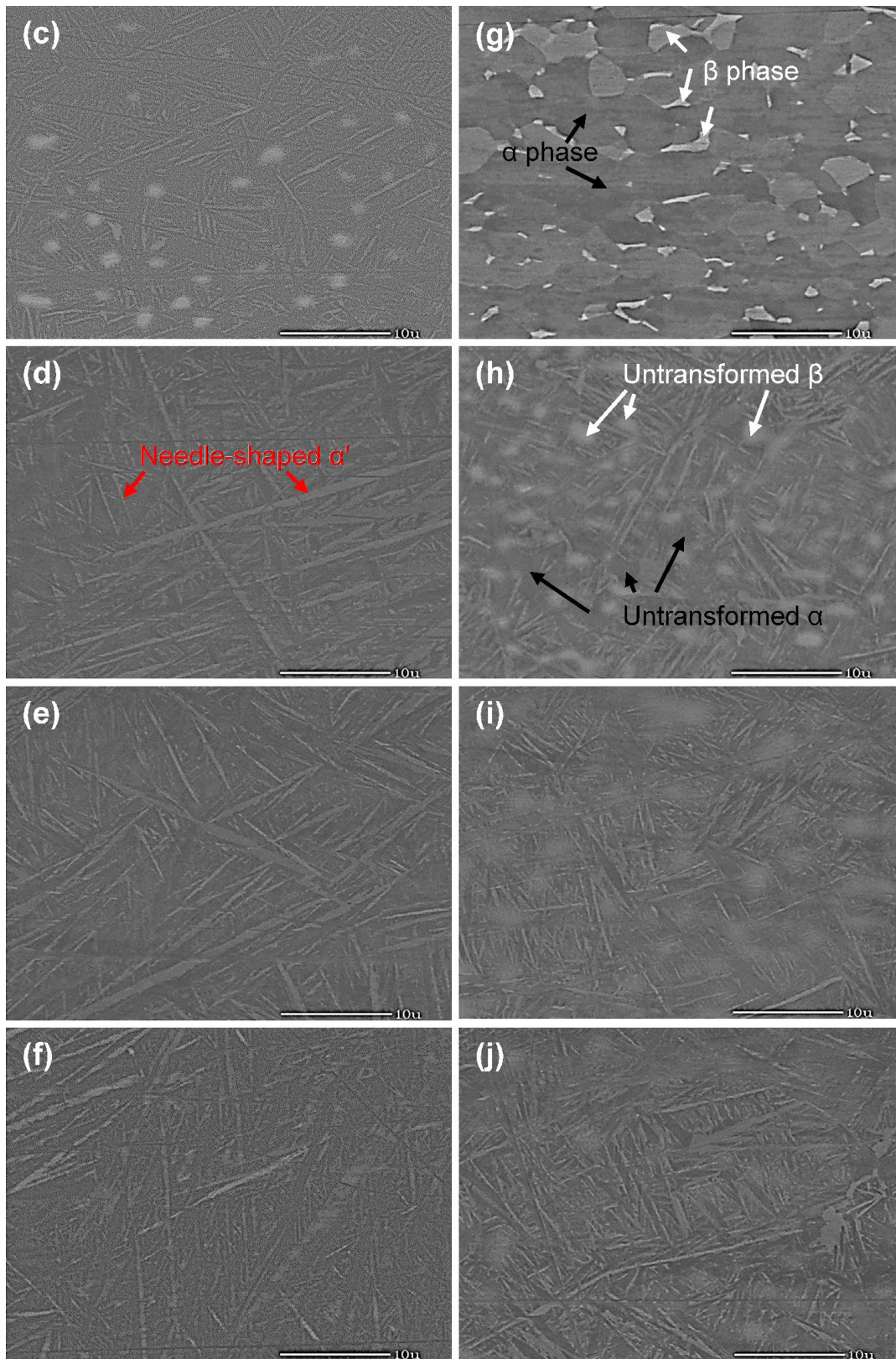


Figure 3.20. SEM microstructure characterization of typical zones selected from Figure 3.19(b).

The HAZ has a lower peak temperature, leading to a solid phase transformation in the Ti6Al4V substrate. In SEM micrographs, the darker region denotes α phase while the lighter region surrounding α phase is representative of β phase. The shape and size of α and β phases are influenced by fabricating methods. For example, the hot-rolled Ti6Al4V substrate exhibits an elongated α -phase along the rolling direction. The β phase was squeezed to the junction of α grains, exhibiting a stub-like morphology (Figure 3.20(g)). The original α grains are decomposed by vanadium diffusion, and the rapid average heating rate of approximately 10^4 K/s leads to partial decomposition of the deformed elongated α grains. As a result, the HAZ is composed of a mixture of newly formed α' martensite and α phase as well as untransformed initial α (Figure 3.20(c,h,i,j)). As clearly illustrated in Figure 3.20(h,i,j), the volume fraction of α' martensite in HAZ increases toward the center due to the overlapping of HAZ (Figure 3.20(j)).

Figure 3.21 presents the predicted microhardness along the two parallel dashed lines illustrated in Figure 3.19(b) as compared to experimental measurements. The two lines were separated by a distance of 200 μm , with the upper line encompassing FZ and HAZ and the bottom line only encompassing the HAZ. The gap between adjacent indentations along either line was set to 100 μm . As shown in Figure 3.21, the overall microhardness prediction is in excellent agreement with the experimental results.

Compared with the upper line, the bottom line has a lower microhardness, which matches the smaller volume percentage of α' martensite detected in the microstructural analysis. For the upper line (Figure 3.21(a)), microhardness prediction indicates a constant peak microhardness value of 427 HV in the FZ, substantiating the cooling rate in FZ has surpassed the upper limit of α' martensitic phase transformation (410 K/s). For the lower line (Figure 3.21(b)), microhardness prediction shows that the maximum microhardness of 389 HV is found near the center of HAZ for the simulation result due to the overlapping of multiple tracks.

Since DED is a multi-track and multi-layer process, depositing the next track will cause part of the previous track to be remelted and resolidified due to the overlapping of subsequent depositions. As the laser beam moves away, the heat dissipates mainly via heat conduction through the substrate and pre-deposited tracks, with less heat being transferred by heat convection and radiation from the free surface of the track due to the argon flow. Therefore, the overlapped regions in HAZ will undergo multiple phase transformation processes. The three-track overlapped zone

will have a higher volume fraction of α' martensite than the two-track overlapped zone, which will be yet higher than the single-track zone due to the accumulation of α' martensites. The martensitic α' phase formed in FZ is unaffected by overlapping of the HAZ from subsequent tracks as the initial melting has already caused the complete transformation to α' phase. In the overlapped FZ areas the cooling rate of the most recent track will control the martensitic α' phase formation.

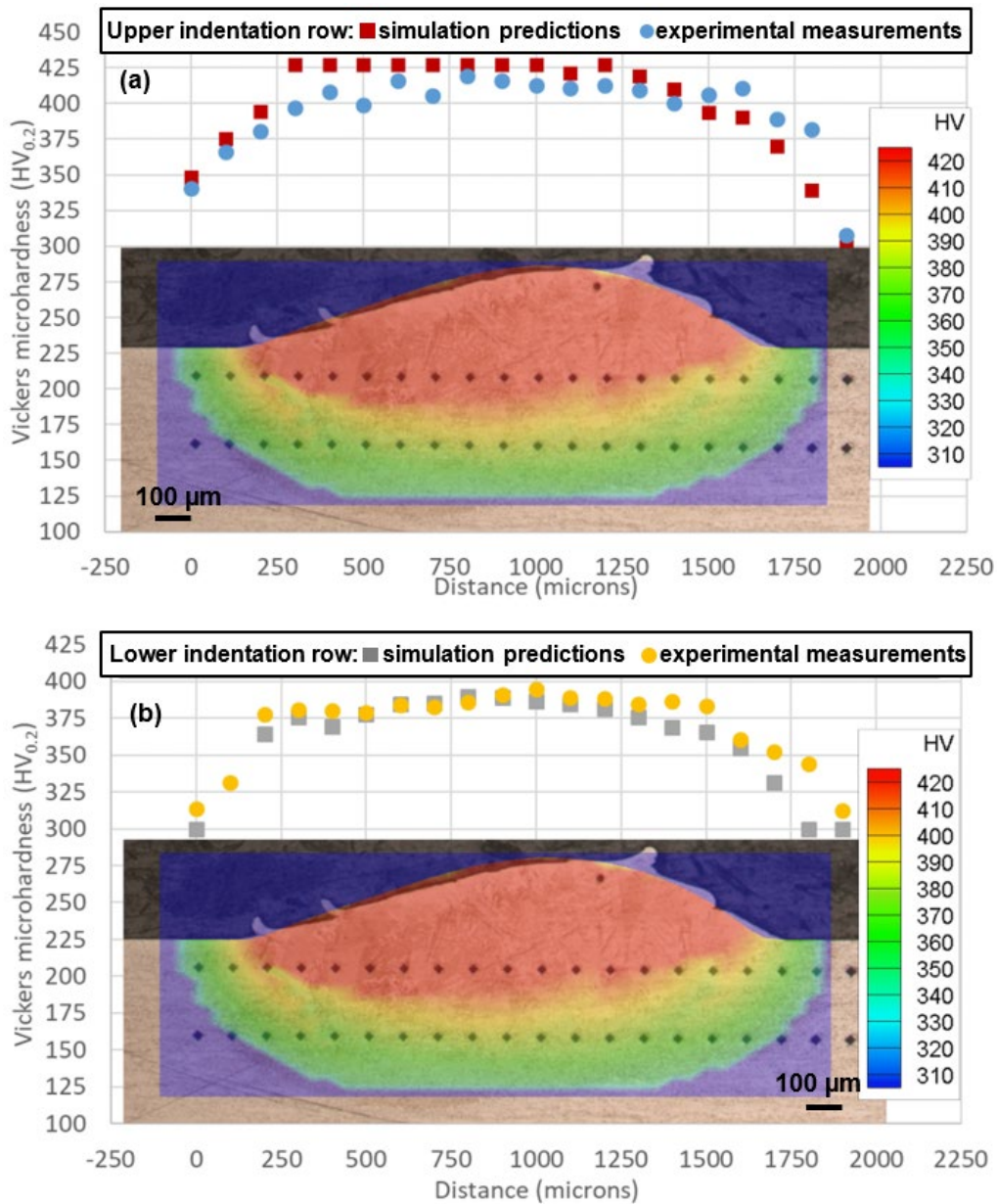


Figure 3.21. Microhardness prediction for DED-deposited three-track Ti6Al4V compared to experimental measurements: (a) upper row measurements and (b) lower row measurements.

3.4 Summary

In this paper, an integrated multi-physics and multi-scale simulation framework was established to model the thermal behavior of the DED process, the resulting β -grain solidification within the molten pool and the solid-state phase transformation of $\beta \rightarrow \alpha/\alpha'$ during the multi-track DED process for Ti6Al4V by combining five predictive tools.

An experimentally validated 3D macro-scale DED model was adopted to simulate the temperature history in the molten pool of a three-track Ti6Al4V deposition. The DED model accurately captured the temporal and spatial temperature fields and heating/cooling rates in different zones in the deposition as well as the molten pool geometry with the free surface, FZ and HAZ boundaries matching the experimental results well.

For the solidification simulation, a 3D macro-scale CA model was used to simulate the as-solidified β -grain structure. Coupled with the temperature profile extracted from the DED model, the 3D CA modeling predicted elongated β grains of columnar shape, which growth epitaxially from the fusion line. While approaching the central zone of the molten pool, the β grains rotated their growth direction to align with the laser scan direction, which has been verified by the microstructure characterization.

On the micro-scale, a thermodynamically-consistent multi-phase and multi-component PF model was adopted to simulate the local competitive polycrystalline growth of β grains and the concentration evolutions of Al and V. The PF model was incorporated with the thermodynamic and diffusion mobility databases of the Ti-Al-V system. In this way, the evolution of Al and V during Ti6Al4V solidification was accurately predicted for the first time, where the solidified β has a slightly higher Al but lower V than the liquid phase, matching the concentration illustrated by the phase diagrams of Ti-Al and Ti-V. After consideration of the cross-diffusion between solutes, the simulated concentration distribution of both Al and V approached the equilibrium state more closely. The increased undercooling from the top to bottom of the molten pool enhanced the growth kinetics linearly while the cooling rate had little influence on the growth rate.

On the meso-scale, an integrated CA-PF model was developed to simulate the grain structure details and solutal evolution on the sub-grain level in response to the temperature history, where the 1D PF component provides the local growth kinetics including the growth velocity and equilibrium solute partition at the solidification front, for the 2D CA component that calculates

dendritic growth variable and concentration distribution. The CA-PF model predicted dendritic morphology within the large β grains and also calculates the concentration distribution of Al and V accurately. Compared with 3D CA modeling, the CA-PF modeling advantages in capturing grain structure details and solutal evolution on the sub-grain level. The advantage of CA-PF modeling over PF models is its remarkable save in computational cost, which improved the calculation efficiency by more than 5 orders of magnitude without losing much accuracy in grain structure and concentration prediction. However, the grain size predicted by 2D CA-PF deviated from the experimental observation by approximately 30%, and 2D CA-PF models lose some capabilities than 3D models. All these limitations should be considered in future research.

When the temperature further drops below the $T_{\beta\text{-trans}}$, a diffusion/diffusionless kinetic 2D phase predict model was used to predict the solid-state $\beta \rightarrow \alpha/\alpha'$ phase transformation. The phase prediction model predicted the volume fractions of α and α' in FZ and HAZ. With the predicted volume fractions of α and α' in the final microstructure, the microhardness was accurately assessed. A consistent peak hardness value in FZ validated the complete formation of α' martensite, which resulted from the high peak temperature and high cooling rate in the FZ during the DED process. The low peak temperature in HAZ led to the incomplete decomposition of initial α phase, which produced a mixture of α' , transformed α phase and untransformed initial α phase in the final microstructure, which resulted in a lower microhardness when compared to the FZ. The overlapped region in HAZ exhibited a higher microhardness, which was attributed to the reheating of previously cooled material and caused additional phase transformation. All these predictions were well validated by experimental measurements. As the deposition can be sliced into a bunch of continuous 2D planes, the α' distribution and microhardness within the entire 3D deposition can be reconstructed.

By applying to Ti6Al4V, this integrated simulation framework demonstrates its feasibility in systematic modeling complex microstructural evolution and phase transformation during the multi-track DED process. Although the framework was applied only to Ti6Al4V in this chapter, it can definitely be extended to other manufacturing processes and various material systems.

4. DIRECTED ENERGY DEPOSITION OF QUATERNARY ZRCUNIAL BULK METALLIC GLASS COMPOSITES

In this chapter, the premixing method is adopted to prepare the ZrNiCuAl powder, which is used as an example to demonstrate the design and fabrication of in-situ bulk metallic glass composite (BMGC) by taking advantage of DED's attribute and thermal behavior as well as the precise control of premixed powder composition. A validated DED model developed by the author's group is introduced to simulate the temperature fields and cooling rates in single-track BMGC, which helps understand the microstructure evolution. Through a proper selection of deposition parameters, a periodic amorphous-crystalline microstructure with about 95.3 vol% amorphous phase and estimated more than 50 vol% crystalline phases in the fusion zone (FZ) and heat affected zone (HAZ) respectively is successfully fabricated. Due to the microstructure heterogeneity in different zones, the indentation tests are employed to characterize the local deformation behavior at the micron/sub-micron length scale.

4.1 Experimental Design

Formation and microstructure of BMG are strongly determined by both composition and cooling rate [276-278]. Before adjusting the DED parameters, the powder composition must be precisely controlled since the composition governs the glass-forming ability [157, 279]. In the current work, the ZrCuNiAl BMG powder was prepared by premixing pure Zr, Cu, Ni and Al metal powders with a prescribed atomic ratio. In spite of its advantages over the pre-alloyed method, partial melting of Zr particles occurred easily with typical gas atomized Zr powders because of its high melting temperature compared with other elements; and also the actual composition can easily deviate from the target composition due to the different flowabilities and densities of each metal powder.

In order to melt Zr particles completely, the as-received 300 μm granular-shaped Zr powders were milled with high energy ball milling to produce flake-shaped Zr powders (Figure 4.1), which increase the surface area and are melted easily. During ball milling, Zr powders were immersed in ethanol and milled at 400 rpm for 2 hours since powdered Zr is highly flammable. The milled Zr powder slurry was then dried using a vacuum drying machine for about 6 hours to remove the

ethanol completely. In order to improve the powder flowability, 75 – 150 μm Zr powders were sieved and mixed with 45 – 150 μm gas atomized Cu, Ni and Al powders, which were manually stirred for 20 minutes, followed by tumbling on a mill roller at 80 rpm for 24 hours. For safety consideration, the powders were handled in a sealed glove box filled with argon.

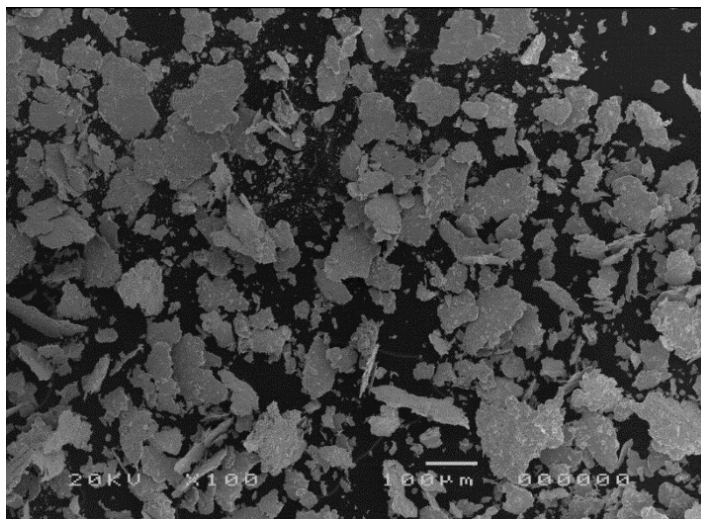


Figure 4.1. High energy ball milled zirconium powders display an irregular flake-shape.

The target composition of BMG in this work is $\text{Zr}_{65}\text{Cu}_{15}\text{Ni}_{10}\text{Al}_{10}$. To obtain this composition, the premixed powder must be a little deficient in Ni and Cu while excessive in Al due to their density differences. Eventually, $\text{Zr}_{66}\text{Cu}_{13}\text{Ni}_6\text{Al}_{15}$ was selected as the premixed composition since it produced an actual composition close to the target composition (Table 4.1). It should be noted that the composition detection in FZ and HAZ must be conducted before etching because the etchant can dissolve some crystalline phases (Figure 4.3(e)), leading to wrong results. As the FZ consisted of about 95.3 vol% amorphous phase (Figure 4.3(d)), which is free from the etchant's corrosion, the detected composition in FZ can be considered as the composition of amorphous matrix. In HAZ, although a large fraction of crystalline phases was produced, the detected composition was comparable to that in FZ. It is hence reasonable to conclude that the average composition of various crystalline phases is similar to the amorphous phase. Since multiple crystalline phases were formed and they were difficult to pinpoint without etching, energy dispersive X-ray spectroscopy (EDX) failed to detect the composition for each phase. Under thus circumstance, X-ray diffraction (XRD) detection was conducted to detect the formed crystalline phases (Figure 4.9, discussed later).

Table 4.1. EDX composition analysis (at.%) in fusion zone (FZ) and heat affected zone (HAZ) of DED-deposited ZrCuNiAl BMGC before etching.

Element	Target	Premixed	Actual	
			FZ	HAZ
Zr	65	66	65.7	66.1
Cu	15	13	15.3	15.5
Ni	10	6	10.4	10.3
Al	10	15	8.6	8.1

ZrCuNiAl samples were built using the Optomec LENS® 750 system, equipped with a 500 W fiber laser. The premixed powders were delivered via argon gas to the laser focal spot through quad nozzles in the working chamber, which also maintained an inert atmosphere of less than 20 ppm oxygen. A 6 mm thick Inconel 625 plate was used as the substrate. Unfortunately, direct deposition of a ZrCuNiAl part on this substrate would cause composition contamination to its bottom layers due to the dilute effect. Therefore, an approximate 2 mm thick ZrCuNiAl layer was intentionally built on the Inconel 625 plate to serve as the blocking layer, onto which BMGC samples were deposited using the parameters given in Table 4.2. After building one layer, the laser scan was rotated by 90 degrees, and the laser focal point was raised in the Z direction by a prescribed distance equal to the layer thickness. Figure 4.2 illustrates the DED process for fabricating ZrCuNiAl BMGC and the fabricated samples.

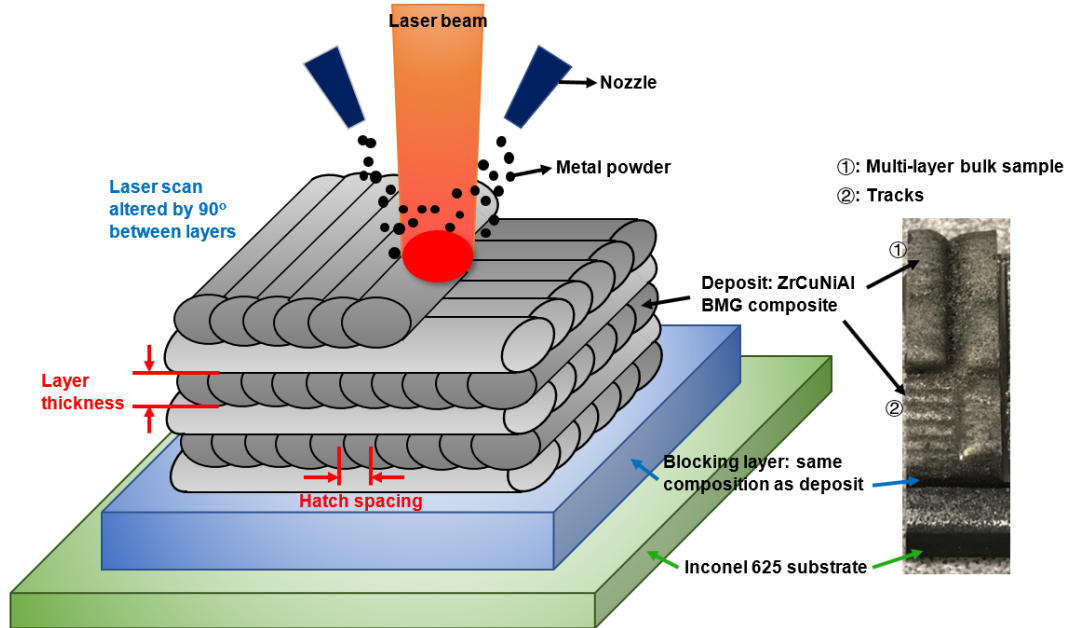


Figure 4.2. Sketch of the DED process for fabricating ZrCuNiAl BMGC and fabricated samples.

Table 4.2. DED parameters for fabricating ZrCuNiAl BMGC.

