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Development of a Rapid Solidification Model for Additive Manufacturing and Application to Al – Si Alloys

적층 제조를 위한 금속 응고 모델 개발 및 Al-Si 합금에서의 응용

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이 논문을 공학석사 학위논문으로 제출함 2023 년 02 월

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Abstract

The prediction of the as-additive manufactured microstructure of alloys depending on the processing parameters and alloy composition is indispensable for the precise control of mechanical properties of the products. In the present study, a rapid solidification model that can be applied to selective laser melting (SLM) is developed by combining various solidification theories and CALculation of PHAse Diagram (CALPHAD) thermodynamic calculations. Using solidification parameters that are determined by Rosenthal equation and a single fitting parameter, the primary dendrite arm spacing (PDAS), primary cell fraction, and solute profile can be predicted in the present model. Single track experiments for Al-12Si binary alloy were also performed under various processing conditions. Using the literature data and the present experimental results, the accuracy of the model for the Al-Si alloy was validated for each part. In case of PDAS model, estimated values were much better than conventional one. To apply our model in a wider range, empirical relationship between fitting parameter and initial concentration was derived for hypo - eutectic case. Also, for practical applications, universal equation between PDAS and cooling rate was suggested. Microsegregation model, which was reported for the first time, was able to predict average solute concentration and phase fraction in a reasonable range.

Keywords : Rapid solidification, Selective laser melting, Primary dendrite arm spacing, Primary cell fraction, Solute profile, Al – Si alloy

Table	of	Contents
-------	----	----------

Abs	strac	ti
Tab	ole of	² Contentsii
Lis	t of H	iguresiv
Lis	t of I	Fables vii
Cha	apter	1. Introduction1
	1.1	Research Objective
	1.2	Organization2
Cha	apter	2. Rapid Solidification Theories
	2.1	Rapid Soldification Theories for Basic Parameters
	2.2	Existing PDAS Model
	2.3	Existing Microsegregation Model
Cha	apter	3. Model Explanation15
	3.1	Thermal Profile in Melt Pool and Solidification Parameters15
	3.2	Primary Dendrite Arm Spacing (PDAS)17
	3.3	Microsegregation
Cha	apter	4. Experimental30
	4.1	Powder Selection
	4.2	Single Track Experiment and Post-Processing
	4.3	Microstructure Observation and Measurement - SEM
	4.4	Microstructure Observation and Measurement - TEM
Cha	apter	5. Results and Discussion40
	5.1	Microstructures of Single Track SLM
	5.2	PDAS Model41
	5.3	Microsegregation Model

Chapte	er 6. Conclusions	64
6.1	Summary	64
6.2	Original Contribution to Knowledge	66
6.3	Future Works	67
Appen	dix	68
Apj	pendix 1. Review of Rosenthal Equation	68
App	pendix 2. Effect of Thermal Diffusivity	69
App	pendix 3. Scheil Cooling Assumptions	70
Apj	pendix 4. Solidification Velocity vs Undercooling	71
Refere	nces	74
Abstra		

List of Figures

Figure 2.1	Schematic of solute	e trapping1	2
------------	---------------------	-------------	---

Figure 2.2 Microstructure estimation using phase field model. (a) Ti-6Al-4V [14], (b) Ni-Nb [13]12

Figure 4.2 Schematics of samples prepared in the present SLM experiments: Al-12 single tracks on pre-Al-12Si blocks on A6061 substrate, and Al-12Si single tracks are formed on Al-12Si blocks.....35

Figure 4.3 Microstructure observation by etching time; (a) 10 s, (b) 20 s.