Parameters	Value	Unit
Laser power	200 – 350	W
Laser scan speed	10	mm/s
Powder feed rate	3 – 5.5	g/min
Hatch spacing	0.02 – 0.035	inch
Layer height	0.008 – 0.018	inch
Time interval between tracks	7	s

In order to produce a high volume fraction of amorphous phase, the parameters listed in Table 4.2 must be critically selected. Decreased scan speeds increase the solidification time of molten pool and provide a longer time for composition homogeneity at the sacrifice of cooling rate. After preliminary tests, 10 mm/s turned out to be an ideal scan speed in balancing the composition homogeneity and cooling rate. Influences of laser scan speeds on the composition homogeneity and phase changes can be found in Ref. [132]. The increase of powder feed rate increases the bead height up to the maximum value determined by the combination of laser power and scan speed. Hatch spacing is the distance between two adjacent tracks. Generally, a larger hatch spacing decreases the layer height since it reduces the overlapping zone of adjacent tracks. When depositing the subsequent layer, the top surface of the previous layer would be remelted; therefore the actual layer thickness was measured by averaging several layers. As the thermal conductivity of amorphous phase is very low (about 5 – 9 W/(m·K)) [280], heat will accumulate with the increase of track and layer numbers, decreasing the cooling rate. A time interval of 7 seconds was hence added between tracks to alleviate the heat accumulation. Zheng et al. [281] numerically proved the positive role of time interval in increasing the cooling rate and decreasing the final temperature of each deposition cycle.

For microstructure characterization, the specimens were cross-sectioned perpendicular to the laser scan direction, mounted in bakelite and polished with a series of SiC sandpapers (#240 – #1200) followed by mirror-polishing via 6 μm diamond and 0.05 μm colloidal silica. Microstructure details were revealed using the aqua regia solution and observed with an optical microscope (Nikon Eclipse LV150), a scanning electron microscope (SEM, JEOL-6400) as well as a high-resolution transmission electron microscope (TEM, FEI TALOS). TEM samples were prepared from the site of interest using focused ion beam (FIB, FEI Nova 200 NanoLab DualBeamTM-SEM/FIB). The composition was analyzed using an energy dispersive X-ray

spectroscopy (EDX), which was attached to the SEM. For phase characterization, the top surface of three-layer BMGC depositions were polished with #800 SiC sandpapers. The XRD machine (Bruker D8) was used to acquire the XRD patterns with 2 theta-angle ranging from 30 to 60 degrees at a scan speed of 8 degrees/min.

Deformation mechanisms and mechanical properties of the deposited BMGC were probed in FZ and HAZ by nanoindentation tests on a NanoTest platform (Micro Materials Ltd., UK). Among the numerous techniques to probe the deformation behavior, nanoindentation provides a large loading range due to its small indent size and is particularly ideal for heterogeneous microstructure. In order to perform accurate measurements, the Berkovich triangular diamond indenter was used to conduct the hardness test by increasing the load to a maximum value of 400 mN with a loading/unloading rate of 20 mN/s. The spherical diamond indenters were used to determine the elastic modulus and analytical indentation stress-strain data, which was obtained by a depth-controlled mode for a target depth of 600 nm. Values of hardness and elastic modulus were obtained from the load-depth curve according to the Oliver and Pharr method [282]. Since the large radius indenters would fail to evaluate a high spatial resolution on the surface [283], a 0.7 μm radius indenter was used to obtain a close elastic modulus for the pure amorphous and crystalline phases while the 100 μm radius tip was adopted for characterizing the average elastic modulus in FZ and HAZ, accounting for their composite nature. The indenter size was chosen based on the actual size of the interested zones characterized by the TEM and optical observations. Vickers microhardness tests were also conducted in FZ and HAZ using a LECO KM 247AT tester with a load of 200 – 500 g and a dwell time of 13 s while a LECO RT-370 Rockwell hardness tester was used to measure the overall macrohardness. Since the regular Rockwell scales would shatter the specimen's surface and slip the measurements, a scale of superficial Rockwell 15 N with a diamond indenter was used instead.

4.2 3D DED Modeling of ZrCuNiAl Bulk Metallic Glasses

In this section, the DED model was used to simulate the single-track DED process of ZrCuNiAl BMGC in order to get the temperature histories and cooling rates in FZ and HAZ. Since the precursor material was prepared by mixing pure Zr, Cu, Ni, Al metal powders, the precise values of some properties cannot be found from literature; therefore, rules of mixtures were

adopted to estimate those unknown material properties of the BMGC built in this work. As the FZ has about 95.3 vol% amorphous phase, the liquidus temperature, thermal conductivity and latent heat of fusion of the solid phase were assumed to be those of pure amorphous phase. Besides, the solidus temperature of the amorphous phase was assumed 10 K lower. In addition, the liquid phase was assumed to have the same density as the solid phase to maintain numerical stability. Table 4.3 summarizes the material properties of ZrCuNiAl BMGC for the DED model.

Table 4.3. Material properties of ZrCuNiAl BMGC for the DED model.

Property	Units	Solid phase	Liquid phase
Density	kg/m ³	6642 [284]	6642 [284]
Specific heat	J/(kg·K)	374 **	556 [285]
Thermal conductivity	W/(m·K)	$k=0.0054T+3.8058$ [286]	55.76 **
Liquid viscosity	kg/(m·s)	-	7.03×10^{-3} **
Thermal expansion coefficient	1/K	4.59×10^{-5} *	-
Absorptivity	-	0.25	-
Emissivity	-	0.3 [170]	-
Latent heat of fusion	J/kg	263800 [286]	-
Solidus temperature	K	1114 ***	
Liquidus temperature	K	1124 [287]	-
Surface tension	N/m	-	1.43 *
Surface tension temperature coefficient	N/(m·K)	-	-2.16×10^{-4} *
Coefficient for the heat convection	W/(m ² ·K)	20 [170, 286]	

*Note: * values were calculated by the rules of mixtures using volume percentage of pure metals; ** values were calculated by the rules of mixtures using mass percentage of pure metals while *** value was hypothesized. The parameter values of pure Zr, Cu, Ni, Al metals can be found in Ref. [288].*

The simulation was performed on a 3D domain that consisted of a bottom ZrCuNiAl amorphous substrate ($12 \times 5 \times 12 \text{ mm}^3$) and a top gas domain ($12 \times 3 \times 12 \text{ mm}^3$). The whole domain was discretized by a uniform mesh ($50 \times 33 \times 50 \text{ }\mu\text{m}^3$) in the deposition region ($6 \times 1 \times 2.5 \text{ mm}^3$) and a non-uniform mesh elsewhere. The initial temperature of the substrate was assumed to be 300 K. The governing equations were solved numerically using a dual-time stepping method. A physical time step was set at $2 \times 10^{-5} \text{ s}$, which consisted of 25 pseudo time steps to approach convergence.

4.3 Results and Discussion

4.3.1 DED-built ZrCuNiAl BMGC Microstructure and Thermal History Prediction

As DED is a track-by-track and layer-by-layer process, the desired microstructure should be maintained from the smallest unit to the bulk structure. Figure 4.3, Figure 4.6 and Figure 4.7 illustrate the microstructures of the DED-built ZrCuNiAl BMGC from single tracks to multiple layers. As the amorphous phase has no grain boundaries or other defects, it owns a remarkable corrosion resistance against the acid attack; therefore, it will exhibit a bright and featureless morphology in optical micrographs after etching. On the contrary, the crystalline phase will show a dark contrast after etching. As clearly shown in these images, FZ exhibits a brighter contrast than HAZ, which indicates a higher fraction of amorphous phase in the FZ but a major fraction of crystalline phases in the HAZ. Comparing Figure 4.3(a) – (c), the increased laser power from 200 W to 350 W widens and deepens the FZ, and also increases the thickness of HAZ, but maintains a consistent microstructure in FZ and HAZ, respectively. The microstructure is also independent of the powder feed rates. The bead built with 300 W is not shown but it maintains the microstructure similarity.

It needs to be noted that FZ consists of a mixture of amorphous and crystalline phases where the 300 nm – 1 μ m round and dendritic crystals are homogeneously embedded in the amorphous matrix (Figure 4.3(d)). The volume fraction of crystalline phases is about 4.7 vol%. The most notable attribute of the amorphous phase is its discontinuous grid-shaped morphology that the 100 – 400 nm wide bright zones serve as the frames, isolating the 1 – 3 μ m inner dark zones. A similar microstructural feature was also observed in the superplastic BMG built by Liu et al. [284], who claimed the uniqueness of this feature compared to the conventional BMG. The color contrast in the amorphous zone was believed to account for the density differences [284]; however, the underlying reason for the different densities and discontinuous microstructure is unclear yet.

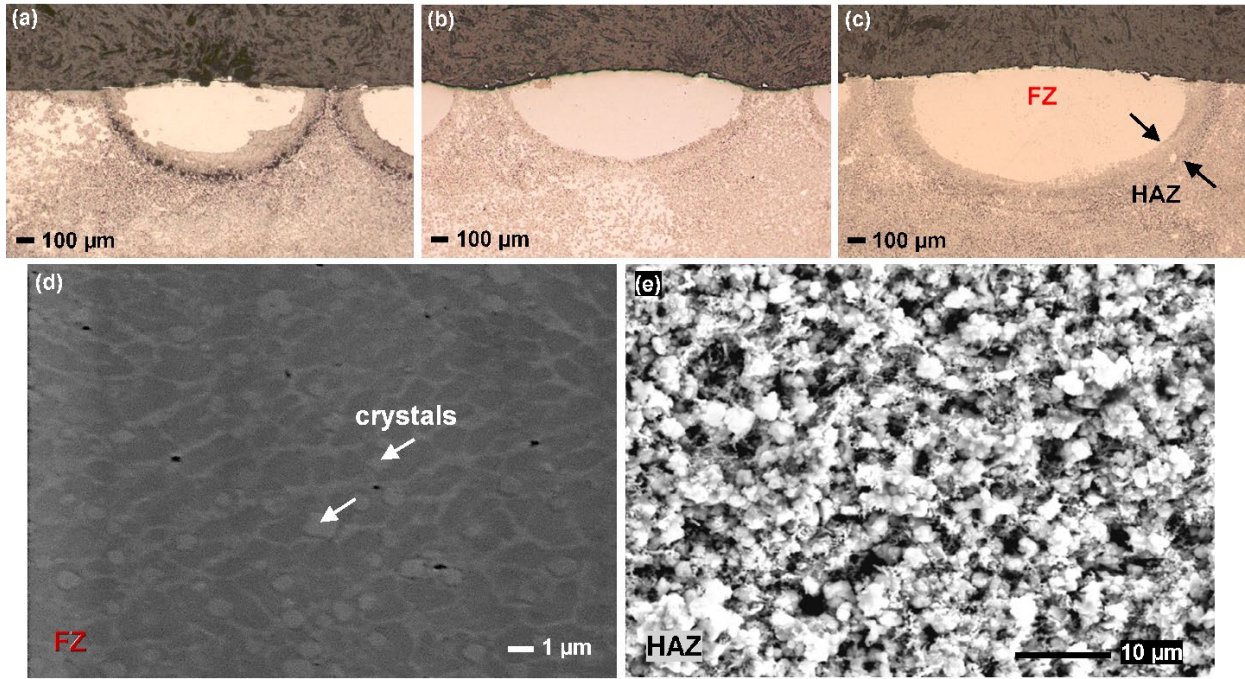


Figure 4.3. Optical micrographs of DED-deposited single-track ZrCuNiAl beads with (a) 200 W, 3 g/min, (b) 250 W, 5.5 g/min and (c) 350 W, 3 g/min. SEM micrographs reveal the microstructure in (d) fusion zone (FZ) and (e) heat affected zone (HAZ) after etching.

Considering the 2 at.% detection error in EDX, a very similar actual composition was obtained in FZ and HAZ (Table 4.1). Without the composition discrepancy, the microstructure difference in these two zones must be attributed to the different thermal histories. Figure 4.4 depicts the temperature fields in the single-track BMGC built with different laser powers. The temperature contour of FZ boundary that matches the liquidus temperature is plotted on Figure 4.4(a) and (b). The temperature profiles along the Y direction (laser scan direction) at four specific X locations illustrated in Figure 4.4(a) and (b) are shown in Figure 4.4(c) and (d) for the BMGC built with 250 W and 350 W, respectively. From the top zone of FZ downwards to the bottom of HAZ, the peak temperature decreases. For the single-track BMGC built by 250 W, the maximum temperature in FZ is 1517 K while that for the track built by 350 W is 1662 K. The peak temperature in HAZ is below the liquidus temperature. Consequently, the material in FZ undergoes a complete melting and solidification while HAZ only experiences the in-process solid phase transformation. As is clearly shown in Figure 4.4(c) and (d), a second temperature peak appears at about $Y = -0.16$ mm, which should be attributed to the amorphous to crystalline phase transformation.

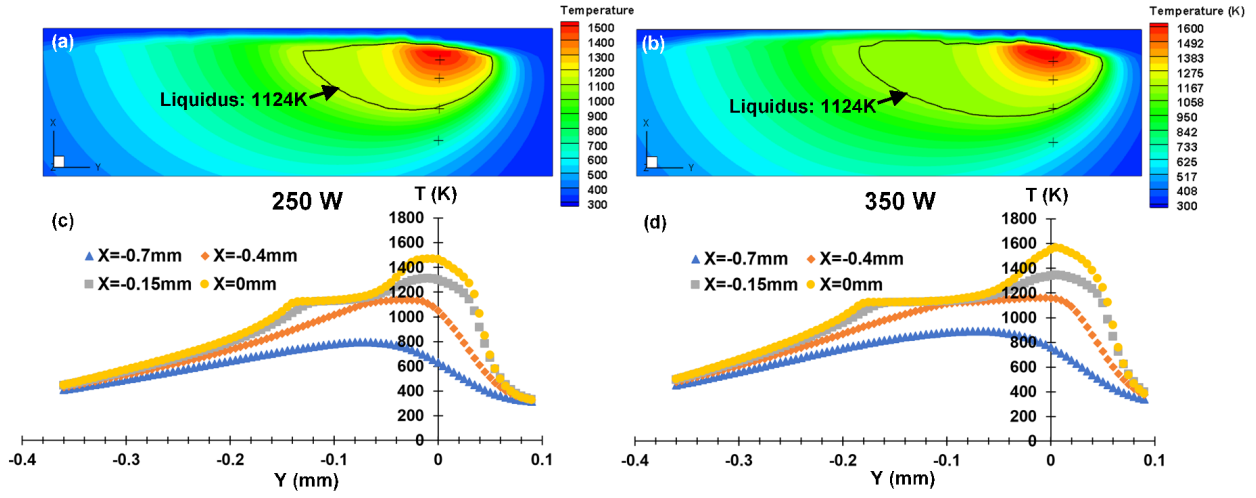


Figure 4.4. Temperature fields of the DED-deposited single-track BMGC built with (a, c) 250 W and (b, d) 350 W: (a, b) side view, (c, d) along the laser scan direction (Y direction) at four specific X locations.

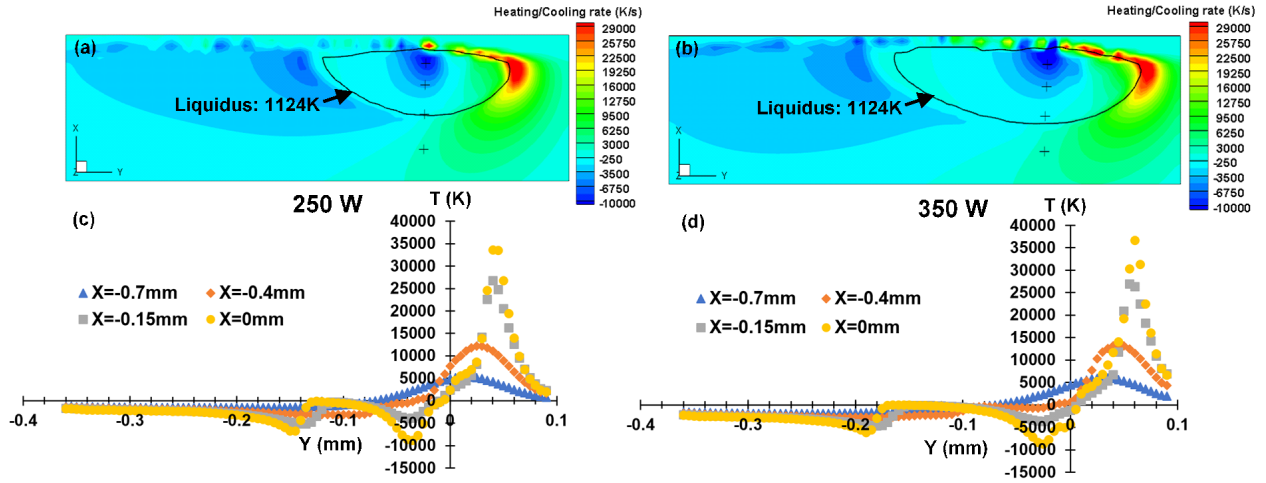


Figure 4.5. Heating/cooling rates of the DED-deposited single-track BMGC built with (a, c) 250 W and (b, d) 350 W: (a, b) side view, (c, d) along the laser scan direction at four specific X locations.

Figure 4.5 presents the heating/cooling rate fields in the single-track BMGC built with different laser powers. Similar to the temperature field, heating/cooling rates also decrease from their maximum near the free surface of FZ to the bottom of HAZ. A cooling rate of $5 \times 10^3 - 10^4$ K/s is produced in the FZ, which is higher than the critical cooling rates of $10^2 - 10^4$ K/s for most BMG materials [129, 289]. Among the various BMG systems, Zr-based BMG is known to have an outstanding glass forming ability. For $Zr_{65}Cu_{15}Ni_{10}Al_{10}$, the reported critical cooling rate was only about 10 K/s [290]. Although 350 W produces a higher peak temperature in FZ, the cooling

rate is still comparable with that for the track built with 250 W, accounting for the similar microstructure produced by different laser powers shown in Figure 4.3(a-c). The underlying reason is associated with the rapid heat dissipation downwards through the blocking layer and upwards through the argon flow convection, which effectively prevents heat accumulation and suppresses the microstructural change.

Figure 4.6 shows the microstructures of single-layer ZrCuNiAl BMGC depositions built with 250 W but different hatch spacings. These single layers maintain the microstructural attribute of single tracks completely. During the deposition of subsequent tracks, a portion of the previous track will be remelted and reheated, becoming the overlapping zone that consists of zones ①, ②, ③ and ④ in Figure 4.6(c). The remelted zones ② and ③ experience resolidification when the molten pool cools down and the fast cooling rate transforms the molten material directly into the amorphous state. It is well known that the amorphous phase is thermodynamically unstable and is prone to relaxing and transforming to crystalline phases when the temperature reaches the crystallization temperature. Consequently, the reheated zones ① and ④ undergo a tempering effect, which facilitates the nucleation and growth of crystalline phases in the amorphous matrix [291]. Due to the repeated heating, the HAZ ④ will have more and larger crystals than zone ①. However, the crystallization transformation is always incomplete due to the high cooling rate of the DED process.

According to the phase transformation occurring in the overlapping zone, a conclusion can be reached that a small overlapping zone induced by a large hatch spacing can help produce more amorphous phase in the bulk structure, as clearly demonstrated by comparing Figure 4.6(b) with Figure 4.6(a). Unfortunately, an excessively large hatch spacing will produce an uneven layer surface (Figure 4.6(b)) and cause a high risk of porosity in the triangular joining zone of adjacent tracks (Figure 4.6(d)). As the size of molten pool varies with the DED parameters (Figure 4.3(a-c)), the hatch spacing should be adjusted accordingly. Table 4.4 lists the optimized hatch spacing values for different laser powers, which produces an overlapping ratio of about 58 vol%.

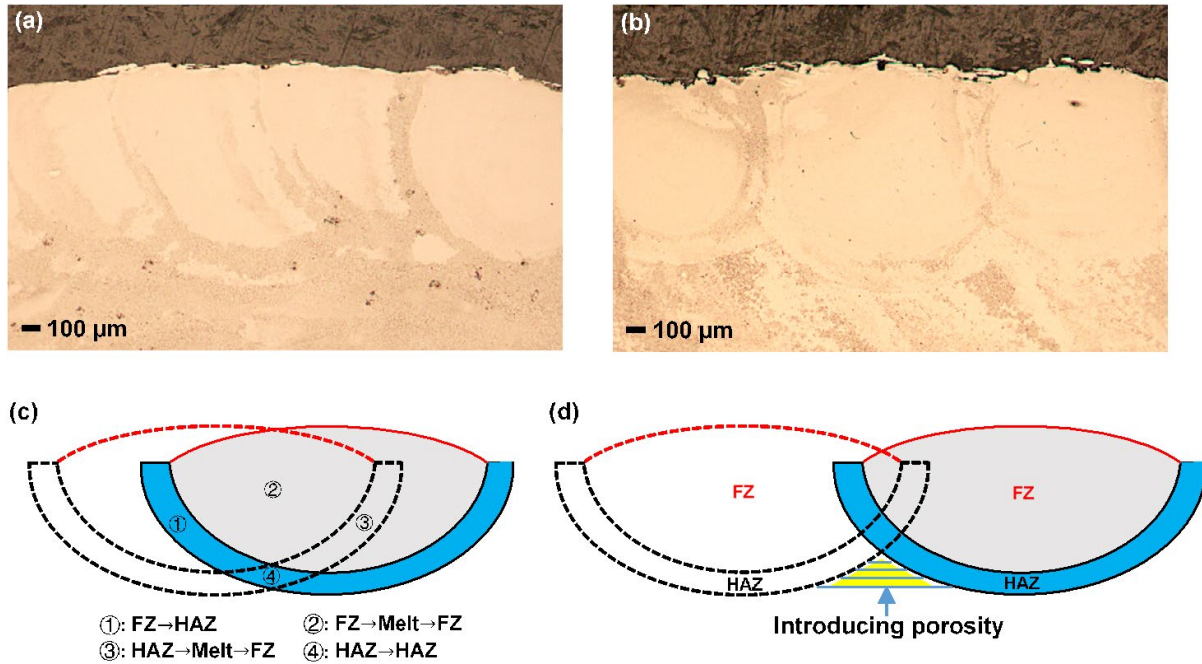


Figure 4.6. Optical microstructures of single-layer BMGC depositions built with 250 W, (a) 0.025-inch hatch spacing and (b) 0.035-inch hatch spacing. (c) Phase transformation in the overlapping zone of adjacent tracks. (d) The design defects of an excessively large hatch spacing.

Table 4.4. Optimized hatch spacings for multi-track ZrCuNiAl BMGC built with different laser powers.

Laser power, W	Value, inch	Overlapping ratio, vol%
200	0.02	61
250	0.025	60
300	0.03	58
350	0.035	56

Resembling the microstructural pattern of single-layer depositions, a representative 5-layer BMGC microstructure is exhibited in Figure 4.7. A periodic microstructure is obtained with a high fraction of amorphous phase and a major fraction of crystalline phases appearing alternately in the FZ and HAZ. Generally, the material initially deposited on the blocking layer experiences a high quenching effect, but this effect will get weakened when depositing subsequent layers due to the reduced cooling rate induced by the heat accumulation. However, this 5-layer sample is free from heat accumulation effect, which must be attributed to the adding of 7-second time interval between tracks. Therefore, it is completely reasonable to expect the manufacture of a bulk structure with a similar microstructural pattern since the time interval can be adjusted accordingly with the increase of layer numbers.

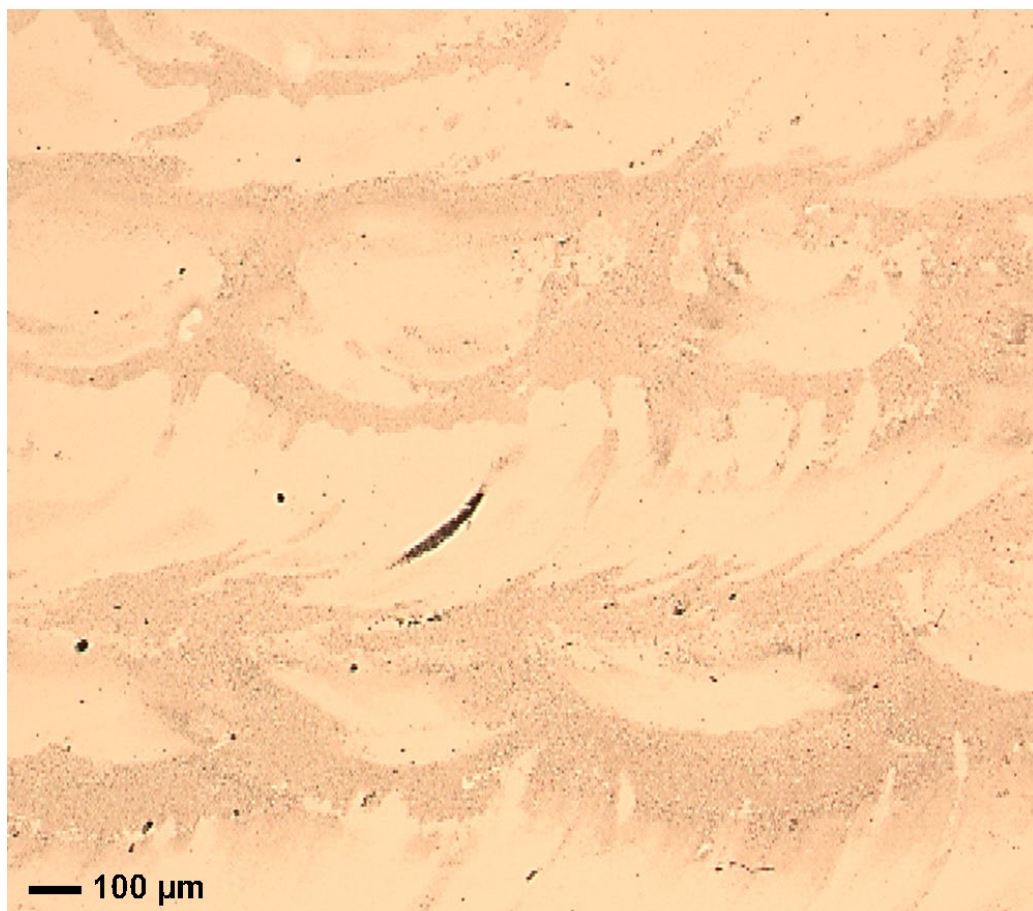


Figure 4.7. The optical microstructure of DED-deposited five-layer BMGC reveals a periodic microstructure with a high fraction of amorphous phase in the fusion zone while more crystalline phases in the heat affected zone.

In order to reveal the microstructure details, a thin slice of sample containing both FZ and HAZ was extracted from the multi-layer specimen using FIB (Figure 4.8(a)) and observed with TEM for the FZ/HAZ boundary (Figure 4.8(b)), FZ (Figure 4.8(c)) and HAZ (Figure 4.8(d)), respectively. The selected-area electron diffraction patterns for the featureless phase in FZ and HAZ are composed of diffuse halo rings superimposed with crystalline patterns, confirming the mixture nature of both zones. Compared with HAZ, FZ has a higher fraction of amorphous phase but fewer crystalline phases. The amorphous phase exhibits an irregularly solidified liquid morphology, in which some round and square crystallized particles are embedded. These crystals are about 100 – 800 nm in FZ (Figure 4.8(c)), while they are in the range of 200 nm – 1.5 μm in HAZ (Figure 4.8(d)), in agreement with the SEM observation (Figure 4.3).

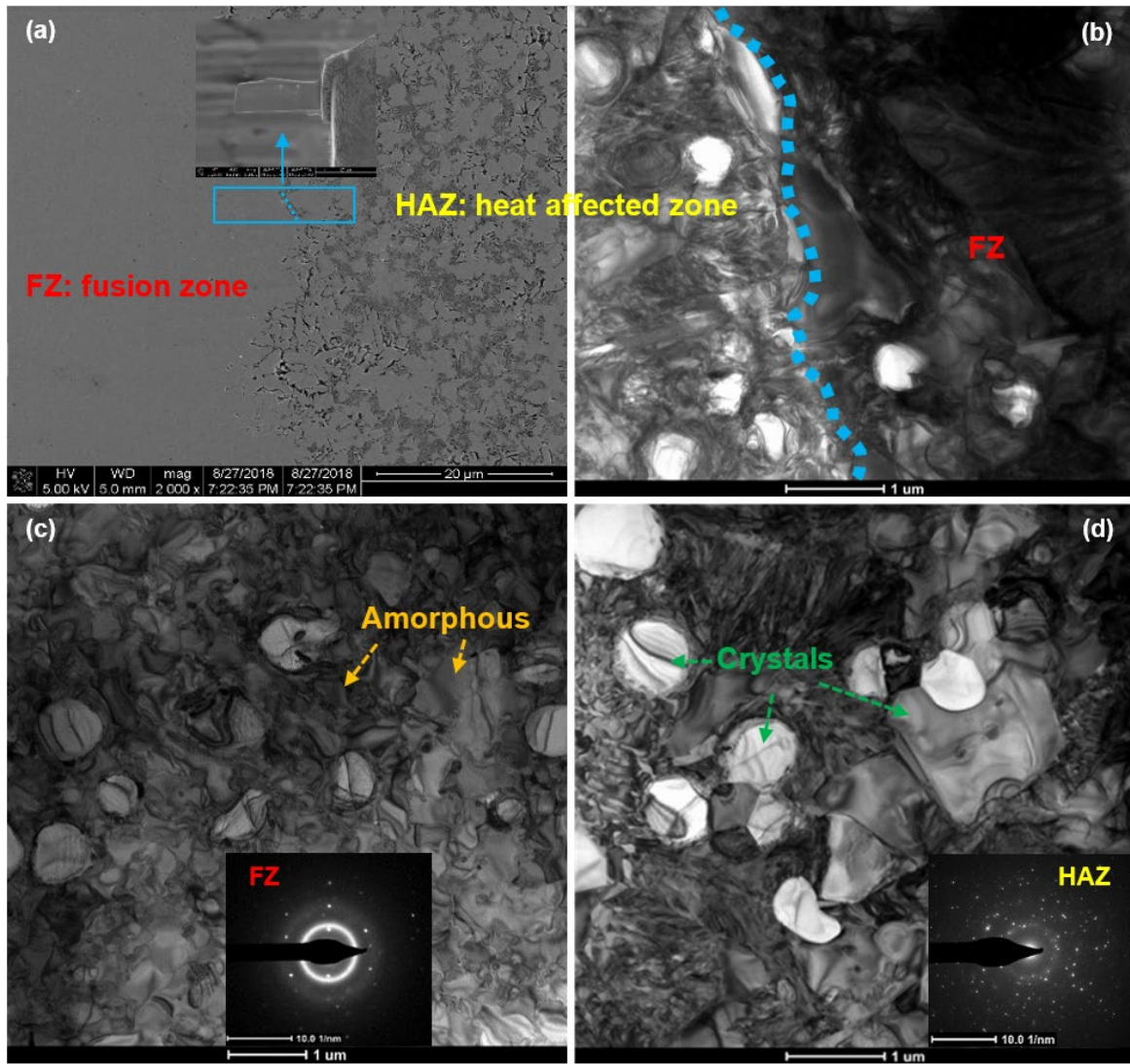


Figure 4.8. (a) TEM sample covers the FZ and HAZ. TEM bright-field images for the (b) FZ/HAZ boundary, (c) FZ and (d) HAZ.

As the precursor material is the premixed powder, different kinds of crystalline phases are expected to form, which are confirmed by the selected-area electron diffraction patterns (insets in Figure 4.8(c, d)) and XRD patterns (Figure 4.9). Several three-layer BMGC depositions built with the deposition parameters shown in Table 4.2 and optimized hatch spacings in Table 4.4 were subjected to the XRD tests. As is clearly shown in Figure 4.9, individual peaks of pure Zr, Cu, Ni and Al are detected for the premixed precursor powder. After interacted with laser, these metals are melted and alloyed. A diffuse broad halo peak that is wide in width and low in intensity, which corresponds to the amorphous phase [132], is observed between 36 – 38 degrees for all the

depositions built with different laser powers. Sharper peaks of crystalline phases that are characterized as NiZr, CuAl₂, ZrCu and Al₂Zr₃ are also superimposed on the amorphous peak. Although the laser power is increased from 200 W to 350 W, the same crystalline phases are formed with a little difference in contents since the relative intensities of different phases can quantify their ratios.

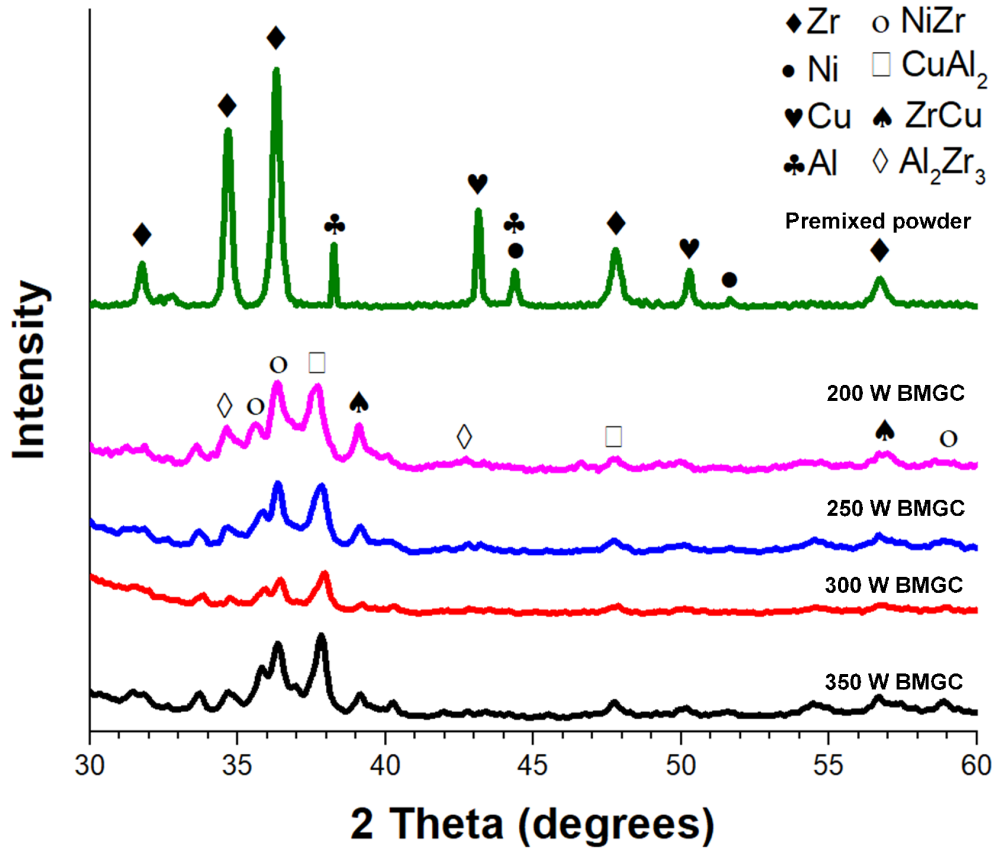


Figure 4.9. XRD patterns of the premixed ZrCuNiAl powder and three-layer BMGC depositions built by different laser deposition parameters.

Since the goal of the current work is to increase the plasticity of the amorphous phase, these formed crystalline phases are highly demanded. The formation of these crystals experiences nucleation and growth. In the DED process, the raw Zr, Cu, Ni, Al metal powders are first melted to form the melt. However, some bigger particles with higher melting temperatures might not be melted completely, becoming the pre-existing nuclei. In addition, the fast heating/cooling rate will produce heterogeneous compositions locally, which are prone to becoming the second-type nucleation sites. The pre-existing nuclei generally grow into larger crystals since they require no

incubation time while relatively smaller crystals grow from the diffusion controlled second-type nuclei [291]. Since the HAZ experienced repeated heating cycles, the crystals are larger than those formed in FZ. As the current work is seeking to introduce crystals in the amorphous matrix, the local inhomogeneity becomes less significant.

4.3.2 Mechanical Property of DED-built ZrCuNiAl BMGC

The mechanical property tests were performed on multiple BMGC parts built with different laser powers, powder feed rates and the corresponding optimal hatch spacings (Table 4.2 and Table 4.4). The mechanical properties turned out to be similar; therefore, the deposition parameters were not specified in this section. Figure 4.10 displays the Vickers microhardness in different zones within one layer. The local microhardness and nanoindentation hardness values along with the overall macrohardness value are summarized in Table 4.5. The average microhardness in FZ is about 620 HV_{0.2} while that in HAZ is only about 450 HV_{0.2}. The higher hardness detected in FZ indicates the decisive role of amorphous phase in enhancing the hardness and strength. The average overall macrohardness of this single-layer sample is approximate 604 HV, which is only 2.6% less than that in FZ. Calculating using rules of mixtures, the FZ turns out to occupy the single layer about 89 vol% with HAZ accounting for 11 vol%.

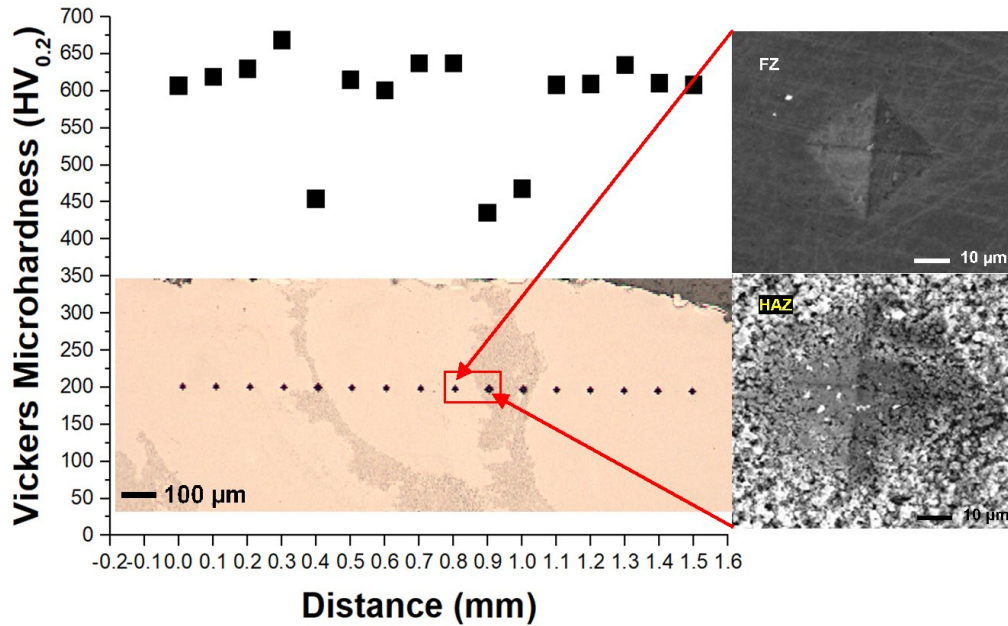


Figure 4.10. Vickers Microhardness results for the DED-deposited single-layer ZrCuNiAl BMGC. Insets show the indents in fusion zone (FZ) and heat affected zone (HAZ).

Table 4.5. Rockwell macrohardness, Vickers microhardness and nanoindentation hardness in fusion zone (FZ) and heat affected zone (HAZ).

Hardness	FZ	HAZ
HV _{0.2}	621.94±18.10	452.62±13.25
Nanoindentation, GPa	5.68 (HV579)	2.37 (HV241)
Rockwell superficial-HR15N	88.2±0.49 (HV604±9)	
Vol.	89%	11%

During indentation, stress will be highly concentrated beneath the indenter. Wavy patterns of shear bands are hence expected to form surrounding the indents [287, 292]. In order to observe the shear bands, increased loads were used for the microhardness test since the increased indentation should have a higher likelihood to produce shear bands. However, no apparent large shear bands were observed for all the indents obtained in FZ and HAZ, as shown in the insets of Figure 4.10. Although the amorphous content in FZ is high, the presence of crystalline phases successfully inhibits the formation and development of shear bands. Similar observations were also revealed in Singh et al.'s work [143], who performed microhardness tests on Zr-based BMG in the as-built glassy and annealed crystalline conditions. A decrease in shear bands was observed in the annealed condition compared to the as-built condition, which was attributed to the presence of nanocrystalline/nanoquasicrystalline phases. The mechanisms related to the improved plasticity have been experimentally revealed in several aspects. While loading, a stress field will first be formed at the crystal-amorphous interface due to their different responses to the applied load, where tiny shear bands will nucleate [134, 138]. In order to alleviate the stress field, the embedded unstable crystals would change their shapes [134]. During the propagation of shear bands, these crystals also serve as barrels, retarding their propagation and promoting new shear bands [141]. Nanocrystals with several nanometers in size can even grow in shear bands since the thickness of shear bands is about 10 nm [293].

To comprehend the hardness and plastic deformation behaviors in different zones at the sub-micro length scale, nanoindentation tests were carried out. Figure 4.11 depicts the change in hardness with the increase of nanoindentation depth in FZ and HAZ for single-track (Figure 4.11(a)) and two-track (Figure 4.11(b)) BMGC. Compared with the single track, the two-track sample exhibits a comparable result in FZ and HAZ, respectively. Furthermore, the hardness values in FZ_A and FZ_C in the two-track sample are also in a good agreement. This consistent hardness indicates the microstructure stability in FZ and HAZ, which are independent of the track and layer

numbers. Therefore, the mechanical property for the bulk structure can be evaluated based on these track results.

As shown in Figure 4.11, the hardness varies with the increasing indentation depth in both FZ and HAZ. The underlying reason is primarily attributed to the indentation size effect that occurs predominantly due to the activation of shear transmission zones, and the concentrated defects in the highly stressed zone associated with the enlarged indent [294, 295]. The commonly used method to address the indentation size effect and calculate the intrinsic hardness is the Nix-Gao model [296], which defines the relationship between indentation hardness and indentation depth as $H/H_0 = \sqrt{1 + h^*/h}$. Here, H is the hardness at indentation depth h , H_0 is the intrinsic hardness at infinite depth, and h^* is the characteristic length parameter. The average H_0 for multiple measurements in FZ is about 5.68 GPa while that in HAZ is only about 2.37 GPa, in a similar trend with the microhardness result (Figure 4.10). Additionally, the formation of various crystalline phases in HAZ increases the heterogeneity, which should be responsible for the larger scatter in hardness values measured in HAZ compared to FZ.

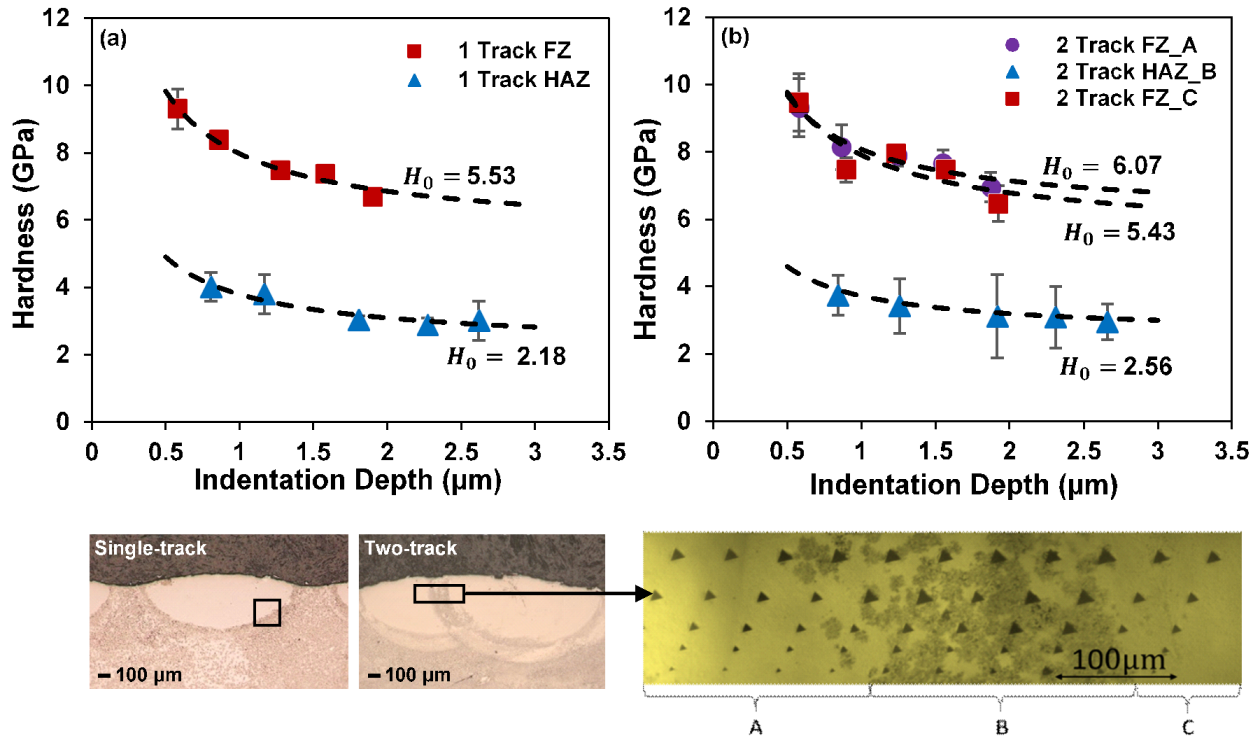


Figure 4.11. Nanoindentation hardness in fusion zone (FZ) and heat affected zone (HAZ) of the DED-built (a) single-track and (b) two-track ZrCuNiAl BMGC. [19]

Table 4.6 summarizes the nanoindentation and compression results for the ZrCuNiAl BMGC built in this work along with those from the literature. Li et al. [287] studied mechanical properties of the cast monolithic $\text{Zr}_{65}\text{Cu}_{15}\text{Ni}_{10}\text{Al}_{10}$ BMG and obtained a nanoindentation elastic modulus of 109.8 GPa and compression ductility of about 3%. Compared with this pure BMG, the measured average elastic modulus in FZ (116.3 GPa) of the $\text{Zr}_{65}\text{Cu}_{15}\text{Ni}_{10}\text{Al}_{10}$ BMGC built in this work is comparable, which indicates that the 0.7 μm indenter is small enough to only cover the amorphous phase. Differently, the author's previous work for this BMGC obtained an improved compression ductility of 5.8% [132]. Since the nominal composition is the same, the improved ductility of BMGC confirms the positive role of crystalline phases in improving the plasticity.