Figure 4.4 Measuring primary cell fraction using image analysis; (a)

Figure 5.2 SEM image of microstructure by process conditions. (a) b1; (b) b2; (c) b3; (d) c1; (e) c2; (f) c3; Eutectic part is a brighter zone and primary cell part is darker zone. As scanning speed increases, cell spacing decreases. On the contrary, primary cell fraction increases..49

Figure 5.3 Magnified microstructure of c3 observed by (a) SEM, (b) TEM, and (c) TEM-EDS mapping......50

Figure 5.5 Optimized A parameter as a function of Si content of hypoeutectic Al-Si binary alloys......52

Figure 5.9 Relationship between *n* value and Si composition.55

Figure A.2 *V* vs undercooling plot for Al-Si alloys; Al-10Si (Black line & square), Al-12Si (Red line & triangle).73

List of Tables

Table 2.1 Result comparison between experiment and estimated PDAS values for various methods.
Table 3.1 Parameters and thermal properties for Al-12Si and AlSi10Mg used to determine partition coefficient, liquidus slope, and tip radius.
Table 4.1 Size distribution of Al-Si SLM powder
Table 4.2 Al-12Si block process condition. 39
Table 4.3 Labels and process conditions for single track fabrication.39
Table 4.4 Polishing condition for Al alloys. 39
Table 5.1 Summary of the present single track SLM experiments for Al-12Si alloy
Table 5.2 The comparison of PDAS between single track experimentresult of AlSi10Mg [38] and modeling result using A=130
Table 5.3 The comparison of PDAS between single track experimentresult of Al-12Si and modeling result using A=233
Table 5.4 Optimized A parameters for various Al-Si alloys
Table 5.5 PDAS comparison between experimental, model, and conventional model
Table 5.6 n value by Si composition. 62
Table 5.7 The comparison of experiment and model primary cell fractions. 62
Table 5.8 Modified eutectic point, maximum solubility, and average concentration inside primary cell for experiment and model. Sample c1

Chapter 1. Introduction

1. 1 Research Objective

Additive manufacturing (AM) technology enables to produce high density and complex structured products by a single process, which significantly reduces design-to-manufacture time and cost [1], and is regarded as one of the future industrial manufacturing technologies. Selective laser melting (SLM), which is a common AM technology, uses a laser to melt metal powder bed to fabricate the product. In the SLM process, a substrate, which is a plate where product is built on, and laser act as a heat sink [1] and high energy source [2], respectively. Thin layer of metal powder is deposited first. Then, laser scanning occurs to melt the metal powder, and a rapid solidification (cooling rate of 10^6 K/s~ 10^7 K/s) happens [3].

Due to its complexity in solidification [4], however, it has been a challenge to predict mechanical properties of AM as-built products. For example, to predict the mechanical properties of as-built products, the precise information of as-built microstructure features such as primary dendrite arm spacing (PDAS), primary cell fraction, eutectic fraction, microsegregation, etc. is essential. Therefore, it is necessary to develop the solidification model to predict as-built microstructure depending on the AM process condition.

Objective for present study is to develop a solidification model to estimate as-built microstructure depending on the AM process condition. To do so, a rapid solidification model for AM process is developed by the modification and integration of several existing solidification theories. The model is let to predict the primary dendrite arm spacing (PDAS), which is an important length scale for AM, microsegregation, and primary and eutectic phase fraction depending on process conditions (laser scanning speed, laser power, and initial alloy composition). To validate the applicability of the model, the single track SLM experiments of Al-12Si binary alloy (12 wt.%Si alloy) were also carried out under various operation conditions. The prediction accuracy of the present model was validated by the present experimental data of Al-12Si alloy, and various Al-Si alloys results available in literature.

1.2 Organization

In chapter 2, basic rapid solidification theories are reviewed. Also, general models for PDAS and microsegregation is explained with existing problems. Chapter 3 explains about the developed rapid solidification model. The model can be divided into three parts: solidification parameters determination, PDAS model, and microsegregation model.

In chapter 4, experiment for model verification is elucidated. Al-12Si single track experiment was done. Afterwards, SEM and TEM was used to observe microstructure and measure various parameters for model verification.

Chapter 5 shows experimental results and compares it with model's prediction. First, microstructure is observed by process conditions. Then, PDAS and microsegregation model validity was certified. Moreover, relationship between PDAS and cooling rate was developed for practical applications.

Finally, chapter 6 summarizes the work done in present study, explains original contribution to knowledge, and suggests available future works.