When using the 100 μm radius tip, the composite microstructure in FZ and HAZ will account for the macroscopic elastic modulus as a result. Consequently, the FZ turned out to have the overall elastic modulus of 107.3 ± 3.0 GPa while it was 117.0 ± 2.2 GPa in HAZ. It should be noted that these elastic modulus values were accurately calculated since the diamond area function of the indenter tip has been calibrated on tungsten sample at a load range from 50 – 500 mN prior to measurements [297, 298]. Therefore, the abnormally high macroscopic elastic modulus in HAZ was believed to be an outcome of residual stresses; however, the authors reserve this opinion and further studies are being conducted to reveal the accurate underlying reason. Moreover, Basu et al.'s study [279] also revealed the influences of crystal morphology and the orientation of phases on the elastic modulus; and Liu et al. [299] also studied the relationship between the grain size and mechanical properties, which however is not the focus of the current work yet. It should be noted that microstructure consists of phases and grains. The current work mainly focuses on the influences of phases other than grains on the mechanical properties since the phase plays a more dominant role than grain structure due to the big difference in volume fractions of amorphous and crystalline phases.

The nanoindentation hardness results for $\text{Zr}_{55}\text{Cu}_{30}\text{Ni}_5\text{Al}_{10}$ and $\text{Zr}_{60}\text{Cu}_{10}\text{Ni}_{15}\text{Al}_{15}$ BMG [300, 301] that are summarized in Table 4.6, where the hardness values of these compositions increase with the formation of crystalline phases, contradict that of the $\text{Zr}_{65}\text{Cu}_{15}\text{Ni}_{10}\text{Al}_{10}$ built in this work. The underlying reason is associated with the formed crystalline phases. For $\text{Zr}_{55}\text{Cu}_{30}\text{Ni}_5\text{Al}_{10}$, $\text{Zr}_{60}\text{Cu}_{10}\text{Ni}_{15}\text{Al}_{15}$ and $\text{Zr}_{50.7}\text{Cu}_{28}\text{Ni}_9\text{Al}_{12.3}$, the commonly formed crystalline phases are thermodynamically stable intermetallic compounds Zr_2Cu [300], Zr_3Al_2 [301], Zr_2Ni [168, 170, 300, 301], $\text{Al}_5\text{Ni}_3\text{Zr}_2$ [162, 167, 170, 300] and Ni_3Zr [302], while NiZr [132] and CuZr [132, 303]

prevail in $Zr_{65}Cu_{15}Ni_{10}Al_{10}$. Some metastable $Cu_{10}Zr_7$ and $CuZr_2$ phases may also form at relatively lower tempering temperatures [138, 168]. It has been observed that the $ZrCu$ phase undergoes the stress-induced transformation, which is the control mechanism for the improved strain hardening and large ductility [134, 137]; while the lack of any transformation during the deformation of Zr_2Cu fails to enhance the ductility [134]. In addition, the stable intermetallic phases produce a strong intercrystalline interface and the lattice misfit between them provides additional hardening against dislocation movement, which increases hardness but weakens ductility [301]. Additionally, the size of the precipitated crystalline phases also affects the mechanical properties. In order to improve the overall mechanical properties of BMGC, the compositions must be carefully selected to control the formed crystalline phases.

Table 4.6. Nanoindentation and compression test properties of $ZrCuNiAl$ systems built with different methods. Com. Strain is short for Compressive engineering strain.

Composition	Build	Zone	Phase	Indentation hardness (GPa)	Elastic Modulus (GPa)	Indenter	Com. Strain
$Zr_{65}Cu_{15}Ni_{10}Al_{10}$ (this work)	DED	FZ	Composite	5.68	116.3/107.3	Spherical , $r = 0.7$ $\mu m/100$ μm	5.8% [132]
		HAZ	Composite	2.37	66.3/117.0		
		Overall (rules of mixtures)		5.32	91.5	-	
$Zr_{55}Cu_{30}Ni_{15}Al_{10}$ [170, 300]	SLM	FZ	Amorphous	6.09 ± 0.23	70.99 ± 3.54	Berkovich	2.3%
		HAZ	Composite	6.27 ± 0.24	75.16 ± 1.58		
$Zr_{65}Cu_{15}Ni_{10}Al_{10}$ [287]	Cast	-	Amorphous	5.67	109.8	Berkovich	3%
		Overall (compression test)		-	85.8	-	
		Overall (ultrasonic measurement)		-	82.3	-	
$Zr_{65}Cu_{15}Ni_{10}Al_{10}$ [292]	Cast	-	Amorphous	4.97 ± 0.05	-	Berkovich	-
$Zr_{60}Cu_{10}Ni_{15}Al_{15}$ [301]	Cast	-	Amorphous	5.95	111.2	Berkovich	-
			Composite	6.80	124.6		
			Crystalline	8.33	131.3		

Note: SLM is selective laser melting, a laser-based powder bed additive manufacturing process. Composite indicates a mixture of amorphous phase and crystalline phases. r means radius.

4.4 Summary

This chapter successfully in-situ built ZrCuNiAl BMGC with a similar hardness but highly improved ductility compared with monolithic BMG using premixed pure Zr, Cu, Ni, and Al metal powders via the DED process. High energy ball milling utilized to prepare the flake-shaped Zr powder solved its incomplete melting issue associated with typical gas atomized Zr particles. The DED model predicted a peak temperature of 1500 – 1662 K and a cooling rate of $10^3 - 10^4$ K/s in FZ, which produced about 95.3 vol% amorphous phase while laser reheating during the subsequent deposition led to partial crystallization in HAZ, resulting in a periodically repeated amorphous-crystalline microstructure. This microstructure was successfully maintained from single-track depositions to multi-layer bulk structures due to the 7-second dwelling time between tracks. The utilization of premixed metal powders produced approximate 4.7 vol% 100 – 800 nm crystalline phases in FZ. These crystalline phases must have a lower hardness than the amorphous phase since the FZ has a higher Vickers microhardness of 620 HV_{0.2} than the 450 HV_{0.2} microhardness in HAZ. Through a proper selection of deposition parameters, the FZ occupied about 89 vol% in the bulk structure and maintained an overall hardness of 604 HV. The indentation stress-strain data accurately corrected by the iterative numerical algorithm using finite-element modeling predict a yield stress of about 1.55 GPa and 0.52 GPa in FZ and HAZ, respectively. Compared with monolithic amorphous phase, the in-situ formed crystalline phases effectively inhibited the nucleation and propagation of shear bands.

5. DIRECTED ENERGY DEPOSITION OF QUINARY COCRFENITI HIGH ENTROPY ALLOYS

In this chapter, three CoCrFeNiTi high entropy alloys (HEAs) with different compositions were designed and synthesized from premixed elemental powders via the directed energy deposition (DED) process. Through a delicate design of composition and powder preparation, different microstructures were formed. H3-Co24.4Cr17.4Fe17.5Ni24.2Ti16.5 was mainly composed of a soft face-centered cubic (FCC)- γ phase while σ -FeCr, δ -NiTi₂, and a small amount of Ni₃Ti₂ were precipitated and uniformly distributed in the FCC matrix for H1-Co22.2Cr16.1Fe19Ni21.8Ti20.9 and H2-Co25.9Cr15Fe17Ni20.8Ti21.3. With a large percent of the secondary phases, H1 exhibited a hardness value of about 853 HV_{0.5}. These HEAs displayed a high oxidation resistance comparable to Inconel 625 superalloy. A detailed evaluation of the hardness, oxidation resistance, and wear resistance of these HEAs were conducted as compared with those of a reference HEA and two popular anti-wear steels.

5.1 Composition Design and Experimental Procedure

The formation of HEA is highly dependent on the constituent elements. In this study, the CoCrFeNiTi HEA feedstock powders were prepared by premixing pure Co, Cr, Fe, Ni, and Ti metal powders with a prescribed atomic ratio. Among these metals, Cr has the highest melting temperature and will experience a partial melting when exposed to the laser processing condition that will be good for melting other lower melting temperature elements. Increasing the laser power density too much to melt Cr powder can result in adverse effects such as evaporation of lower melting temperature elements and turbulent molten pool. In authors' previous study on in-situ synthesis of ZrCuNiAl bulk metallic glasses [19], using flake-shaped Zr powders successfully solved the incomplete melting problem of Zr powders because the flake shape has a larger surface area than spherical ones and small particle size could be conducive to melting. Similarly, 45 – 75 μ m flake-shaped Cr powders instead of regular gas-atomized spherical powders, obtained from Reade Advanced Materials®, were used as a raw material. As for Co, Fe, Ni, and Ti powders, it has no strict requirements on particle shape and size. All of these four powders (45 – 150 μ m) were

obtained from Atlantic Equipment Engineers® with Co and Ni powders in spherical shape while Fe and Ti are irregular.

Another issue for the blown-powder AM of premixed metal powders is the deviation between the actual and premixed compositions due to the different flowability and density of each metal powder during deposition. The reference HEA for the current study is Co_{1.5}CrFeNi_{1.5}Ti (Co₂₅Cr_{16.7}Fe_{16.7}Ni₂₅Ti_{16.7} in at.%) [206]. Based on this reference HEA, three different HEA compositions named H1, H2, and H3 were eventually designed. Table 5.1 summarizes the premixed and actual compositions of these HEA alloys. The actual composition is referred to as the overall average composition characterized by the energy-dispersive X-ray spectroscopy (EDX) in the mapping model for almost the entire cross-section of a specimen, and it must be detected before etching because the etchant may dissolve some constituents. H1 was designed with the premixed composition same as that of the reference HEA, but the actual composition turned out to be lower in Co, Ni, and Ti while higher in Fe. After increasing the atomic ratio of Co and Ni but decreasing Cr and Ti in the premixed composition, the actual composition approached the reference HEA. Considering the 2 at.% detection error in EDX, H3 achieved an actual composition quite similar to the reference composition. An interesting finding between H2 and H3 is that a tiny change in the atomic ratio of Cr, Fe, and Ti led to a significant deviation in the actual compositions. This finding implies the reaction among these elements and distinctively different microstructures between these HEA alloys can occur with the slight changes of premixed powder composition.

Table 5.1. EDX analysis of overall average composition (in at.%) of DED-built CoCrFeNiTi HEA alloys before etching.

Element	H1		H2		H3	
	Premixed	Actual	Premixed	Actual	Premixed	Actual
Co	25	22.2	28	25.9	28	24.4
Cr	16.7	16.1	16	15	15	17.4
Fe	16.7	19	14	17	16	17.5
Ni	25	21.8	28	20.8	28	24.2
Ti	16.7	20.9	14	21.3	13	16.5

The three HEA alloys were synthesized using the Optomec LENS® 750 system, equipped with a 500 W fiber laser. The premixed powders were delivered via argon gas to the laser focal spot through quad nozzles. Argon was also used to provide an inert atmosphere of less than 20

ppm oxygen in the sealed working chamber. A 6 mm thick 304L stainless steel plate was used as the substrate, onto which 7 mm cubes of HEA alloys were deposited. After building one layer, the laser scan was rotated by 90 degrees, and the laser focal point was raised in the Z direction by a preset distance equal to the layer thickness, which was calculated by averaging the total height of several layers. Scan speed is a key factor affecting the composition homogeneity. Based on the authors' previous work on the DED-synthesized bulk metallic glass composites using premixed elemental powders [19], 10 mm/s was chosen as an ideal scan speed in homogenizing the composition. Large laser power and small scan speed would always produce a relatively dense part. Hatch spacing is the distance between two adjacent tracks and optimal hatch spacing can result in a suitable layer height and a smooth surface finish. Table 5.2 summarizes the optimized DED deposition parameters after preliminary tests.

Table 5.2. DED deposition parameters for CoCrFeNiTi HEA alloys.

Parameters	Value	Unit
Laser power	350	W
Laser scan speed	10	mm/s
Powder feed rate	3.7	g/min
Hatch spacing	305	μm
Layer height	254	μm

After the specimens were built, they are cross-sectioned, mounted in bakelite, and polished using the standard metallographic technique for microstructure characterization. Microstructure details were revealed using the aqua regia solution and observed with an optical microscope (Nikon Eclipse LV150), and a scanning electron microscope (Quanta 650 FEG) equipped with an EDX detector. The top surface of the specimens was polished with #800 SiC sandpapers and exposed to the X-ray diffractometer to acquire the XRD patterns with 2 theta-angle ranging from 20 to 75 degrees at a scan speed of 5 degrees/min. Vickers microhardness tests were conducted using a LECO KM 247AT tester with a load of 500 g and a dwell time of 13 s. A continuous oxidation test was performed at 800 °C for 24 h followed by air cooling in a tube furnace open to the air. The heating rate was 10 °C/min. Before the oxidation test, the as-built HEA blocks were polished to achieve smooth surfaces and made into a regular rectangular shape such that the surface area could be accurately measured. Masses of the specimens before and after oxidation tests were measured to calculate the weight gain (mg/mm²).

5.2 Results

Figure 5.1 illustrates the SEM secondary electron (SE) images of H1. Due to the track-by-track feature of the AM process, distinct fusion zones (FZ) and heat-affected zones (HAZ) are observed where HAZ exhibits a darker contrast than FZ after etching (Figure 5.1(a)). Representative regions covering both the FZ and HAZ outlined by the solid frame in Figure 5.1(a) are shown with higher magnification in Figure 5.1(b) and (c) for FZ and HAZ, respectively. Quite different microstructures are observed for the FZ and HAZ. For the FZ, a relatively denser phase with a light color occupies almost the entire micrograph. Only at the local etched tiny regions, a dark phase is revealed. Different from FZ, the light phase becomes much sparser and coarser in the HAZ, exposing overall a large area of dark phase. EDX detection reveals a higher concentration of Cr and Fe but lower Ni and Ti in the dark phase while the light phase displays a contrary composition distribution. It is hence reasonable to conclude that two different phases that are rich in (Fe, Cr) and (Ni, Ti) were formed.

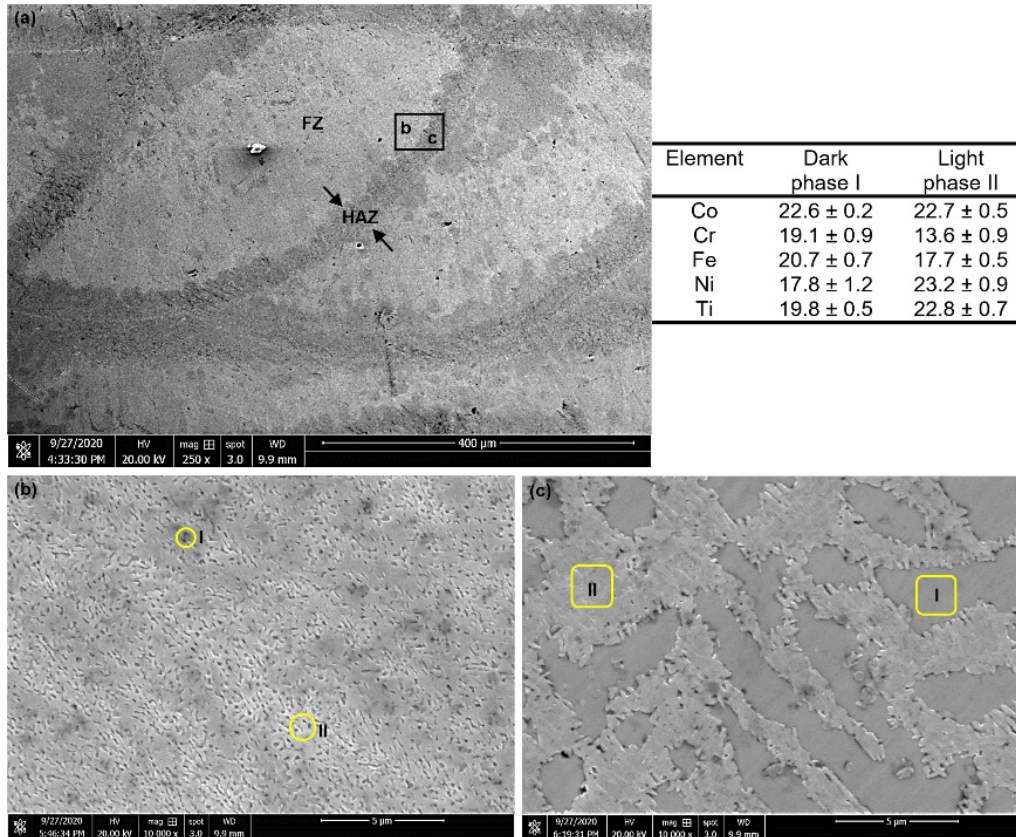


Figure 5.1. SEM secondary electron images and EDX results for different phases of H1: (a) low magnification reveals a distinct microstructure between fusion zone (FZ) and heat-affected zone (HAZ), (b) FZ and (c) HAZ with high magnification for the selected region outlined by the frame in (a).

Figure 5.2 shows the SEM secondary electron (SE) images of H2. With a different actual composition from H1, H2 reveals a quite distinct microstructure, where the light dendrites are homogeneously embedded in the matrix (Figure 5.2(a)). Comparing the microstructures in FZ and HAZ, the dendrites in HAZ grew coarser because of the repeated heating cycles. When observing the amplified images for FZ (Figure 5.2(b)) and HAZ (Figure 5.2(c)), the matrix displays a discontinuous grid-shaped morphology, consisting of small isolated islands with a size of about 400 nm – 1 μ m. These small islands are encompassed with a light-color phase. Due to its similar color contrast to the dendrites, it is believed to have the same composition as the dendrites because the color contrast accounts for the composition difference. The EDX results confirm the formation of (Fe, Cr, Ni)-rich phases in dendrites and Ti-riched phases in the matrix; however, the small size of the light-color phase isolating the islands in the matrix is beyond the capability of EDX.

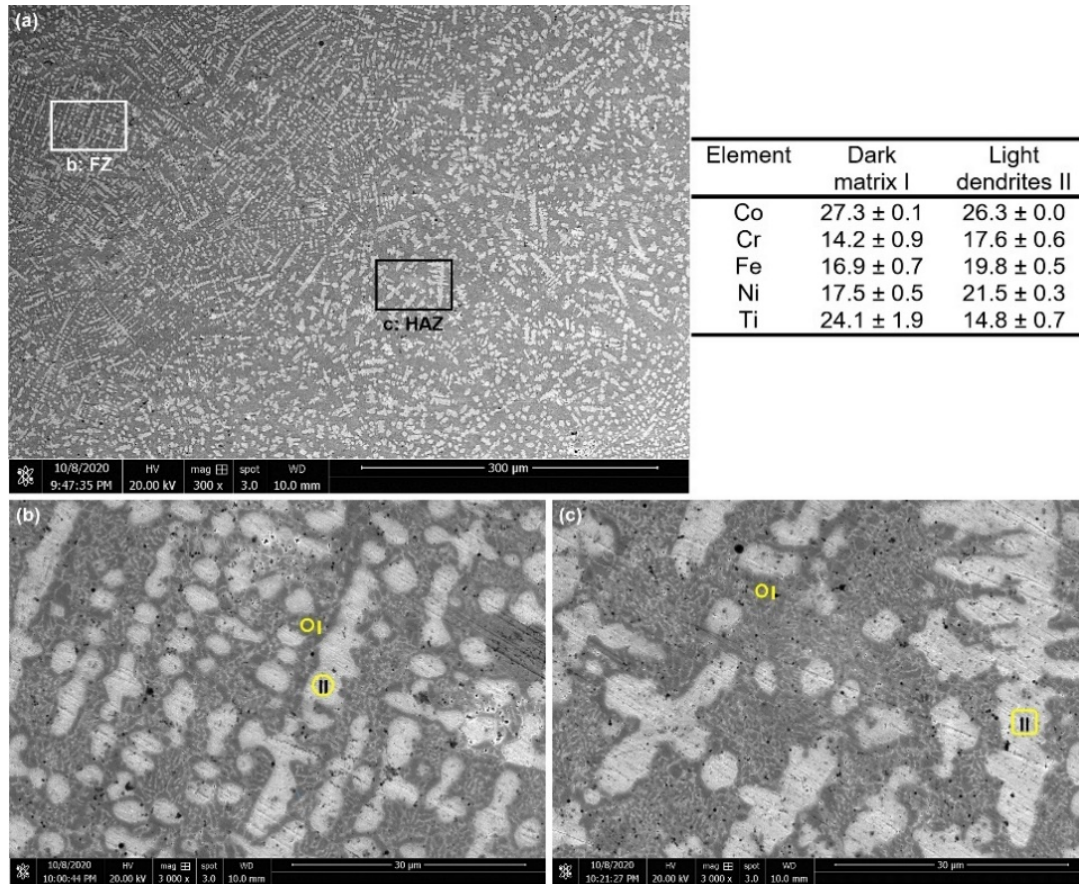


Figure 5.2. SEM secondary electron images and EDX results for different phases of H2: (a) low magnification microstructure of fusion zone (FZ) and heat-affected zone (HAZ), (b) FZ and (c) HAZ with high magnification for the selected regions outlined by the frames in (a).

The SEM SE images of H3 is exhibited in Figure 5.3. Compared with H1 and H2, a completely different microstructure is produced. Although it is still the dendritic phases that dominate the microstructure, different from H2 (Figure 5.2), the dendrite arms have a darker contrast while the interdendritic regions reveal a slightly lighter color (Figure 5.3(b) and (c)). The EDX results reveal similar Co and Ni concentrations in these two phases, but the dendrite arms have a little higher concentration of Fe and Cr but lower Ti than the interdendritic regions. Compared with H1 and H2, the color contrast and composition deviation between two different phases are relatively small. Amplifying the microstructure in the outlined region in (c) with a higher magnification (Figure 5.3(d)), it can be seen that quite a few isolated spherical nano-precipitates are dispersed throughout the entire microstructure. Due to their small size compared with the EDX probe size, the composition acquisition of these nano-precipitates is beyond the capability of EDX. In addition, some needle-like and plate-shaped phases are also observed in the interdendritic regions. Although the amplified image in (b) is not shown in Figure 5.3, it exhibits a similar microstructure to (d).