2

Chapter 2. Rapid Solidification Theories

This chapter focuses on the basic rapid solidification theories that are adopted in general researches. Difference between conventional solidification and rapid solidification is explained, and velocity dependent equations for basic solidification parameters, such as partition coefficient, liquidus slope, and dendrite tip radius, are explained. Moreover, general models adopted in other studies are elucidated. Specifically, PDAS and micrsegregation models are described and problems of the models are analyzed too.

2. 1 Rapid Solidification Theories for Basic Parameters

When solidification occurs, various parameters are important, and among all those parameters, partition coefficient and liquidus slope are significant. Thus, determination of these parameters is essential. For conventional solidification, local equilibrium at the solid-liquid interface is assumed, and the parameters are independent to solidification velocity. However, in case of rapid solidification, this concept can't be applied due to its high cooling rate and fast solidification velocity. Hence, to analyse phenomenon occurred during rapid solidification, departure from equilibrium should be well considered. Various researchers made different models, and the model by M. J. Aziz [5], and the model by P. K. Galenko [6] are the most well-known models. Aziz et al. proposed a concept called "solute trapping" to explain the modified solute distribution occurred by rapid movement of solid-liquid interface. Unlike conventional solidification, due to the rapid locomotion of

the interface, some solute atoms won't have enough time to diffuse back to liquid to make local equilibrium. Instead, they'll be trapped inside the solid, which increases partition coefficient (fraction between solid and liquid concentration at the interface) (Fig. 2.1). Amount of trapped solute will differ by solidification velocity, so partition coefficient will be dependent to solidification velocity. Assuming sharp interface and utilizing diffusive-type rate equations, equation for partition coefficient will be:

$$k = \frac{k_e + V/V_{DI}}{1 + V/V_{DI}} \tag{1}$$

where k is modified partition coefficient, k_e is equilibrium partition coefficient, V is solidification velocity, and V_{DI} is interface diffusive speed. According to equation (1), when V approaches to zero, k will approach to k_e , and when V approaches to infinity, k will become 1, which means that partitionless solidification occurs.

However, in several experiments, partitionless solidification occurred at finite solidification velocity [7, 8], leading to limitation of Aziz model. To solve this drawback, P. K. Galenko developed the model with additional consideration: no local equilibrium at bulk liquid phase. Using several assumptions and equations from irreversible thermodynamics (mass balance & evolution equation), reformed equation for partition coefficient was derived:

$$k = \begin{cases} \frac{(1 - V^2 / (V_D)^2) k_e + V / V_{DI}}{1 - V^2 / (V_D)^2 + V / V_{DI}} & , V < V_D \\ 1 & , V \ge V_D \end{cases}$$
(2)

where V_D is bulk diffusive speed. If solidification velocity surpasses bulk diffusive speed, diffusionless solidification will occur, which matches well with experiment results stated previously. Additionally, due to departure from equilibrium, liquidus slope also becomes dependent to solidification velocity. To derive modified equation for liquidus slope, non-equilibrium part should be considered at chemical potential equivalency. With this consideration, velocity dependent liquidus slope will be:

$$m = \begin{cases} \frac{m_e}{1 - k_e} \left\{ 1 - k + \ln\left(\frac{k}{k_e}\right) + (1 - k)^2 \frac{V}{V_D} \right\}, V < V_D \\ \frac{m_e \ln k_e}{k_e - 1}, V \ge V_D \end{cases}$$
(3)

where m is modified liquidus slope and m_e is equilibrium liquidus slope. Similar to equation (2), equation becomes different when velocity is faster than diffusive speed.