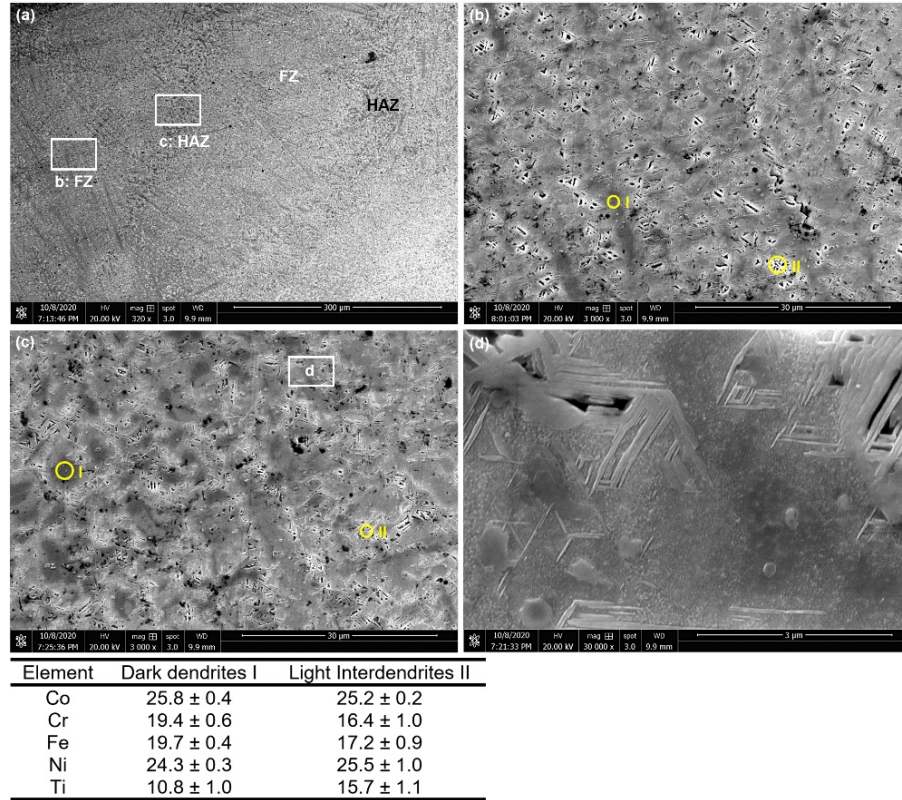


Figure 5.3. SEM secondary electron images and EDX results for different phases of H3: (a) low magnification image, (b) fusion zone (FZ), and (c) heat-affected zone (HAZ) for the selected regions outlined by the frames in (a), (d) a high magnification image of the outlined region in (c).

Figure 5.4 displays the XRD patterns of three HEA alloys synthesized in this study. The premixed feedstock materials are composed of pure Co, Cr, Fe, Ni, and Ti elemental powders. After interacting with the laser, these metals are melted and alloyed. However, a local heterogeneous composition is easy to form due to the premixed precursor material and the unique nonuniform thermal history of AM processes, and therefore a large amount of background noise is observed. All of the three XRD patterns present dominant FCC- γ peaks. A similar primary phase was also found in the reference Co_{1.5}CrFeNi_{1.5}Ti HEA built by casting followed by aging [206]. However, the reference HEA contains an η -Ni₃Ti phase as the secondary hardening phase, which is not detected in the current study. Instead, peaks corresponding to σ -FeCr, δ -NiTi₂, and metastable Ni₃Ti₂ are detected, confirming the EDX results for the (Fe, Cr)-rich phase and Ti-rich phases in the three HEA alloys. It should be noted that a tiny amount of Ni₄Ti₃, Ni₃Ti, and NiTi may be formed because of a large amount of heterogeneous composition but no clear peaks were detected. From H1 to H3, the peak intensity of these secondary phases is gradually decreased, implying a reduced volume percent since the relative intensities of different phases can quantify their ratios. As for H3, it is mostly composed of the FCC- γ solid solution with a small amount of σ -FeCr phase and neglectable δ -NiTi₂ and Ni₃Ti₂. This XRD analysis for H3 is consistent with the EDX detection as both phases have a quite similar Co and Ni concentration (Figure 5.3). As for H1 and H2, the EDX results only display a difference in Ni contents between different phases but a similar Co content. Although Co and Ni were reported to substitute each other in the alloying process due to their similar atomic size and chemical property [304, 305], the substitution seems not to occur for the HEA alloys synthesized in this study.

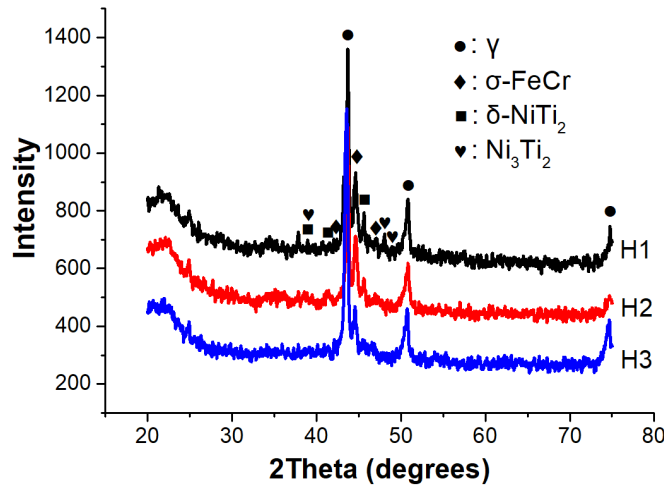


Figure 5.4. XRD patterns of three HEA alloys synthesized by the DED process.

To comprehend the hardness in different zones at a small length scale, Vicker's microhardness tests were carried out. Because of the heterogeneous microstructure in FZ and HAZ, a large number of indentations were measured to evaluate the average hardness of the alloy. Table 5.3 summarizes the average hardness of the three DED-synthesized HEA alloys compared with the reference HEA and two high wear-resistant steels. The local heterogeneous composition should be responsible for the large scatter in hardness values. With a more uniform composition from H1 to H3, the standard deviation is hence decreased. H1 has the highest hardness of about 853 HV_{0.5}. Compared with H1, the average microhardness of H2 is lower by about 200 HV_{0.5} while H3 has the lowest hardness of about 513 HV_{0.5}. As the hardness of the soft FCC- γ phase is about 500 HV [206], which is close to that of H3, this further confirms H3 to be almost only composed of the γ phase. With the formation of the hard σ -FeCr and δ -NiTi₂ intermetallic phases, H1 and H2 are expected to own a much higher hardness. As illustrated in Table 5.3, the hardness of H1 is comparable to that of AISI M2 high-speed steel and is about 130 HV higher than that of AISI 52100 bearing steel. Both of these two steels are commonly used wear-resistant materials. Therefore, H1 is believed to possess a positive anti-wear performance. As H2 has similar hardness, oxidation resistance, and constituent elements to the reference HEA, they are hence expected to have comparable wear resistance.

Table 5.3. Vickers microhardness of DED-synthesized HEA alloys compared with the reference HEA and two typical wear-resistant steels.

HEA composition	Vickers microhardness HV
H1	852.95 $\pm$ 36.36
H2	669.22 $\pm$ 20.47
H3	513.09 $\pm$ 11.23
Reference Co _{1.5} CrFeNi _{1.5} Ti HEA	654 $\pm$ 7 [206]
AISI M2 high-speed steel	890 [206]
AISI 52100 bearing steel	722 [206]

Note: The reference HEA was manufactured with casting followed by aging.

Figure 5.5 shows the oxidation results of the three DED-synthesized HEA alloys compared with the reference Co_{1.5}CrFeNi_{1.5}Ti HEA, AISI M2 high-speed steel, and AISI 52100 bearing steel after oxidation at 800 °C for 24 h in air. The oxidation resistance was characterized by the weight gain (mg/mm²) such that a low weight gain value corresponds to high oxidation resistance. All three DED-synthesized HEAs have comparable weight gain values to the reference HEA and the

Inconel 625 superalloy despite the slightly larger weight gain values of H1 and H3. This positive oxidation result indicates the potential of the HEA alloys for their high-temperature applications. On the contrary, the weight gain of AISI M2 and AISI 52100 steels are more than 20 times and 30 times higher, revealing a much higher oxidation rate at elevated temperatures. Combined with the microhardness and oxidation results, the DED-synthesized HEA alloys are also expected to possess a high wear resistance although the tribological test was not performed in this study. Further discussion linking the composition, microstructure, hardness, and oxidation resistance, as well as wear resistance, is given in Section 5.3.

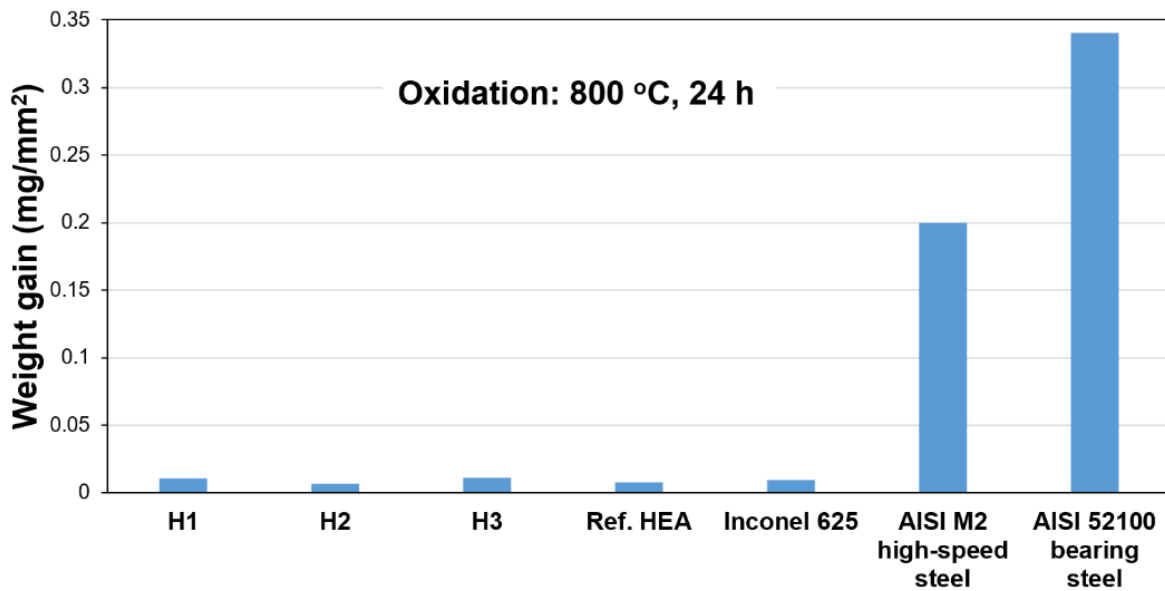


Figure 5.5. Oxidation results of DED-synthesized three HEA alloys, reference HEA [206], Inconel 625 [306], AISI M2 high-speed steel [206], and AISI 52100 bearing steel [206] at 800 oC for 24 h.

5.3 Discussion

The three HEA alloys designed in this study are directly synthesized using the DED AM process from elemental powders. Due to the unique thermal history of the AM process, a portion of the previous track and layer will be remelted or reheated during the deposition of subsequent tracks and layers. The tempering effect experienced in the HAZ will lead to the coarsening of grains, resulting in a non-uniform heterogeneous microstructure (Figure 5.1 – Figure 5.3). Therefore, the overall mechanical properties must be evaluated by averaging the substantial number of measurements in different regions of the microstructure.

The selected compositions were based on the reference $\text{Co}_{1.5}\text{CrFeNi}_{1.5}\text{Ti}$ HEA, which was reported to be an ideal candidate material for anti-wear applications [206]. The underlying reason associated with the high wear resistance is attributed to the constituent phases that result in high hardness and super oxidation resistance. First, a large ratio of strong FCC formers, Co and Ni, were added to the CoCrFeNi HEA system to enhance the formation of a soft FCC primary phase [307], which endows the alloy with high workability by plastic deformation [308]. Second, additional Ti was added to facilitate the formation of hard intermetallic $\eta\text{-(Ni, Co)}_3\text{Ti}$ phase such that the precipitation hardening induced by the η phase will enhance the hardness and wear resistance of the alloy. A similar design idea was adopted in this study for the primary FCC- γ phase. As for the introduction of secondary hardening phases, the current study adopted the blown-powder DED process instead of casting to directly synthesize the novel HEA alloys by alloying elemental powders. The advantage of premixed elemental powders against prealloyed powders has been discussed in the introduction section. The key advantage is its high effectiveness in forming various crystalline phases because of the local heterogeneous composition [19]. Since one target property of the HEAs synthesized in this study is the wear resistance, forming complex secondary hardening phases is very much needed.

As illustrated by the EDX results in Table 5.1 and Figure 5.1 – Figure 5.3, H3 was designed with an actual composition close to the reference HEA. It turned out to be mainly composed of the FCC- γ phase with few secondary phases. After varying the atomic ratios of the five constituents, a large amount of $\sigma\text{-FeCr}$ and $\delta\text{-NiTi}_2$ secondary phases were formed in H1 and H2 (Figure 5.4). The σ phase can be precipitated under 600 – 1000 °C and is prevalent in (Fe, Cr)-contained alloys since the strong ferrite stabilizer Cr facilitates the formation of σ easily [309-312]. Different from the reference HEA, the $\eta\text{-Ni}_3\text{Ti}$ phase was not detected. Instead, $\delta\text{-NiTi}_2$ is prevalent in AM-built (Ni, Ti)-contained alloys [14, 313, 314]. In addition, metastable Ni_3Ti_2 was also detected. Compared with H2, the higher percent of secondary phases in H1 leads to a much higher hardness of H1 (852.95 ± 36.36). It is worthwhile to note that XRD is only able to capture the signal of regular-size phases, leaving nano-crystalline phases not discernable [315]. Therefore, the light-color phase isolating the small islands in the matrix of H2 (Figure 5.2) and the nano-precipitates in the matrix of H3 (Figure 5.3) may not be detected via XRD. However, the authors reserve this opinion, and further studies are required to clarify these phases.

The formed hard secondary phases play a critical role in governing the wear resistance of a material. For example, the high hardness and super wear resistance of AISI M2 high-speed steel and AISI 52100 bearing steel mainly result from the hard carbides [316-318]. σ -FeCr is known to lead to an embrittlement of the material due to its much higher hardness [308, 319, 320], and δ -NiTi₂ intermetallic phase has a favorable hardness and wear resistance [14, 321, 322]. Therefore, the formed σ -FeCr, δ -NiTi₂ and Ni₃T₂ intermetallic phases must be the decisive reason for the high hardness of H1 and H2. In general, a material with a high hardness roughly has positive wear resistance. Reinforced with hard particles, the abrasive wear resistance of the soft matrix can hence be improved substantially [323]. However, hardness is not the only qualification indicator for wear resistance. The reference HEA was discovered to have a comparable wear resistance with AISI M2 high-speed steel and twice wear resistance that of AISI 52100 bearing steel despite its much lower hardness than these two materials [206]. The wear mechanism of the reference HEA was reported to be the mild oxidational wear [206, 324, 325]. Due to the sliding frictional effect, the local contact point could reach a temperature of more than 800 °C under certain sliding conditions [326]. With such high temperatures, the oxidation resistance and high-temperature stability must be considered to evaluate the material's anti-wear performance. Metals with low oxidation activity would wear out slowly [327]. A dense oxidation layer would protect the base material from the degree of adhesive wear [328], and the formation of hard ceramic oxides like Al₂O₃ and TiO₂ at the contact surface could further reduce the wear rate [329, 330].

Although the tribology test is not carried out in this study, it is completely reasonable to expect a similar wear resistance of H2 to the reference HEA due to their similar hardness and oxidation resistance. Since H1 has a much higher hardness and comparable oxidation resistance compared with the reference HEA, H1 must possess an even better anti-wear performance. On the contrary, since the dominant phase of H3 is the soft FCC- γ phase with a low hardness of about 513 HV, it would suffer from severe abrasive wear due to its high plastic deformation [323]. In addition to the anti-wear performance, the three HEA alloys synthesized in this study also show great potential for high-temperature applications due to their matched oxidation resistance with Inconel 625.

5.4 Summary

This chapter adopted the DED process to directly in-situ synthesize three CoCrFeNiTi HEAs, which were designed for high-temperature and anti-wear applications. Because of the use of elemental powders, the actual composition had a big deviation from the premixed composition. For H3 with an actual composition of Co_{24.4}Cr_{17.4}Fe_{17.5}Ni_{24.2}Ti_{16.5}, the microstructure was dominated by the soft FCC- γ phase and a small amount of σ -FeCr phase, resulting in low hardness of about 513 HV_{0.5}. The increased Ti and decreased Co and Ni in the premixed composition led to the formation of σ -FeCr, δ -NiTi₂, and a small amount of Ni₃Ti₂ for H1-Co_{22.2}Cr_{16.1}Fe₁₉Ni_{21.8}Ti_{20.9} and H2-Co_{25.9}Cr₁₅Fe₁₇Ni_{20.8}Ti_{21.3}. With the highest volume percent of the secondary phases, H1 owned a high hardness of about 853 HV_{0.5} close to that of AISI M2 high-speed steel. With a decreased amount of the secondary phases, the hardness of H2 was lower by about 200 HV_{0.5} than H1 and a distinct microstructure with isolated dendrites uniformly dispersing in the matrix was formed. All three HEAs exhibited a comparable oxidation resistance to the reference HEA and Inconel 625 superalloy, which was roughly 20 times higher than the AISI M2 and 30 times higher than the AISI 52100 bearing steel. Since H1 and H2 had a higher or matchable hardness with the reference HEA with the same constituent, which was reported to possess a better wear resistance than AISI M2 and AISI 52100 anti-wear steels, H1 and H2 were believed to own great potential for anti-wear applications.

6. A NOVEL 3D CA-PF MODELING OF EFFICIENT MICROSTRUCTURE PREDICTION DURING SOLIDIFICATION IN A LARGE DOMAIN

In this chapter, a novel 3D CA-PF model that can accurately predict the dendrite formation in a large domain, which combines a 3D CA model with a 1D PF component. In this integrated model, the PF component reformulated in a spherical coordinate is employed to accurately calculate the local growth kinetics including the growth velocity and solute partition at the solidification front while the 3D CA component uses the growth kinetics as inputs to update the dendritic morphology variation and composition redistribution throughout the entire domain. Taking advantage of the high efficiency of the CA model and the high fidelity of the PF model, the 3D CA-PF model saves the computational cost more than five orders of magnitude compared to the 3D PF models without losing much accuracy. By coupling the thermodynamic and kinetic calculations into the PF component, the CA-PF model is capable of handling the microstructure evolution of any complex multi-component alloys. Al-Cu binary alloys with 2 wt.% and 4 wt.% Cu are first used to validate the 3D CA-PF model against the Lipton-Glicksman-Kurz analytical model and a 3D PF model. Then, the 3D CA-PF model is applied to predicting the dendrite growth during large-scale solidification processes of directional solidification of Al-30wt.%Cu and laser welding of Al-Cu-Mg and Al-Si-Mg alloys. In addition to the drastic saving in computational cost over the PF modeling, quantitatively accurate results are also obtained compared to the experimental microstructure.

6.1 Model Description

In this study, the 3D dendrite solidification of multi-component alloys is modeled via a newly developed 3D CA-PF model. This hybrid model is established by the combination of a 3D CA component and a 1D PF component. The 3D CA component captures the dendrite growth and solutes evolution within the entire simulation domain, while the 1D PF component calculates the growth kinetics including the growth velocity at the solidification front and the solute partition at the S/L interface. The growth kinetic data serve as the inputs to the CA component, which also provides the local solidification condition containing the local curvature, composition, and

temperature for the PF component. The PF component is coupled with the thermodynamic data of a multi-component alloy system; therefore, the established 3D CA-PF model is applicable of predicting the 3D dendritic growth and solutes evolution during solidification for any complex alloys. A detailed flow chart of the integrated 3D CA-PF models is illustrated in Figure 6.1.

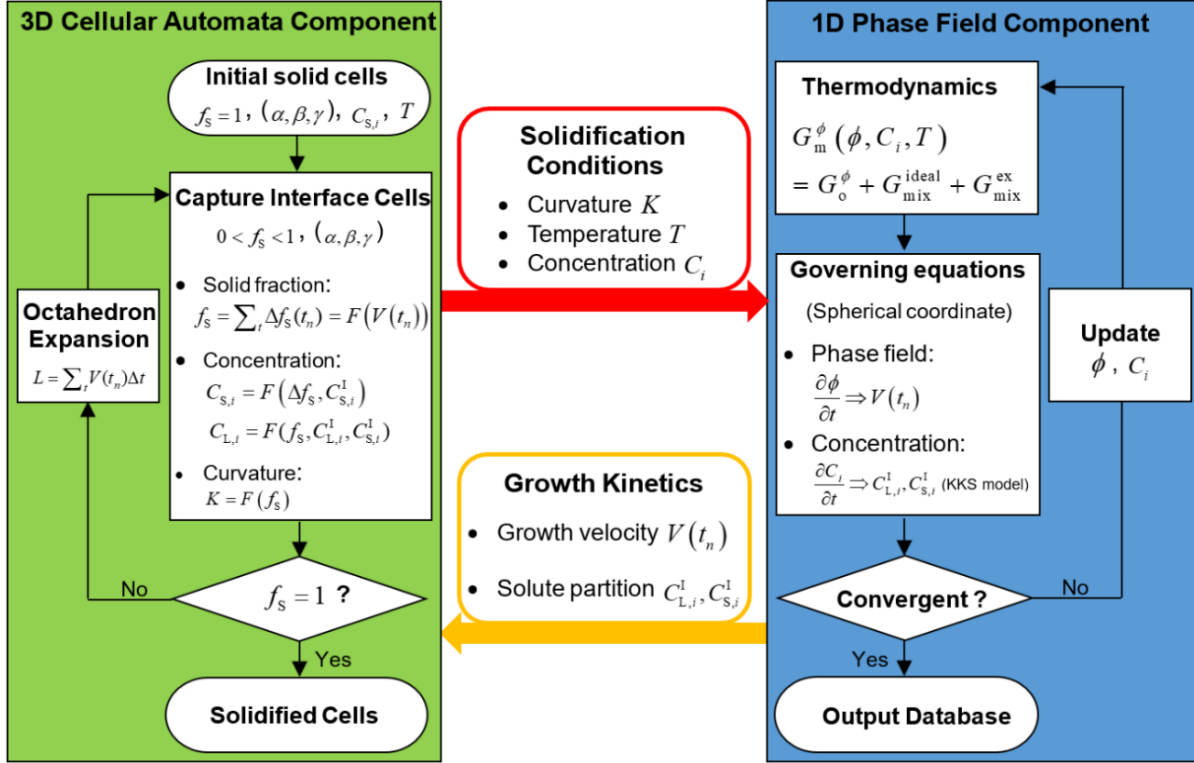


Figure 6.1. Flow chart of the integrated 3D Cellular Automata-Phase Field model.

6.1.1 3D CA Component

6.1.1.1 Dendrite Growth

For the 3D case, the domain is created with uniform cubic cells. Each cell carries several variables, such as solid fraction (f_s), concentration (C_i), crystallographic orientation (characterized by three Euler angles α , β , γ), temperature (T), and growth velocity (V). During solidification, the phase state of a cell changes from liquid ($f_s = 0$), to interface ($0 < f_s < 1$), and eventually to solid ($f_s = 1$). Therefore, S/L interface can be implicitly tracked by the solid fraction within each CA interface cell. At the beginning of the simulation, seeds with random

crystallographic orientations are manually placed or automatically generated in the undercooled melt. These seeds are initialized with solid compositions (C_{is}) while the melt has an initial composition of C_{i0} .