To analyze solidification, dendrite (or cell) tip radius (r) is also a crucial parameter, like partition coefficient and liquidus slope. In case of conventional solidification, criterion called "marginal stability" was applied to determine r [9]. However, when deriving the equation, assumptions were based on small Peclet number (slow solidification velocity). Therefore, the equation can't be directly applied to rapid solidification cases, which have high Peclet number. Thus, W. Kurz, B. Giovanola, and R. Trivedi developed the model (KGT model) by considering stability functions that are dependent to Peclet number [10]. Moreover, P. K. Galenko expanded the model to non-equilibrium at both the interface and bulk phases [11]. Thus,

KGT model is modified as follow:

$$Gr^{2} + 2rm\xi_{c}C_{d}(1-k)P_{c} + 4\pi^{2}\Gamma = 0$$
(4)

with,

$$P_c = \frac{Vr}{2D_L} \tag{5}$$

$$\xi_{c} = \frac{1 - \left[1 + \left(1 - \left(\frac{V}{V_{D}}\right)^{2}\right)\left(\frac{2\pi}{P_{c}}\right)^{2}\right]^{\frac{1}{2}}}{\left[1 - \left(\frac{V}{V_{D}}\right)^{2}\right]\left[1 - 2k - \left[1 + \left(1 - \left(\frac{V}{V_{D}}\right)^{2}\right)\left(\frac{2\pi}{P_{c}}\right)^{2}\right]^{\frac{1}{2}}\right]}$$
(6)

$$C_d = \frac{C_0}{1 - (1 - k)Iv(P_c)}$$
(7)

$$D_L = D_0 \exp\left(\frac{Q}{-RT}\right) \tag{8}$$

$$Iv(P_c) = P_c \exp(P_c) \exp(P_c)$$
(9)

where *G* is thermal gradient, P_c is Peclet number, Γ is Gibbs-Thomson coefficient, C_0 is initial concentration, D_L is liquid diffusion coefficient, D_0 is exponential factor, $\exp(P_c)$ is exponential integral, and $Iv(P_c)$ is Ivantsov's solution. By using solidification velocity dependent *k* and *m*, KGT model could be well applied to rapid solidification conditions.

2.2 Existing PDAS Model

In case of selective laser melting (SLM), which is a type of additive manufacturing (AM), and laser welding, primary dendrite arm spacing (PDAS) is a crucial parameter that's directly related to mechanical properties. As a result, there were various trials to estimate PDAS in both laser welding and AM by using analytic equations or simulations.

One of the most famous equation used for estimating PDAS is Kurz & Fisher model [9]. The model assumes cell/dendrite shape as an ellipsoid, and they're close packed together. Utilizing these geometrical properties, formula for PDAS is:

$$\lambda_1 = \left(\frac{3\Delta T'r}{G}\right)^{\frac{1}{2}} \tag{10}$$

 λ_1 is PDAS, G is thermal gradient, r is tip radius, and $\Delta T'$ is defined as temperature difference between tip and root of the cell. For small Peclet number, tip radius could be written as follow by using KGT model:

$$r \approx \left(\frac{4\pi^2 D_L \Gamma}{\Delta T_0 kV}\right)^{\frac{1}{2}} \tag{11}$$

where ΔT_0 is equilibrium solidification range. With additional assumption that $\Delta T' \approx \Delta T_0$, and substituting equation (11) to (10), the result will be:

$$\lambda_1 \approx \frac{4.3 (\Delta T_0 D_L \Gamma)^{0.25}}{k^{0.25} V^{0.25} G^{0.5}}$$
(12)

In many cases, equation (12) is utilized to predict PDAS for laser welding and additive manufacturing products. However, for laser welding and additive manufacturing, solidification occurs rapidly. Thus, Peclet numbers are high for this case, which is controversial to assumption made during derivation. As a result, deviation exists between prediction and experimental results for various alloys (Table 2.1). Errors are in the range of 16% to 57%, which is quite large. Moreover, these results are just for single process parameter, so it couldn't be ensured that the model could be applied to various process parameters. Conclusively, the model should be modified, and verified in various cases to be applied at rapid solidification.

Another method that could be utilized to predict PDAS is simulations. Various simulations can be used however, the most common method is phase field model. Phase field model is a powerful method applied in solidification, which could solve interfacial problems in phase transformation [12]. The method helps researchers to understand the dynamics of solidification and simulate complex morphologies (Fig. 2.2). Therefore, it is widely used not only in conventional solidification, but also in rapid solidification. This was done for various kinds of alloys [13, 14] and it predicted morphology quite well. However, as shown in Table 2.1, estimated values are not that accurate. Additionally, phase field model is a time-consuming process, so to predict the length scale of the microstructure, a more accurate but less time-consuming method is required. This is same for other simulations like cellular automaton [15] (see Table 2.1 [13-18] for compared result).