Once the melt temperature becomes lower than the liquidus temperature, solidification will be invoked. In the beginning, the closest liquid neighboring cells around the seeds will be captured as the interface cells. After these interface cells are fully solidified, they will begin to capture new interface cells. The algorithm to capture interface cells is usually manipulated by the expansion of an independent envelope [195]. In the 3D space, this envelope is a de-centered regular octahedron with its diagonal aligned with its crystallographic orientation, as shown in Figure 6.2(a) for the interface cell P_0 . The envelope expands according to [195, 331]:

$$L = \sum_t V(t_n) \Delta t \quad (6.1)$$

where L is the half-diagonal of the octahedron envelope, t is the time duration when the phase state remains interface, Δt is the time step, and $V(t_n)$ is the growth velocity along the preferential growth direction (normal direction) at the time t_n , which is calculated by the 1D PF component.

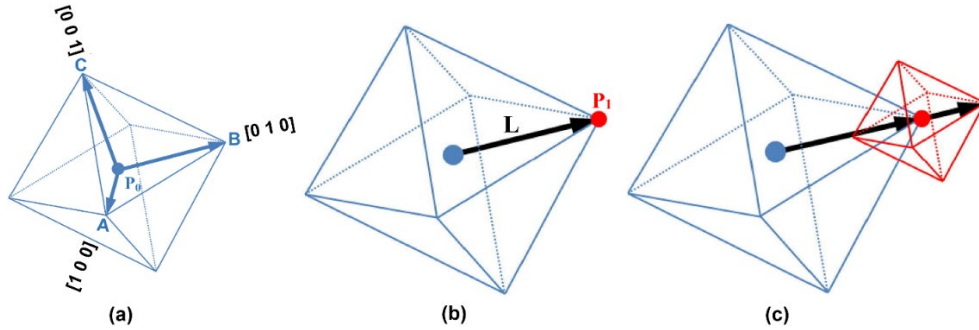


Figure 6.2. 3D cellular automata growth algorithm tracked by the expansion of 3D de-centered octahedron envelope: (a) parent cell P_0 expands its octahedron envelope, (b) parent envelope captures new interface cell P_1 , (c) interface cell B expands its new envelope. Grain grows with equal preferential growth direction $1\ 0\ 0$ aligned with all diagonals. $L = \sum_t V(t_n) \Delta t$.

Given certain time duration, the envelope will grow out of this interface cell and its diagonal tip (point P_1 in Figure 6.2(b)) will touch the neighboring cells. If the touched cell is a liquid cell, it will be captured as a new interface cell and inherit the crystallographic orientation from the capturing cell. The envelope of this newly captured interface cell is centered at the

diagonal tip of the capturing envelope and grows with its own growth velocity (Figure 6.2(c)). For the octahedron envelope, all of its six tips participate in capturing cells. An interface cell will eventually become solid when its solid fraction f_s reaches 1, which is approximated as:

$$f_s = \sum_i \Delta f_s(t_n) \cong \frac{L}{\Delta x (|\sin \beta| + |\cos \beta|)} \quad (6.2)$$

where $\Delta f_s(t_n)$ is the increment of the solid fraction at time t_n , Δx is the mesh size of the cubic CA cell, and β is one Euler angle (details are explained in Section 6.1.1.3). To stabilize the calculation, a necessary limitation should be added to $\Delta f_s(t_n)$ as $\Delta f_s(t_n) = \min(\Delta f_s, 1 - \sum_i \Delta f_s(t_n))$.

6.1.1.2 Curvature Calculation

Curvature determines the growth velocity. To deal with the dendrite growth, the curvature for each CA interface cell should be accurately calculated and updated for every time step. With the curvature calculated from the CA module, the growth velocity at the S/L interface can be calculated by the PF module. In the 2D CA-PF model [200], the S/L interface is determined by the explicit virtual front tracking method. However, it is very difficult to directly extend this method to 3D since tracking the S/L interface advancement requires an accurate implementation of the two principal curvatures in the two principal directions for a 3D surface. Instead, an implicit weighted mean curvature proposed by Pan and Zhu [332] is adopted in this work.

In the Gibbs-Thomson equation for anisotropy crystals, the weighted mean curvature (K) is defined as [333]:

$$K = \left(a(\vec{n}) + \frac{\partial^2 a(\vec{n})}{\partial \theta^2} \right) \cdot K_1 + \left(a(\vec{n}) + \frac{\partial^2 a(\vec{n})}{\partial \varphi^2} \right) \cdot K_2 \quad (6.3)$$

where θ and φ are spherical coordinate angles in two principal directions of curvature, K_1 and K_2 are the two principal curvatures in these two directions. $\vec{n}$ is the normal vector of the interface, described by $\vec{n} = n_x \vec{i} + n_y \vec{j} + n_z \vec{k}$ for a 3D surface. $a(\vec{n})$ is the anisotropy function with the expression [202, 332, 334]:

$$a(\vec{n}) = (1 - 3\zeta) \cdot \left(1 + \frac{4\zeta}{1 - 3\zeta} (n_x^4 + n_y^4 + n_z^4) \right) \quad (6.4)$$

where ζ is the strength of anisotropy, commonly set as $\zeta = 0.04$ or $\zeta = 0.03$.

CA models are sharp interface models, which explicitly track the S/L interface; therefore, all these parameters must be precisely determined for quantitative simulations. Unfortunately, it is very complex to accurately quantify the two principal curvatures and principal directions for a point on a 3D surface. In Pan and Zhu's paper [332], K is calculated based on the surface divergence of the Cahn-Hoffman ξ -vector and $\vec{n}$ is calculated concerning the local solid fraction f_S as $\vec{n} = \nabla f_S / |\nabla f_S| = n_x \vec{i} + n_y \vec{j} + n_z \vec{k}$. Consequently, K becomes a function only related to the first and second derivatives of f_S , which successfully avoids the complicated calculation of θ , φ , K_1 , and K_2 . Instead, K can be easily solved by a finite difference method in the Cartesian coordinates. The K is denoted as:

$$K = (3\zeta - 1) \cdot (\partial_x n_x + \partial_y n_y + \partial_z n_z) - 48\zeta \cdot (n_x^2 \cdot \partial_x n_x + n_y^2 \cdot \partial_y n_y + n_z^2 \cdot \partial_z n_z) + 12\zeta \cdot Q \cdot (\partial_x n_x + \partial_y n_y + \partial_z n_z) + 12\zeta \cdot (n_x \cdot \partial_x Q + n_y \cdot \partial_y Q + n_z \cdot \partial_z Q) \quad (6.5)$$

where $n_x = \partial_x f_S / |\nabla f_S|$, $n_y = \partial_y f_S / |\nabla f_S|$, and $n_z = \partial_z f_S / |\nabla f_S|$. ∂_x , ∂_y , and ∂_z indicate the first derivatives. $|\nabla f_S| = \sqrt{(\partial_x f_S)^2 + (\partial_y f_S)^2 + (\partial_z f_S)^2}$. $Q = n_x^4 + n_y^4 + n_z^4$.

6.1.1.3 Crystallographic Orientation

Note that CA models simulate the dendrite growth with the preferential growth directions, denoting it as $\langle 1 \ 0 \ 0 \rangle$, parallel to the axes of the rotated body Cartesian coordinates, [335, 336]. For non-directional growth, dendrites always have random crystallographic orientations; therefore, the body Cartesian coordinates (A, B, C) should be defined associated with an arbitrary orientation. When plotting the microstructure, the grains are exhibited in the global fixed Cartesian coordinates (X, Y, Z) . The transformation from the body (A, B, C) coordinates to the fixed (X, Y, Z) coordinates can be realized by three Euler angles α , β , γ , $Vector|_{XYZ} = R_Z(\gamma)R_Y(\beta)R_X(\alpha)Vector|_{ABC}$ [337], as shown in Figure 6.3. The Euler transformation matrix S is defined as [205]:

$$S = \begin{pmatrix} \cos \gamma & -\sin \gamma & 0 \\ \sin \gamma & \cos \gamma & 0 \\ 0 & 0 & 1 \end{pmatrix} \cdot \begin{pmatrix} \cos \beta & 0 & \sin \beta \\ 0 & 1 & 0 \\ -\sin \beta & 0 & \cos \beta \end{pmatrix} \cdot \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos \alpha & -\sin \alpha \\ 0 & \sin \alpha & \cos \alpha \end{pmatrix} \quad (6.6)$$

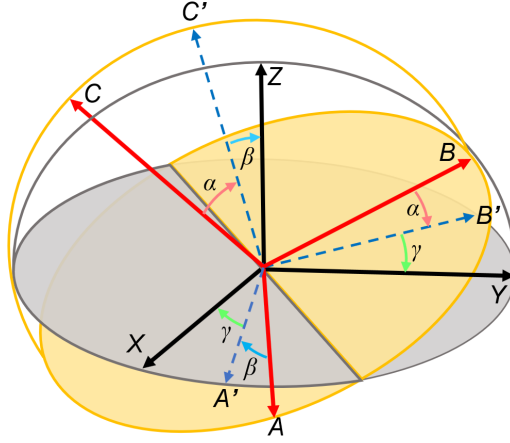


Figure 6.3. Crystallographic orientation of the grain in the global fixed (X, Y, Z) coordinates is characterized by three Euler angles (α, β, γ) related to the rotated body Cartesian (A, B, C) coordinates.

In Pan and Zhu's study [332] for 3D sharp interface modeling of solutal dendrite growth, the Euler transformation was applied to the first and secondary derivatives of the solid fraction, f_s . With these transformations, the crystallographic orientation is directly incorporated into the curvature calculation. Although this algorithm is easy to understand, the transformation calculation for the second derivatives of f_s adds significant complexity to the model. In the current study, the dendrite growth is tracked by the growth velocity, which is aligned with the axes of the rotated body (A, B, C) coordinates [205]; therefore, the crystallographic orientation can be easily handled by applying the S matrix to the velocity vector as $V|_{XYZ} = S \cdot V|_{ABC}$, so that the crystallographic orientation can be displayed in the fixed (X, Y, Z) coordinates. It should be noted that $V|_{ABC}$ is calculated by the 1D PF component [205].

6.1.1.4 Solute Evolution

Since solid and liquid phases usually have different solute concentrations, solute redistribution will occur as solidification proceeds. In general, the governing equation of solute diffusion for an N -component alloy is defined as:

$$\frac{\partial C_{\phi,i}}{\partial t} = \nabla \cdot \left(\sum_{j=1}^{N-1} D_{\phi,ij} \nabla C_{\phi,j} \right) + \frac{\partial f_s}{\partial t} (C_{L,i}^I - C_{S,i}^I) \quad (i, j = 1, 2, \dots, N-1) \quad (6.7)$$

where $C_{\phi,i}$ and $D_{\phi,ij}$ are the concentrations and solute diffusion coefficients in liquid ($\phi = L$) and solid ($\phi = S$). Since CA models are sharp interface-based models without the interface phase, Eq. (6.7) will cause a property jump at the S/L interface [243, 332]. To solve this problem, similar to the 2D CA-PF model (Section 3.2.4.1), an effective method is to treat the entire domain as one single phase by defining the equivalent composition $C_{e,i}$ and equivalent diffusion coefficient $D_{e,i}$ [200, 243, 332]. Eq. (6.7) is thus updated as:

$$\frac{\partial C_{e,i}}{\partial t} = \nabla \cdot \left(\sum_{j=1}^{N-1} D_{e,ij} \nabla C_{e,j} \right) + \frac{\partial f_s}{\partial t} (C_{L,i}^I - C_{S,i}^I) \quad (i, j = 1, 2, \dots, N-1) \quad (6.8)$$

together with:

$$\text{For liquid cells: } C_{e,i} = C_{L,i}, \quad D_{e,ij} = D_{L,ij} \quad (6.8a)$$

$$\text{For interface cells: } C_{e,i} = C_{L,i}, \quad D_{e,ij} = D_{L,ij} \quad (6.8b)$$

$$\text{For solid cells: } C_{e,i} = C_{S,i}, \quad D_{e,ij} = D_{S,ij} \quad (6.8c)$$

To simplify the calculation, the cross-diffusion coefficients are assumed to be zero ($D_{ij} = 0, i \neq j$) in the current study. It should be noted that for interface cells, $C_{L,i}$ is the concentration in the liquid portion while $C_{S,i}$ is the concentration in the solid portion and is:

$$C_{S,i} = \frac{\sum_t \Delta f_s(t_n) C_{S,i}^I(t_n)}{\sum_t \Delta f_s(t_n)} \quad (6.9)$$

When the interface cell becomes solid, its concentration will be updated with $C_{S,i}$. $C_{L,i}^I$ and $C_{S,i}^I$ are the solute partition at the S/L interface, which will be provided by the 1D PF component. The last term on the right-hand side of Eq. (8) hence indicates the amount of solute rejected at the

S/L interface. Eq. (8) is solved through the finite volume method with MPI parallel computing capabilities, and the time step is set as [338]:

$$\Delta t \leq 0.25 \min \left(\frac{\Delta x}{V}, \frac{\Delta x^2}{D_{L,i}}, \frac{\Delta x^2}{D_{S,i}} \right) \quad (6.10)$$

In the current study, $\Delta t = 10^{-6}$ is chosen as the time step for the CA component throughout the entire simulations.

6.1.2 1D PF Component

6.1.2.1 1D PF Model in Spherical Coordinates

The PF component is responsible for the calculation of the growth kinetics at the S/L interface under the local solidification conditions including temperature, concentration, and curvature. Based on the growth velocity, the new position of the S/L interface for the next time moment can be tracked. It is clear that the movement of the S/L interface is governed by the growth velocity in the normal direction; therefore, the local interface growth can be well captured by a 1D approximation.

The interpretation of the 1D PF equations in a Cartesian coordinate is to simulate the solidification of a planar interface. For a 3D dendrite, whose interface varies in continuous concave or convex shapes, a planar interface approximation will generate a large error since it degrades the effect of the curvature on growth velocity. Zhang et al. [334] proposed that the growth velocity increases with the increase of curvature. Tan et al. [200] also supported the positive effect of the curvature on growth velocity from the view of solute diffusion. As a result, the planar interface approximation will underestimate the growth velocity for the interface with a convex shape while overestimating the growth of a concave interface. Therefore, the current work formulates the 1D PF model in the spherical coordinate as:

$$\frac{1}{L_\phi} \frac{\partial \phi}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left(\varepsilon^2 r^2 \frac{\partial \phi}{\partial r} \right) - \frac{\partial G_m}{\partial \phi} \quad (6.11)$$

$$\frac{\partial C_i}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \sum_{j=1}^{N-1} \left(D_{ij} \frac{\partial C_j}{\partial r} \right) \right) + \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \sum_{j=1}^{N-1} \left(M_{ij} \frac{\partial^2 G_m}{\partial C_j \partial \phi} \right) \frac{\partial \phi}{\partial r} \right) - \nabla \cdot j_i \quad (i, j = 1, 2, \dots, N-1) \quad (6.12)$$

where r is the local radius for a spherical interface and ϕ is the phase field variable, which is equal to 1 or 0 for the solid and liquid phase respectively while $0 < \phi < 1$ for the S/L interface. L_ϕ is the phase field mobility. M_{ij} is the solute diffusion mobility and is solved inversely from $D_{ij} = \sum M_{ij} \frac{\partial^2 G_m}{\partial C_i \partial C_j}$ [259]. ε is the coefficient of surface gradient energy and has the expression of $\varepsilon = \varepsilon_0$ (free from anisotropy for 1D case), where $\varepsilon_0 = \sqrt{3\sigma \cdot 2\lambda/2.2}$ [18], σ is the interface energy, and 2λ is the width of the S/L interface. G_m is the molar free energy density and is calculated as:

$$G_m(\phi, C_i, T) = \frac{1}{V_m} \left(h(\phi) G_{S,m}(C_{S,i}^I, T) + (1 - h(\phi)) G_{L,m}(C_{L,i}^I, T) \right) + \omega g(\phi) \quad (6.13)$$

where T is temperature and will be provided by the 3D CA component. V_m is the molar volume, and the subscript m denotes molar. $h(\phi) = \phi^3(6\phi^2 - 15\phi + 10)$ is used to link the difference in energy between the liquid and solid phases. $g(\phi) = \phi^2(1 - \phi)^2$ is the double-well function, and ω is the width of the double well, having the expression of $\omega = 6 \times 2.2\sigma/2\lambda$ [18]. $G_{S,m}(C_{S,i}^I, T)$ and $G_{L,m}(C_{L,i}^I, T)$ are the Gibbs free energies of solid and liquid phases, which are generated based on the system thermodynamics (CALPHAD method). The CALPHAD equations and parameters for the aluminum alloys studied in the current study are well established from the literature [205, 259, 334, 339]. For brevity, only relevant publications instead of details of the materials' thermodynamic database are listed in this study. The material parameters used for PF modeling are summarized in Table 1. $C_{S,i}^I$ and $C_{L,i}^I$ are the local solute partition at the S/L interface that will be calculated for the 3D CA component. To calculate $C_{S,i}^I$ and $C_{L,i}^I$, the Kim, Kim, and Suzuki (KKS) model [225] is adopted, which defines the phase interface with the same chemical potential μ_i but different compositions as:

$$C_i = h(\phi) C_{S,i}^I + (1 - h(\phi)) C_{L,i}^I \quad (6.14)$$

$$\mu_i = \frac{\partial G_{S,m}(C_{S,i}^I, T)}{C_{S,i}^I} = \frac{\partial G_{L,m}(C_{L,i}^I, T)}{C_{L,i}^I} \quad (6.15)$$

j_i in the last term on the right-hand side of Eq. (12) is the anti-trapping current term, which is added to alleviate the solute trapping experienced at the S/L interface [231]. j_i is given by [205]:

$$j_i = \frac{1}{2\sqrt{2}} C_{\infty,i} (C_{S,i}^I - C_{L,i}^I) (2\lambda) e^{u^i} \frac{\partial \phi}{\partial t} \frac{\nabla \phi}{|\nabla \phi|} \quad (i=1, 2, \dots, N-1) \quad (6.16)$$

where C_{∞}^i is the far-field solutal concentration, u^i is a dimensionless parameter. Details about the anti-trapping current term are referred to [231].

Table 6.1. Model parameters and material properties for 1D PF model.

Parameter	Units	Symbol	Al-Cu	Al-Cu-Mg	Al-Si-Mg
Initial concentration	wt. %	$C_{\infty,i}$	2, 4 or 30 Cu	4.5 Cu, 1.5 Mg	0.6 Si, 1.0 Mg
Diffusion coefficient of Cu in liquid	m ² /s	$D_{L,Cu}$	3×10^{-9} [338]	$1.06 \times 10^{-7} \exp(-24000/RT)$ [340]	-
Diffusion coefficient of Cu in fcc Al	m ² /s	$D_{S,Cu}$	3×10^{-13} [338]	$4.44 \times 10^{-5} \exp(-133900/RT)$ [340]	-
Diffusion coefficient of Mg in liquid	m ² /s	$D_{L,Mg}$	-	$9.9 \times 10^{-5} \exp(-71600/RT)$ [340]	
Diffusion coefficient of Mg in fcc Al	m ² /s	$D_{S,Mg}$	-	$1.49 \times 10^{-5} \exp(-120500/RT)$ [340]	
Diffusion coefficient of Si in liquid	m ² /s	$D_{L,Si}$	-	-	$1.34 \times 10^{-7} \exp(-30000/RT)$ [340]
Diffusion coefficient of Si in fcc Al	m ² /s	$D_{S,Si}$	-	-	$1.38 \times 10^{-5} \exp(-117600/RT)$ [340]
Anisotropy strength	-	ζ	0.03 [332] or 0.04 [205]*		
Molar volume	m ³ /mol	V_m	1.06×10^{-5} [341]		
Interface energy	J/m ²	σ	0.093 [341]		
Interface width	m	2λ	$10 \Delta x$ [200]		
Mesh size	m	Δx	5×10^{-9} [200]		
Time step	s	Δt	10^{-9} [200]		
Slope of the liquidus curve	K/wt. %	m_L	-2.6 [342]		
Equilibrium liquidus temperature at the initial composition	K	T_L^{Eq}	$933.602 + m_L \times \text{wt. \%}$	922	925 [205]

Note: *Two different values are used to be consistent with the benchmarking problems of Ref. [332] and Ref. [205], where the values of 0.03 and 0.04 were used respectively.

The partial differential equations in Eq. (6.11) and Eq. (6.12) are solved with the Tri-Diagonal Matrix Algorithm (TDMA) solver to ensure the convergence through parallel computation capabilities (MPI) on ten processors. A list of model parameters and material properties of all aluminum alloys studied in this study are summarized in Table 6.1.

6.1.2.2 Composition Interpolation for 1D PF Component

Solute diffusion dominates the diffusion-controlled dendrite growth; therefore, the 1D concentration profile along the normal vector of the interface is another input for the PF modeling. This concentration profile is provided by the 3D CA component. To calculate this 1D concentration profile, the algorithm proposed by Tan et al. [200] for 2D dendrite growth is adapted to the 3D case. As shown in Figure 6.4, a normal vector is generated for the CA interface cell of interest (cell A). The end of the vector extrudes into infinity, where the concentration can be approximated to be the initial concentration. Therefore, the 1D concentration profile along the vector can be expressed as:

$$C_i(\rho) = C_{\infty,i} + (C_{L,i}^I - C_{\infty,i}) \exp(-A_i \rho) \quad (6.17)$$

where ρ is the distance from the interface into the melt, $C_{L,i}^I$ is the liquid concentration at the S/L interface from the last step, $C_{\infty,i}$ is the concentration at infinity. A_i is a variable that describes the steepness of the concentration variation. By selecting several points along the 1D concentration vector and calculating their concentrations, the concentration profile denoted by Eq. (6.17) can be obtained. For instance, the solid point **P** is one selected point. Its concentration is updated by interpolation of the concentrations from the closest eight neighboring CA cells (B, C, D, E, F, G, H, I). The 1D concentration profile is then re-mapped onto the 1D PF domain with the PF interface at $\phi = 0.5$ located at $r = 1/K$ in the 1D spherical coordinate.

The last required input for the PF component is the temperature from a CA interface cell. Since the mesh size of the 1D PF domain is 5×10^{-9} m, which is more than two orders of magnitude smaller than the CA mesh, the temperature is thus assumed isothermal for the entire PF domain. After receiving the curvature, concentration, and temperature inputs from a CA interface cell, the PF component requires several iterations to march from the received concentration to the

converged concentration. Within this time duration, the average growth velocity calculated by the advanced distance at $\phi = 0.5$ divided by the time duration will be returned to the CA interface cell for the growth preparation for the coming time step, together with the calculated $C_{L,i}^I$ and $C_{S,i}^I$ after convergence.