Conclusively, development of analytical model for rapid solidification is necessary to estimate PDAS faster and more accurately.

2.2 Existing Microsegregation Model

Like PDAS, solute distribution, primary, and secondary phase amounts are also important factors that affect mechanical property. Moreover, when additional heat treatment is applied to as-built products, these quantities are directly related to the final microstructure. Therefore, estimating each part is important and essential. Like PDAS estimation, due to its rapid solidification velocity, modification of microsegregation model from conventional solidification is needed to engage the model at rapid solidification cases. Liang et al. [19] developed a microsegregation model that could be applied in rapid solidification by considering non-equilibrium and supersaturation. The model is based on Brody and Flemings' model which is:

$$C_s^* = k_e C_0 [1 - (1 - 2\alpha k_e) f_s]^{\frac{k_e - 1}{1 - 2\alpha k_e}}$$
(13)

$$\alpha = \frac{D_s t_f}{L^2} \tag{14}$$

where C_s^* is solute concentration in the solid, C_0 is initial concentration, f_s is solid fraction, α is back-diffusion coefficient, D_s is solid diffusion coefficient, t_f is solidification time, and L is total system length. To consider non-equilibrium, velocity-dependent partition coefficient and liquidus slope from Aziz [5] was adopted. Additionally, to take supersaturation into account, KGT model [10] was used to calculate tip radius, then add tip undercooling considering the shape of the tip. Therefore, equation (13) will conform as:

$$C_{s}^{*} = kC_{0}A\left(1 - (1 - 2\alpha' kAf_{s})\right)^{\frac{kA-1}{1-2\alpha' kA}}$$
(15)

$$\alpha' = \frac{4D_s\Delta T}{\lambda_1^2 GV} \tag{16}$$

$$A = \frac{1}{1 - (1 - k)Iv(Pc)}$$
(17)

$$Pc = \frac{Vr}{2D_L} \tag{18}$$

 λ_1 is PDAS, ΔT is solidification range, Pc is solute Peclet number, and Iv(Pc) is Ivantsov function for solute Peclet number. By comparing with empirical results by Liang et al., the model showed a better validity than conventional solidification theories, in rapid solidification conditions.

The model effectiveness was proved to the range $\sim 10^4$ K/s, however, in case of SLM, cooling rate increases to $10^6 \sim 10^7$ K/s. Moreover, to consider supersaturation, Liang's model included only tip undercooling. Nonetheless, for alloys that have low solubility (ex. Al-Si alloys), eutectic undercooling should also be calculated because solidification ends at eutectic temperature (Fig. 2.3). Additionally, due to high cooling rate and rapid solidification velocity, large eutectic undercooling will exist, and by that, amount of supersaturation will change. Therefore, additional undercooling should be considered. However, in the author's knowledge, there's no model for predicting amount of supersaturation by solute trapping and large undercooling due to rapid solidification. There're only some experimental observation for supersaturation [20, 21], and evidence for eutectic point modification [22, 23]. Even though, microsegregation for SLM products could be calculated by using phase field model, absolute value is not that

accurate [24] or the validity is not that clear [25]. On top of that, the process is extremely time-consuming as mentioned before. Hence, a new model is required to predict microsegregation in both faster solidification velocity and low solute solubility with a less time-consuming work.

As mentioned before, primary dendrite fraction and secondary phase fraction are also critical factors that affect mechanical properties of as-built products. Nevertheless, in the author's knowledge, there's no model to predict each value. Thus, only Scheil cooling calculation based on thermodynamics is available for prediction. Conclusively, if integrated model that could estimate both solute distribution and primary dendrite fraction (or secondary phase fraction) is developed, it'll be a huge breakthrough for additive manufacturing.



Figure 2.1 Schematic of solute trapping.