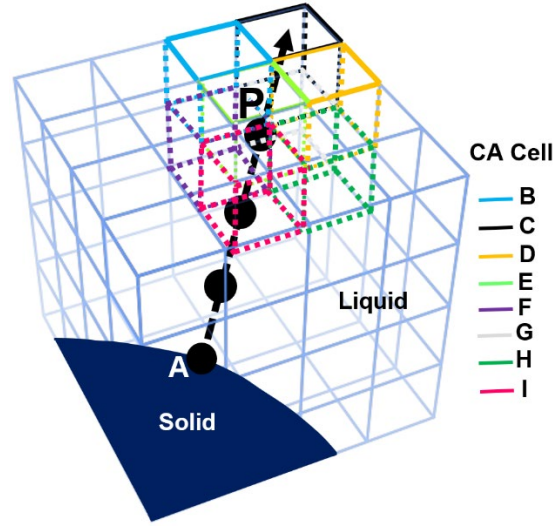


Figure 6.4. 1D concentration profile along the normal vector of the solid/liquid interface generated by the CA component for the PF component. The concentration of each point (e.g. point P) on the profile is produced by concentration interpolation of its eight closest neighboring cells (e.g. cell B-I).

It is readily noticed that the PF component must be called to calculate the growth kinetics for every CA interface cell within every time step. To save the substantial computational cost, a growth kinetics database is established in advance as in Ref [200]. Some sample problems with preset solidification conditions are selected to calculate the sample growth kinetics. The solidification condition for an alloy with N components includes curvature K , temperature T , concentration $C_{L,i}^I$ and steepness variables $A_i, (i=1,2,\dots,N-1)$. To ensure accuracy, an adequate number of sample conditions should be selected. Although the establishment of this database requires a high computational cost, once it is established, the actual growth kinetics can be easily determined by the interpolation of the database, and this database is only required to establish once.

6.2 Model Validation

The Al-Cu binary system has been extensively studied as a benchmark example. To validate the 3D CA-PF model, the simulation is hence first applied to the Al-Cu alloy and validated against the 3D PF model and the Lipton-Glicksman-Kurz (LGK) analytical result. The CA-PF model is then used to simulate the columnar dendrite growth in the directional solidification of Al-30 wt.%Cu. Eventually, the CA-PF model is expanded to the ternary Al-Cu-Mg and Al-Si-Mg alloys and applied to laser welding cases with a predefined thermal condition or coupled with a predicted thermal history from a laser welding model. All the application cases are quantitatively compared against the experimental observation.

Figure 6.5 illustrates the simulated steady-state grow velocity and tip radius of Al-2wt.%Cu as a function of melt undercooling, which are compared with the LGK analytical result. The dendrite tip selection parameter σ^* for the LGK model is set to 0.0847 and the anisotropy strength is $\zeta=0.03$ [332]. For brevity, the LGK model is not explained in the current work. Please refer to Ref. [332] for more details. The mesh size of the CA component in the CA-PF model is set to be 0.1 μm . The entire CA domain is specified with a constant undercooled temperature. A seed with the size of one cell is placed at the center of the domain, which grows with the crystallographic orientation of 0° . As the tip growth velocity in the 3D CA-PF model is calculated by the PF component and is updated for every time step, the tip grows at a varied velocity that is also related to the solid fraction and tip curvature; therefore, an average instead of the transient growth velocity is calculated every 50-time steps based on the advancement of the dendrite tip with $f_s = 0.5$ and a total of 6 calculations are carried out. For the measurement of the tip radius, $f_s = 0.5$ is also used to outline the dendrite tip. A number of points along the dendrite tip are probed on the central cross-section of the dendrite. After using a fourth-order polynomial to fit the points into a fin-shape curve, the radius of the fin tip can be calculated.

As shown in Figure 6.5, the steady-state growth velocity increases while the tip radius decreases with the increased undercooling. Overall, the growth velocity matches the LGK result well but the error of the tip radius predicted by the 3D CA-PF model becomes larger at smaller undercooling. It should be noted that a reasonable deviation from the LGK analytical model is acceptable since the LGK model itself is not perfect because the selection of the σ^* value directly

determines the Ivantsov parabola in the LGK model, which is used to approximate the dendrite tip geometry. This Ivantsov parabola is an approximation of the dendrite shape [342] and σ^* has no agreed value in literature [332, 342].

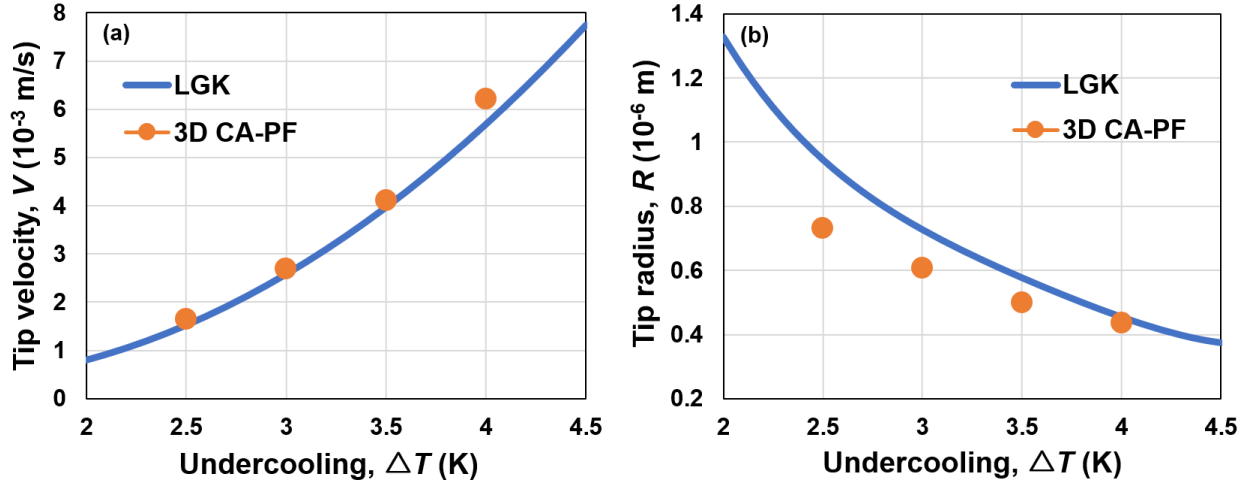


Figure 6.5. Comparison of the steady-state (a) growth velocity and (b) tip radius of Al-2 wt.%Cu alloy under different undercooling between the Lipton-Glicksman-Kurz (LGK) analytical result [332] and the 3D CA-PF result. $\sigma^*=0.0847$ and $\zeta=0.03$ [332].

Figure 6.6 depicts the 3D CA-PF modeling of the freely-grown dendrite with the concentration of copper at the dendrite surface compared with the PF result from Ref. [205]. The Al-4wt.%Cu alloy solidifies at 900 K and the anisotropy strength is 0.04 [205]. After solidification for 1.5×10^{-4} s, the primary arm length of both dendrites reaches roughly $6.7 \mu\text{m}$. The mesh size of the PF model is $0.02 \mu\text{m}$ and the time step is 10^{-8} s, while that of the CA component in the CA-PF model is set as $0.1 \mu\text{m}$ and 10^{-8} s. In the comparison of the dendritic morphology, the dendrite size and shape predicted by CA-PF modeling match the PF result with reasonable agreement. However, the CA-PF modeling reveals fewer feature details than the PF modeling. The underlying reason associated with the difference in the dendritic morphology is mainly related to the mesh size and the number of interface cells. The mesh size of PF models is in the length scale of $10^{-8} - 10^{-9}$ m and the interface generally crosses over 4 to 8 cells. In PF modeling, a small artificial noise factor is always added to encourage the growth of secondary arms. Because of the small mesh size in PF modeling and several layers of interface cells, the instability at the solidification front is always enhanced. However, for CA and CA-PF models, the mesh is about two to three orders of magnitude larger, and only the closest neighboring liquid cells are captured as the interface cells. Without

several layers of interface cells growing simultaneously, the concentration field at the S/L interface and the curvature of the dendrite tip are different [342]; consequently, the solute rejected by the solid phase at the solidification front diffuses away easily, and the predicted concentration value of Cu at the dendrite surface is therefore only about a half of that predicted by the PF modeling. Free from the high-concentration solute accumulated at the S/L interface, the secondary dendrite arms could grow closer and even merge together, leaving no obvious side-branching as revealed by the CA-PF dendritic morphology (Figure 6.6(b)).

Although the dendritic morphology details are not perfectly reproduced compared with the PF modeling, the computational cost is drastically reduced with the CA-PF modeling. It took roughly about 4 days on 19 processors to obtain the PF result [205], while the CA-PF modeling only requires about 4 minutes on 1 processor. This is mainly because the CA model is an engineering model that has a much looser constraints on the mesh size and time step. Moreover, CA models calculate the dendritic variation via an engineering cellular automata rule instead of physics-based partial differential equations in PF modeling, which also accelerates computational efficiency. After combined with PF modeling to calculate the local growth kinetics for the CA interface cells, the CA-PF model successfully improves the accuracy in capturing the dendrite growth and solute evolution. The balanced efficiency and accuracy endow the CA-PF model with the capability to carry out the simulation of microstructure evolution on a large scale over a reasonable amount of computational cost, e.g., directional solidification and solidification within the entire molten pool during AM or welding processes (to be shown in the next section), which is far beyond the capabilities of current PF models.

To maintain consistency, a multi-equiaxed dendrite solidification was also performed for the Al-4wt.%Cu alloy freezing at the same solidification condition of Figure 6.6(b). Figure 6.7 presents the predicted Cu concentration at the dendrite surface. The simulation is run on one processor and requires about 19 CPU minutes of computational time. At the beginning of the simulation, the undercooled liquid is seeded with seven seeds assigned with random crystallographic orientations. Each seed has a size of one cell. The dendrite growth lasts for a physical time of 1.5×10^{-4} s and the primary arm length reaches about 6.7 μm . Since the entire domain is set with a constant temperature of 900 K, the large undercooling of about 23 K stimulates the coarsening of the primary trunks. Therefore, after growing for a physical time of 1.5×10^{-4} s, all the dendrites exhibit

a diamond equiaxial shape without obvious branching or secondary arms. As solidification proceeds, the dendrites will be fully developed eventually.

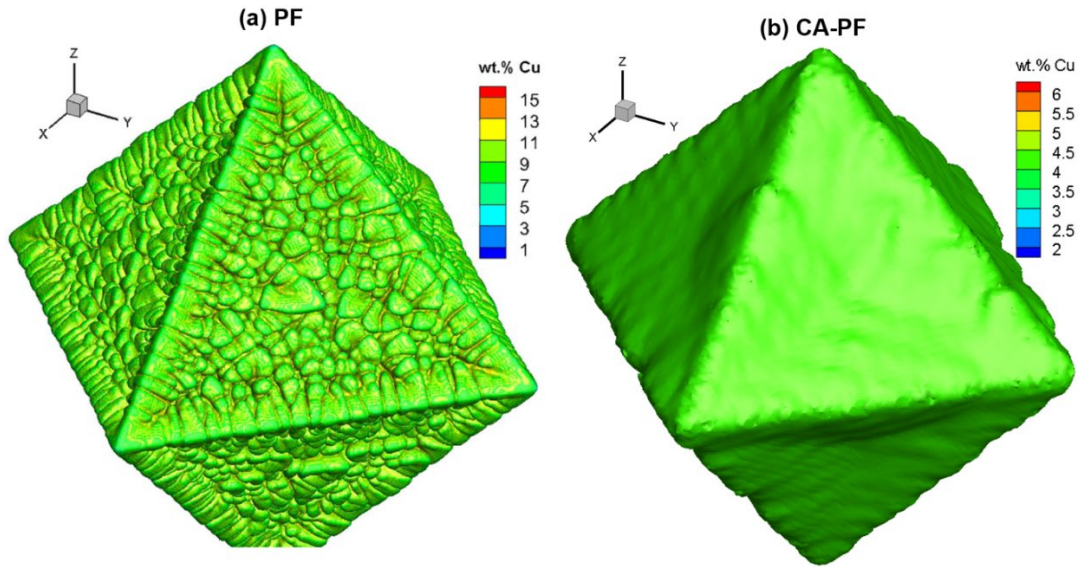


Figure 6.6. Predicted Cu concentration at the dendrite surface for Al-4wt.%Cu alloy freezing at 900 K, $\zeta=0.04$ for a physical time of 1.5×10^{-4} s: (a) 3D PF result [205], (b) 3D CA-PF result. The primary arm length of both dendrites is about $6.7 \mu\text{m}$.

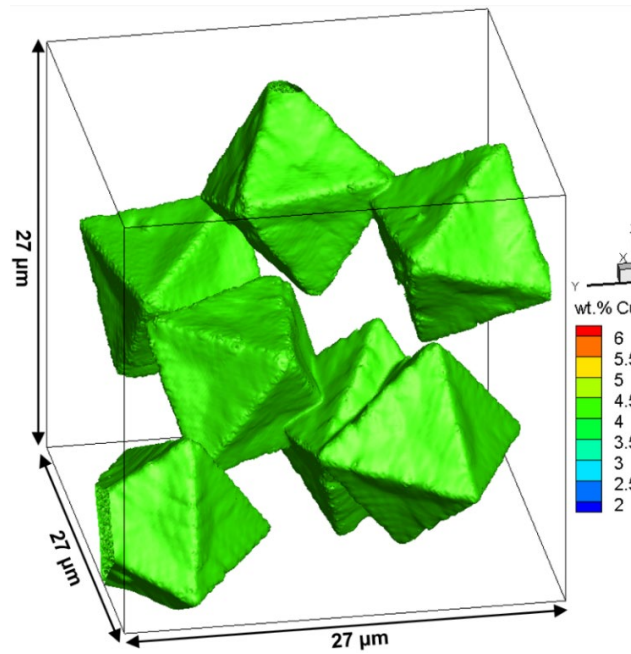


Figure 6.7. Predicted Cu concentration at the multi-equiaxed dendrite surface for Al-4 wt.%Cu alloy freezing at 900 K (undercooling ~ 23 K), $\zeta=0.04$ for a physical time of 1.5×10^{-4} s. The primary arm length of both dendrites is about $6.7 \mu\text{m}$.

6.3 Model Application

After validating the 3D CA-PF model in the Al-Cu binary alloy system, the model was extended to ternary systems. In this section, the CA-PF model is applied to large-scale dendritic solidification of three aluminum alloys in both directional solidification and laser welding processes. The simulated microstructures are compared against experimental observations.

6.3.1 Directional Solidification

The 3D CA-PF model was first applied to duplicating the columnar dendrite growth in the directional solidification of an Al-30 wt.%Cu alloy, which is observed by the experimental microstructure obtained via the time-resolved X-ray imaging technique [343], as shown in Figure 6.8. The simulation is carried out on the CA domain of $475\text{ (X)} \times 100\text{ (Y)} \times 800\text{ (Z)}\ \mu\text{m}^3$ with a temperature gradient of 27 K/mm and an initial undercooling of 2 K. To accommodate the large simulation domain, a larger mesh size of $\Delta x = 0.5\ \mu\text{m}$ is selected for the CA domain. It is clear that the columnar dendrites are well developed with asymmetric secondary arms formed. The width of the realistic secondary arms is in the range of 5 – 30 μm and the average secondary arm spacing is roughly 16.6 μm for the experimental dendrites. The 3D CA-PF result captures the dendritic morphology and size with a reasonable agreement, where the average simulated secondary arm spacing is about 25.2 μm and the width of the secondary arms is 10 – 50 μm .

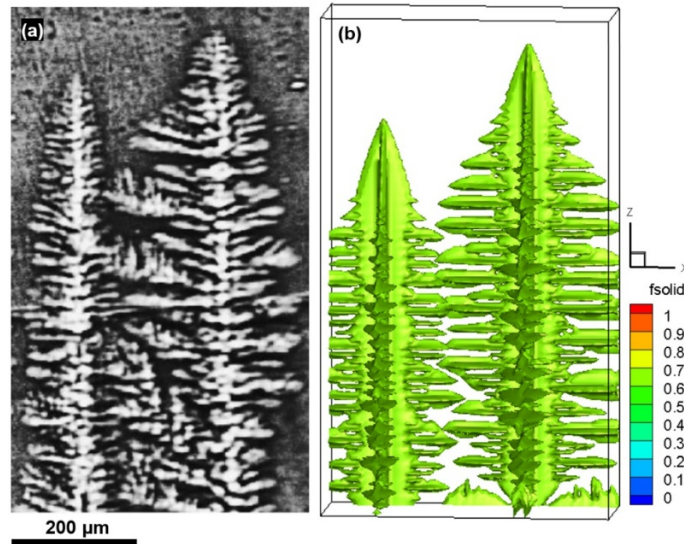


Figure 6.8. Columnar dendrite growth in the directional solidification of Al-30 wt.%Cu alloy freezing at a temperature gradient of 27 K/mm: (a) experimental microstructure obtained via the time-resolved X-ray imaging technique [343], (b) 3D CA-PF modeling result.

6.3.2 Laser Welding

The CA-PF model was also applied to simulating the as-solidified microstructure during a laser welding process. Welding and AM processes are known for their large temperature gradients and rapid heating/cooling cycles. The most dominant influence of a large temperature gradient on the grain morphology is the unique texture resulting from the directional growth. To understand the as-solidified welding and AM microstructure, it is vital to simulate the entire molten pool. As the smallest unit, the single scan has a dimension of millimeter-scale, which is far beyond the computational capability of PF modeling. This study, therefore, applies the 3D CA-PF model to a welding case to demonstrate its capability in both computational efficiency and accuracy.

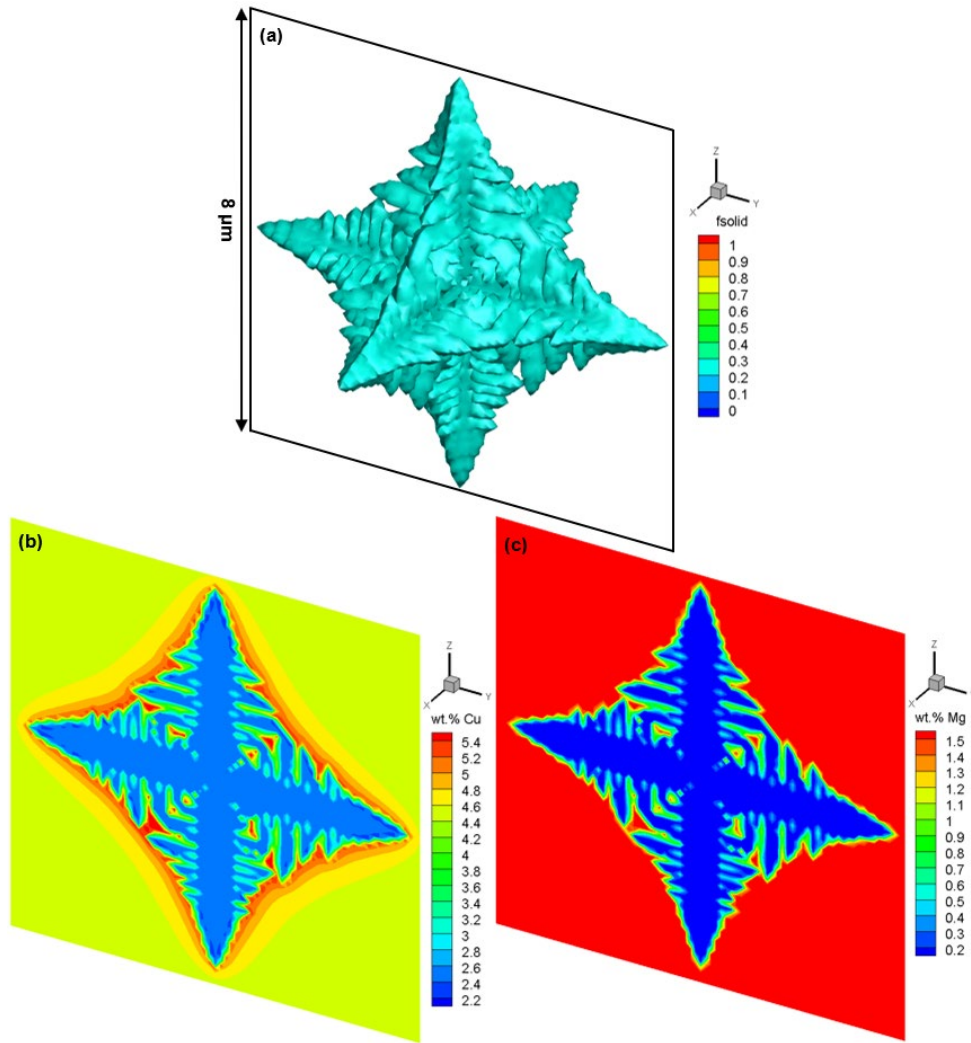


Figure 6.9. Simulated single dendrite of Al-4.5wt.%Cu-1.5wt.%Mg alloy freezing at a temperature gradient of 5×10^5 K/m and a cooling rate of 10^4 K/s: (a) dendritic morphology, (b) Cu concentration field and (c) Mg concentration field in the slice of (a).

The simulation was first carried out for Al-4.5wt%Cu-1.5wt%Mg ternary alloy. The thermodynamic database of Al-Cu-Mg system is well developed and can be found in Ref. [259, 334]. Figure 6.9 shows the predicted single 3D dendritic morphology and the concentration distributions of Cu and Mg in a 2D slice of the dendrite. The CA domain is an $8^3 \mu\text{m}^3$ cube with a mesh size of $0.1 \mu\text{m}$. A divergent temperature field with a temperature gradient of $5 \times 10^5 \text{ K/m}$ and a cooling rate of 10^4 K/s was predefined to approximate the thermal history in a welding process. At the beginning of the simulation, a seed with a crystallographic orientation of 0° was manually planted at the center of the CA domain. After freezing for a physical time of $4 \times 10^{-4} \text{ s}$, the free dendrite is fully developed and branches into secondary arms. The as-solidified dendrite has a lower Cu and Mg concentrations compared with the liquid phase. As the S/L interface advances, the solid keeps repelling the solutes into the liquid phase, generating a concentration gradient close to the S/L interface of dendrite arms. Microstructure evolution in alloys is mainly governed by solute diffusion. This high-concentration solute trapped in the inter-dendrites makes these regions to solidify the last and is consequently responsible for the micro-segregation commonly observed in the dendritic microstructure.

After applying the 3D CA-PF model to free dendrite growth, the model was then utilized to simulate the microstructure evolution during solidification in a real welding process. The example material is AA6061, the composition of which is simplified to Al-0.6wt%Si-1.0wt%Mg. Details of the thermodynamic database of Al-Si-Mg can be found in Ref. [339]. AA6061 Al alloy is a well known precipitates-strengthened alloy and the precipitates include GP cluster-MgSi, β'' -Mg₅Si₆, β' -Mg₉Si₅, and β -Mg₂Si [344-348]. When a molten pool is formed during laser welding, these precipitates are first completely dissolved. In the following solidification process, the primary α phase (face-centered cubic Al solid solution saturated with Si and Mg) is formed first [349]. Some of the nano-scale GP cluster, β'' , β' , and β secondary particles may precipitate out from the α -Al matrix under certain thermal conditions [350-352]. Simulation of the formation of secondary intermetallic phases is beyond the scope of the current study; therefore, the formation of these nano-precipitates are not considered.