Figure 2.2 Microstructure estimation using phase field model. (a) Ti-6Al-4V [14], (b) Ni-Nb [13]



Figure 2.3 Schematics of phase diagram and solidification range by maximum solubility (C_{sol}) . T'_m and T'_e are melting and eutectic temperature which considered undercooling respectively. (a) $C_{sol} > C_0$; (b) $C_{sol} < C_0$

		(%) Reference		57 [18]	7 [17]	8 [16]	31.6 [14]	[13]	[15]		
		Error (24~5	19.1	15.3	12.8~3	'	575	0.40	
	Experimental	PDAS	(mm)	$1.0 \sim 1.8$	1.038	1.3	$1.13 \sim 1.5$	$0.5 \sim 1.0$	5 46	2	
	Method Alloy Estimated PDAS (µm)		$1.57 \sim 2.23$	1.237	1.5	$1.28 \sim 1.96$	$0.14 \sim 1.6$	8 33	0.00		
			Inconel 718	AA5456	Al-Mg	Ti64	Inconel 718	AL-Cu	n>		
			Analutical	Equation	Equation	Phase field	model	Cellular	automaton		

Table 2.1 Result comparison between experiment and estimated PDAS values for various methods

Chapter 3. Model Explanation

This chapter discusses about developed rapid solidification model presented in this study. First, thermal distribution equation utilized in this study is elucidated to transform process parameters (laser power, scanning speed, initial concentration) to solidification parameters (solidification velocity, thermal gradient, cooling rate). Next, various solidification theories are integrated and modified to estimate PDAS and microsegregation of SLM products' microstructure.

3.1 Thermal Profile in Melt Pool and Solidification Parameters

Two important process parameters of SLM are laser power and scanning speed. However, solidification microstructure is determined by thermal gradient (G), solidification velocity (V), and cooling rate (CR), which are known to be solidification parameters. Therefore, conversion of SLM process parameters to solidification parameters is firstly necessary to model the solidification microstructure. In the present study, the Rosenthal equation [26] which has been widely accepted for explaining thermal distribution of a moving heat source, was chosen for the connection.

The Rosenthal equation was initially developed to calculate temperature profile for welding. In fact, SLM process is essentially a manufacturing process similar to welding process. Several studies [27, 28] already applied the Rosenthal equation to SLM process to predict the melt pool formation and showed that solidification parameters in SLM were well predicted by the equation (Appendix 1). For example, the schematic diagram of the melt pool formation in SLM process is presented in Fig. 3.1. Using the Rosenthal equation, the temperature distribution in the melt pool can be calculated:

$$T = T_0 + \frac{cP}{4\pi k} \frac{\exp\left(-\frac{vR}{\alpha}\right)\exp\left(-\frac{vx}{\alpha}\right)}{R}$$
(18)

, where T_0 is the initial temperature before laser scanning, *x* and *z* the distance from laser scanning direction in parallel and orthogonal to substrate surface, respectively, and y orthogonally directed to *x* and *z*, R the distance from heat source, which is defined as $\sqrt{x^2 + z^2}$, *v* the velocity of heat source, *k* thermal conductivity, P heat source power, c absorptivity, and α thermal diffusivity. To define solidification parameters in the melt pool center (MPC), y can be set to be zero.

Differentiating the equation (18) with x and z, thermal gradient in x direction G_x , z direction G_z , and total value G can be determined as below [28]:

$$G_x = \frac{\partial T}{\partial x} = \left(1 + \frac{x}{(x^2 + z^2)^{\frac{1}{2}}} + \frac{2\alpha x}{v(x^2 + z^2)}\right) \left(\frac{-cPv}{4\pi k\alpha} \frac{1}{(x^2 + z^2)^{\frac{1}{2}}}\right) \exp\left[-\frac{v}{2\alpha} \left(x + (x^2 + z^2)^{\frac{1}{2}}\right)\right]$$

(19)

$$G_{z} = \frac{\partial T}{\partial z} = \left(1 + \frac{2\alpha}{v(x^{2} + z^{2})^{\frac{1}{2}}}\right) \left(\frac{-cPv}{4\pi k\alpha} \frac{z}{x^{2} + z^{2}}\right) \exp\left[-\frac{v}{2\alpha} \left(x + (x^{2} + z^{2})^{1/2}\right)\right]$$
(20)

$$G = \sqrt{G_x^2 + G_z^2} \tag{21}$$

Typically, solidification direction is opposite to thermal gradient. Thus, solidification velocity V (see Fig. 3.1 (a)) can be calculated as [22]:

$$V = v \cdot \cos\beta \tag{22}$$

where $\beta = tan^{-1} \left(\frac{G_z}{G_x} \right)$.

Then, cooling rate ($CR = G \cdot V$) can be easily derived. That is, for a given SLM process condition, solidification parameters at a given position of melt pool can be calculated by using the Rosenthal equation. Of course, solidification in melt pool occurs in the solidification temperature range of a given alloy (between liquidus temperature, T_m and eutectic temperature, T_e). Therefore, average values of V and G of a given position during the solidification can be calculated for the present solidification model. The depth of MPC is set to be half of the depth of melt pool (Fig. 3.1 (b)).

3.2 Primary Dendrite Arm Spacing (PDAS)

As explained in Section 2.1, although the equilibrium distribution of solute between solid and liquid phase is usually assumed at the solid/liquid interface in the conventional solidification condition, departure from local equilibrium happens at the solidification front in a rapid solidification process like SLM due to the fast movement of the interface [2]. As a result, solidification related coefficients such as partition coefficient (k) and liquidus slope (m) become solidification velocity dependent. In present study, equations by Galenko [2] (Eqs. (2) - (3)) were adopted to determine k and m. The value of each parameter used to determine k and m are listed in Table 3.1 [2, 29-33].

One of the parameters also important in solidification is dendrite tip radius (*r*). Kurz, et al. [10] proposed theoretical model (known as KGT model) to calculate *r*, which could be applied for directional rapid solidification (for high Peclet number). For the present study, this KGT model (Eqs. (4) - (9)) was applied at undercooled temperature to calculate *r*.

$$T = T_m - \Delta T_n - \Delta T_r - \Delta T_K = T_m - C_0 (m_e - m) - \frac{2\Gamma}{r} - \frac{V}{\mu_K}$$
(23)

$$\mu_k = \frac{\nu_s Q_s}{RT_m^2} \tag{24}$$

where μ_k kinetic growth coefficient, Q_s latent heat, and v_s sound of speed. exp $i(P_c)$ in Eq. (13) is exponential integral of P_c , and $Iv(P_c)$ is Ivantsov's solution. In the case of Ivantsov's solution, it could be approximated to series of polynomials: In this study, it is taken from Ref. [9].

Thermal diffusion term in the KGT model for solidification velocity range of SLM process (~ 1 m/s) is negligible (Appendix 2). Therefore, thermal stability function in the model [2] is neglected for this study. Several undercoolings occur for rapid solidification: undercooling by change of liquidus slope ($\Delta T_n = C_0(m_e - m)$), curvature undercooling ($\Delta T_r = \frac{2\Gamma}{r}$), and kinetic undercooling ($\Delta T_K = \frac{v}{\mu_K}$). The temperature dependence in liquid diffusion coefficient is also considered. The morphology of solidification can be changed depending on the solidification parameters. According to the solidification map [20], local solidification in the MPC results in a fine cellular morphology, due to the rapid cooling rate and high ratio of G to V (G/V) of SLM process. Therefore, PDAS is important dimensional scale for SLM products. For the calculation of PDAS, Kurz and Fisher model (Eq. (10)) is chosen, where $\Delta T'$ is temperature difference between tip and root of the cell ($\Delta T' = T_{tip} - T_{root}$) :

 T_{root} can be eutectic temperature in conventional solidification. But, due to the fast solidification speed in SLM, eutectic undercooling becomes significant, and therefore both eutectic undercooling and kinetic undercooling should be taken into account for the calculation of T_{root} [34]:

$$T_{root} = T_e - \Delta T_e - \Delta T_K \tag{25}$$

$$\Delta T_e = A\sqrt{V} + (m - m_e)C_e \tag{26}$$

where T_e is equilibrium eutectic temperature, ΔT_e eutectic undercooling, ΔT_K kinetic undercooling (V/μ_K), and C_e equilibrium eutectic concentration. *A* is complex equation related to eutectic microstructure, and the details can be found in the study by Kurz and Trivedi [34]. It should note that this *A* parameter is used as a fitting parameter in the present model later.