The experimental observation reveals that the grain morphology varies according to the laser power and welding speed [200]. To predict the microstructure evolution corresponding to a certain welding condition, the thermal history should be coupled to the CA-PF model. An experimentally validated welding model developed in the authors' group [205, 353] is thus adopted to predict the

temperature gradient and cooling rate within the molten pool. The experimental condition for generating the experimental microstructure as well as for modeling is 800 W laser power and 500 mm/min laser scan speed. Figure 6.10 shows the predicted temperature field in the laser welding of AA6061 and the extracted temperature file (Figure 6.10(c)) outlined by the rectangular frame in Figure 6.10(a) that will be used for microstructure prediction. This temperature field is produced after the simulation reaches quasi-steady-state; therefore, the predicted temperature field will remain consistent as the laser moves. Since the mesh size of the laser welding model ($30\text{ }\mu\text{m}$) is two orders larger than that of the 3D CA-PF model, the temperature data are mapped onto the CA-PF mesh through linear interpolation. At each time step of the CA-PF model, the temperature of each mesh in the CA-PF domain is updated by interpolating the temperature data at its current position due to the movement of the laser beam. In this way, the transient feature of thermal history is naturally considered in the microstructure prediction.

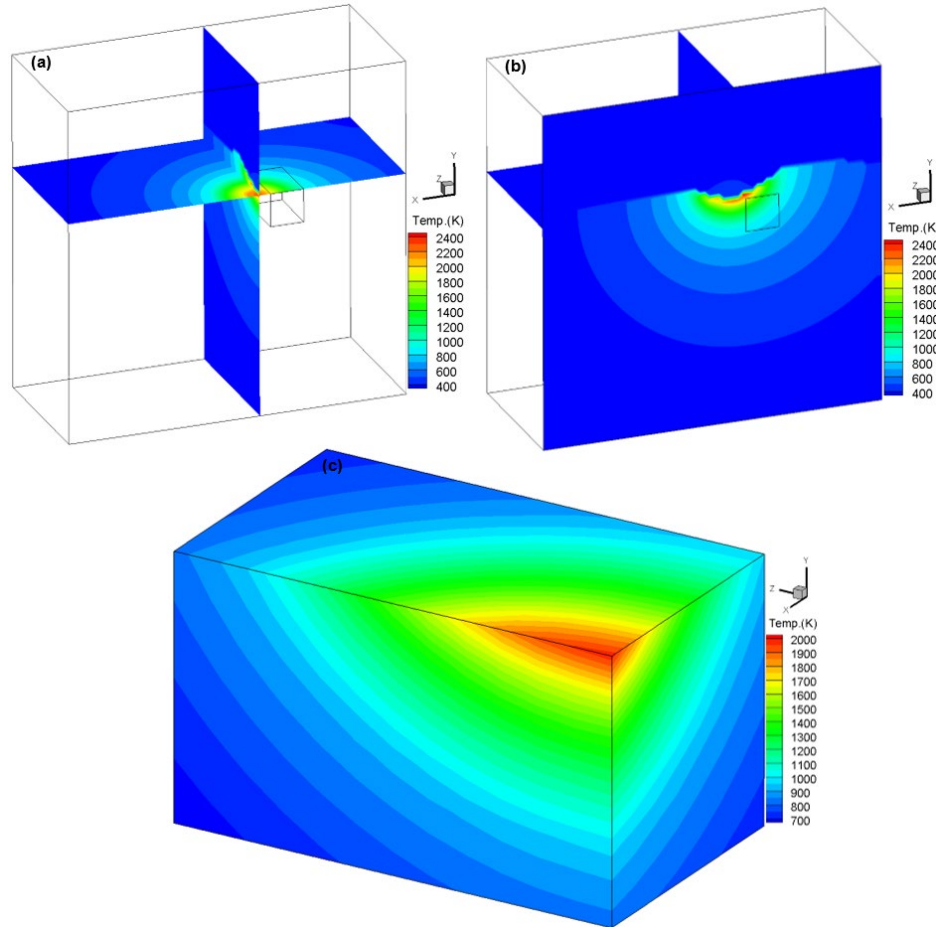


Figure 6.10. Predicted temperature field taken from a laser welding model: (a) XZ and YZ planes and (b) XY plane located in the molten pool center, (c) extracted temperature field of the rectangular frame in (a).

Figure 6.11 exhibits the predicted fully solidified microstructure with regard to the extracted temperature field shown in Figure 6.10(c). The simulation is carried out on a $160\text{ (X)} \times 164\text{ (Y)} \times 276\text{ (Z)}\ \mu\text{m}^3$ domain with a cubic mesh of $0.3\ \mu\text{m}$. In total, the simulation was carried out for a physical time of $1.85 \times 10^{-2}\text{ s}$, taking a computational time of roughly 3.6 CPU days on 10 2.6 GHz processors. On the contrary, Bailey et al. [205] in the authors' group conducted 3D PF modeling of AA6061 using the same laser welding model after simplifying the alloy into a pseudo-binary alloy to save the computational cost, but it required 60 CPU days of computation time on 20 2.6 GHz processors to complete the simulation only for a small domain of $28 \times 14 \times 8\ \mu\text{m}^3$. Therefore, the 3D CA-PF model improves the computational efficiency by more than five orders of magnitude than the 3D PF model.

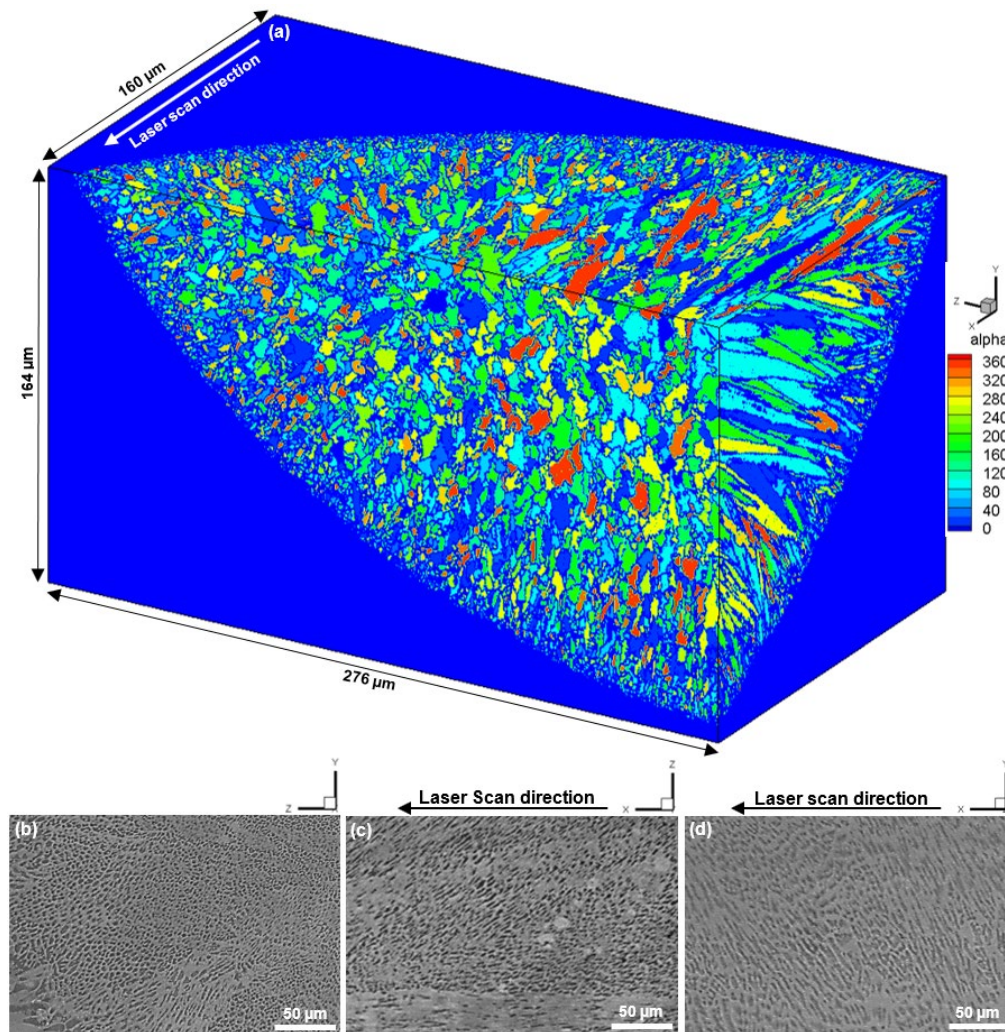


Figure 6.11. (a) 3D CA-PF modeling of the fully solidified microstructure during laser welding of AA6061 Al alloy and (b-d) SEM micrographs for different views in three directions.

As shown in Figure 6.11(a), dense and small nuclei seeds with random crystallographic angles are initially formed on the molten pool boundary. During solidification, all grains competitively grow towards the favorable thermodynamic conditions with the strongest temperature and concentration gradients. This high density of the initial seeds will definitely result in a strong interaction of the diffusion field. As time advances, the growth of certain grains will be suppressed if their crystallographic orientations are not aligned with the favorable thermodynamic conditions. Eventually, a balance is reached among the interaction of survived grains, and the grain size and dendrite arm spacing become stable. For the cross-section YZ and the top longitudinal-section XZ, the grains are primarily formed into cellular dendrites while columnar dendrites are produced on the central horizontal-section XY. During solidification, the growth of the columnar dendrites is aligned with the laser scan direction. The cellular dendrites revealed on the YZ plane and XZ plane seem to be the truncation of the short axis of the columnar dendrites.

To quantitatively validate the predicted microstructure on the three planes: YZ, top XZ, and central XY of Figure 6.11, a welded single scan was polished to show the corresponding views using the standard metallurgical sample preparation procedure followed by a vibratory polishing in colloidal silica for 4 hours. The microstructure was revealed by the Weck's reagent and observed by a scanning electron microscope (Quanta 650 FEG). Figure 6.11(b-d) present the SEM microstructure for almost the entire fusion zone against the three revealed planes in (a). For the cross-section YZ plane, the SEM micrograph (Figure 6.11(b)) displays oval grains with the long axis perpendicular to the molten pool boundary while the predicted microstructure (Figure 6.11(a)) qualitatively captures the grain morphology with irregular grains shapes. For the longitudinal-section XZ plane, the columnar grains at the very central zone of the molten pool are completely aligned with the laser scan direction (Figure 6.11(c)). With a distance from the central zone, grains are still prone to being along with the scan direction but with a gradually increased rotation angle when it is away from the molten pool center. This growth pattern is well captured by the simulation result (Figure 6.11(a)). While for the central horizontal-section XY plane, the grains are still aligned with the scan direction but grow into elongated columnar grains with a large aspect ratio (Figure 6.11(c)). The simulation result (Figure 6.11(a)) predicts the grain morphology similar to the experimental result. The unique grain growth pattern is attributed to the consistency of the preferred growth direction with the maximum temperature gradient direction. This particular microstructure is also prevalent in AM-built and welded various steel materials [194, 195] and

Titanium alloys [331, 354]. Compared with the experimental results, the grain growth pattern and grain texture predicted by the 3D CA-PF model display a qualitative agreement. The seemingly different morphologies are possibly due to the fact that the simulation results show a snap shot of the fusion zone, while SEM images are for continuous scanning (welding). The large percent of small grains formed at the fusion zone boundary in the simulation result should be ascribed to the many nuclei seeds.

A quantitative comparison of the grain size and 2D crystallographic orientation was performed at selected regions between the simulation results and experimental observation, as shown in Figure 6.12. The grains were first characterized and extracted using the ImageJ FIJI software with MorphoLibJ plug-in followed by the Matlab processing to calculate the grain size and crystallographic orientation. For the grain size, a similar probability is obtained between the simulation and experimental results for the top XZ (Figure 6.12(k) and central XY (Figure 6.12(l)) planes while the 3D CA-PF model predicts a larger volume percent of small grains in $0 - 10 \mu\text{m}^2$ but a smaller volume percent of $10 - 20 \mu\text{m}^2$ grains than the experimental data for the front YZ plane (Figure 6.12(j)). As for the 2D crystallographic orientation distribution for the front YZ plane (Figure 6.12(m)), the experimental microstructure is primarily composed of dendrites with $0 - 60^\circ$ growth orientations while the simulation result reveals a larger distribution range. For the top XZ plane (Figure 6.12(n)), a good agreement is revealed for the crystallographic orientation between simulation and experimental results. The simulation result displays a primary $-40 - -20^\circ$ crystallographic angles for the central XY plane (Figure 6.12(o)) while $-60 - -40^\circ$ grains dominate the experimental microstructure. Overall, the grain size distribution and grain texture predicted by the 3D CA-PF model display a reasonable agreement with the experimental data; however, the predicted grains have a little larger size range than the experimental result. Smaller mesh sizes at the expense of increased computational time could possibly improve the size uniformity and produce smoother grain boundaries [355]. As for some deviations in the dominant crystallographic orientations, it could be related to the selected regions not being exactly identical.

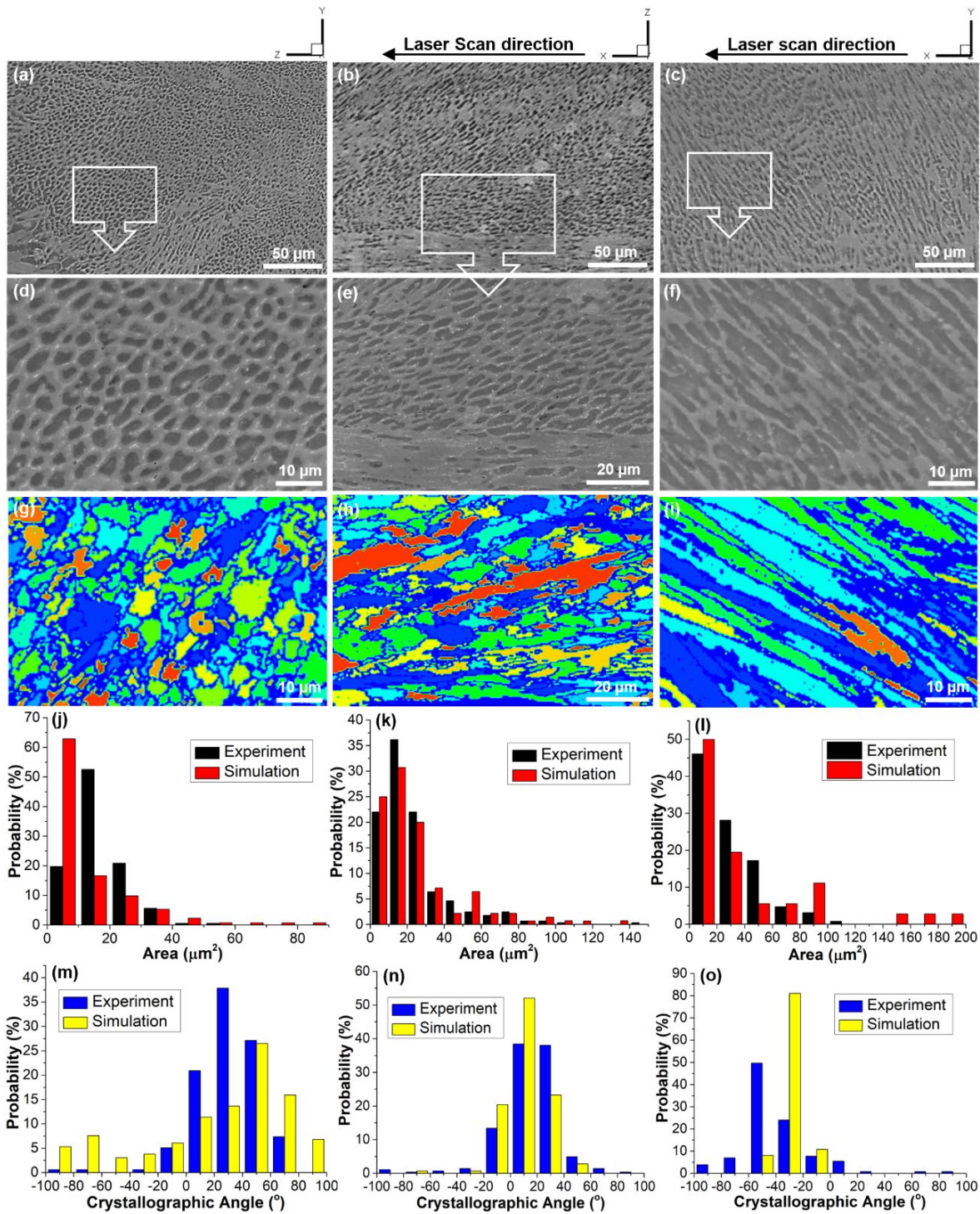


Figure 6.12. A comparison of grain size distribution and crystallographic orientation at selected regions between the simulation and experimental results. The left column is for the cross-section YZ plane, the middle column is for the top longitudinal-section XZ plane, and the right column is for the central horizontal-section XY plane. (a-c) SEM micrographs with small magnification, (d-f) enlarged SEM micrographs at selected regions, (g-i) simulation results at selected regions, (j-l) grain size distribution between (d-f) and (g-i), (m-o) 2D crystallographic orientation distribution between (d-f) and (g-i).

6.4 Summary

A novel 3D CP-PF model was proposed in this study to predict the 3D microstructure morphology in a large domain, e.g. entire fusion zone, which integrates a 3D CA component and a 1D PF component to simulate the dendrite growth during the solidification of multi-component alloys. Binary Al-Cu and ternary Al-Cu-Mg and Al-Si-Mg Al alloys were used as the example materials to present the as-solidified dendritic microstructure during different solidification processes. The primary conclusions are summarized below:

1. The fidelity of the 3D CA-PF model is well validated by the LGK analytical model concerning the growth velocity at the dendrite tip and tip radius.
2. For isothermal solidification, the 3D CA-PF model decently captures the dendrite shape and size compared with the PF result but reveals fewer morphology features.
3. For directional solidification on a large-scale domain, the dendritic morphology predicted by the 3D CA-PF model agrees well with the experimental observation. The 3D CA-PF model applied to the laser welding process was able to predict the fully developed free-growing dendrites with secondary arms formed.
4. While incorporating the thermal history predicted by a laser welding model to the 3D CA-PF model, the dendrite growth during the solidification of the entire molten pool of AA6061 Al alloy could be simulated. The predicted grain growth pattern and grain size distribution on cross-section YZ plane, top XZ plane, and central XY plane all matched the experimental results with a reasonable agreement, but the quantitative comparison reveals a larger size range and some deviated crystallographic orientation for the simulation results.
5. Compared with the 3D PF modeling, the 3D CA-PF model reduces the computational cost by five orders of magnitude with reasonable accuracy in capturing dendritic morphology and concentration distributions, confirming its high capability of predicting the microstructure evolution on a large-scale domain.

7. FUTURE WORK AND RECOMMENDATIONS

Both experimental syntheses of high-performance multi-component materials using AM techniques and numerical simulation of large-domain microstructure evolution have profound research values to the materials and engineering communities.

7.1 Experiments

For experimental research, different HEA systems with outstanding synergistic combinations of mechanical, high-temperature, corrosion, and anti-wear performances are the focus of research interests. For structural applications, the materials should have both high strength and high ductility. In general, HEA with a single FCC structure like CoCrFeMnNi [40, 356, 357], CoCrFeNi [32], and Al_{<0.3}CoCrFeNi [358] will achieve good plasticity (40% – 60%) but poor strength (200 – 500 MPa) while the HEA alloys with single BCC structures such as AlCoCrFeNi [359], NbMoTaWV [183], NbMoTaW [182, 183] possess high strength (1800 – 2300 MPa) but low ductility (<1%). Therefore, BCC HEAs are always subjected to compressive tests. With the attempt to achieve excellent balanced strength and tensile ductility, the microstructure should possess ductile FCC (or ordered L1) phases and hard BCC (or ordered B2) phases or/and hard intermetallic phases such as hard Laves phase. Several promising HEA alloys with superior mechanical properties are exhibited in Figure 7.1. Some of these HEA alloys, e.g. Fe₂₀Co₂₀Ni₄₁Al₁₉ and CrFeCoNi_{2.1}Al have better mechanical properties than forged Ti6Al4V, which has an ultimate tensile strength of about 1200 MPa and an elongation of about 16%.

Although refractory HEA alloys that are composed of elements Cr, Hf, Mo, Nb, Ta, Ti, V, W [182-185], Zr such as MoNbTaV, MoNbTaTiV, MoNbTaVW, and NbTaHfZrTi have poor ductility, they exhibit great high-temperature strength, stability, and creep resistance, which is better than the commonly used superalloy Inconel 718 and Haynes 230 [36]. Therefore, refractory HEA alloys are expected to have superior potentials for extreme environment applications. For example, the (W, Mo)-contained refractory HEA like MoNbTaVW and MoNbTaW that are free

from Al, Cu, and Cr are expected to present outstanding corrosion resistance in the world if subjected to the most severe high-temperature molten salt corrosion environment.

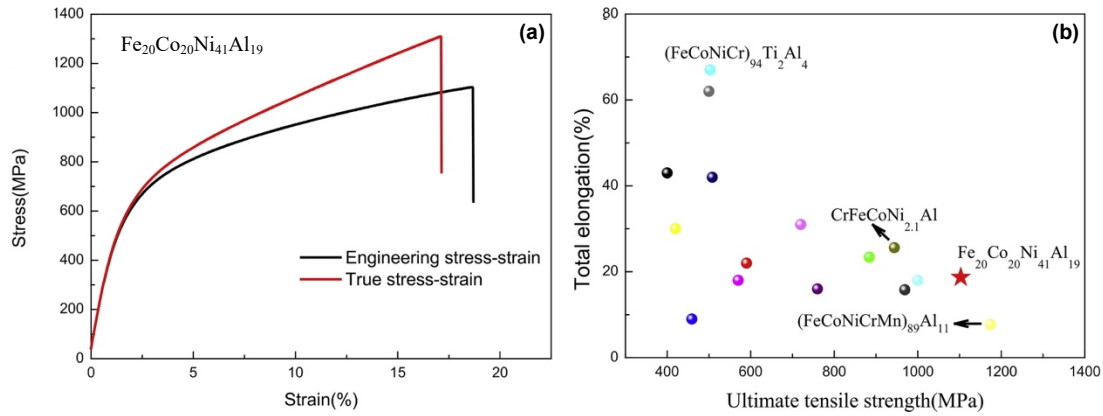


Figure 7.1. A Room-temperature tensile stress-strain curve of Fe₂₀Co₂₀Ni₄₁Al₁₉ alloy; (b) total elongation-ultimate tensile strength map of some HEAs prepared by casting. [360]

7.2 Microstructural Simulation

In future research of large-domain microstructure modeling, the 3D CA-PF model is recommended to simulate the solidification of multi-component HEA alloys during AM processes. For most HEA alloys, the thermodynamic and mobility databases are lacking due to the booming of new HEA compositions and the depleted research on HEA alloy systems; therefore, the thermodynamic and mobility databases should be established first. One popular software to conduct the calculations is CALculation of PHase Diagrams (CALPHAD). The current 3D CA-PF model has been successfully applied to simulating the solidification of ternary alloys during laser welding and laser additive manufacturing (Chapter 6). To extend the component numbers, only the 1D PF component in the 3D CA-PF model should be updated accordingly. Since the PF model implemented in the 3D CA-PF model is a multi-phase and multi-component PF model, it will be easy to involve more phases and constituent components.

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