To calculate T_{tip} , various undercoolings should be also considered [2]:

$$T_{tip} = T_m - \Delta T \tag{27}$$

$$\Delta T = \Delta T_C + \Delta T_r + \Delta T_n + \Delta T_K + \Delta T_t \tag{28}$$

where ΔT_c is constitutional undercooling, ΔT_r curvature undercooling, ΔT_n undercooling occurred by departure of local equilibrium, ΔT_K kinetic undercooling, and ΔT_t thermal undercooling. Constitutional undercooling is calculated [2]:

$$\Delta T_{\mathcal{C}} = k \Delta_{\nu} \frac{l \nu(P_{c})}{1 - (1 - k) l \nu(P_{c})}$$
⁽²⁹⁾

, where k partition coefficient (see Eq. (6)) and Δ_v is solidification range. As can be seen in Fig. 3.2, Δ_v has two different expressions depending on initial alloy composition C_0 and maximum solute solubility in solid phase C_{sol} .

$$\Delta_{\nu} = \begin{cases} \frac{mC_{0}(k-1)}{k}, \ C_{0} < C_{sol} \\ T'_{m} - T'_{e}, \ C_{0} > C_{sol} \end{cases}$$
(30)

 T'_m is modified melting temperature, which is same as Eq. (27), and T'_e is undercooled eutectic temperature, which is same as Eq. (25). Thermal undercooling is:

$$\Delta T_t = \frac{Q_s}{c_p} I v(P_T) \tag{31}$$

$$P_T = \frac{Vr}{2\alpha} \tag{32}$$

where P_T thermal Peclet number, and c_p heat capacity at solidification region.

In summary, PDAS in Eq. (10) can be calculated based on *r* and *G* from Eqs. (2) to (9) and Eqs. (23) to (24), and $\Delta T'$ from Eqs. (25) to (32). *A* in Eq. (25) is the only fitting model parameter used in the present study which is a function of alloy composition.

3.3 Microsegregation

Solid and liquid fraction can be changed during solidification process. According to solidification theory, once primary cell spacing (λ_1) is established in the cellular tip formation, no change of λ_1 can be assumed during or after solidification [9]. As shown in Fig. 3.3 (a), therefore, the length of system for the solidification can be fixed as $\lambda_1/2$. If solid domain length, x_s , for each time step is determined, solid and liquid fraction could be calculated while solidification occurs. In this study, 1-dimensional (1D) model scheme is chosen to calculate the solidification of alloy:

$$f_s = \frac{x_s}{\lambda_{1/2}}, \text{ and } f_l = 1 - \frac{x_s}{\lambda_{1/2}}$$
(33)

where f_s and f_l are solid and liquid fraction, respectively. Solidification begins at T'_m , and ends at T'_e . When it reaches T'_e , the remaining liquid transforms to eutectic structure. Thus, total primary cell fraction f_c and eutectic fraction f_e in the end of solidification can be defined as:

$$f_c = \frac{x_{s,f}}{\lambda_{1/2}}, \quad f_e = 1 - \frac{x_{s,f}}{\lambda_{1/2}}$$
 (34)

For the determination of solid domain length, mass balance concept is adopted from the previous study by Paliwal and Jung [35]. In their study, microsegregation in Mg alloys in conventional solidification was successfully predicted by assuming a back diffusion in solid phase, no concentration gradient in liquid phase, and equilibrium partition coefficient (*k*) at solid/liquid interface. In the present study for rapid solidification for SLM, we assume (i) no back diffusion in solid phase because solidification ends rapidly (within 1~10 µs) and consequently negligible solid-state diffusion can occur, (ii) no concentration gradient in the liquid due to perfect mixing by Marangoni flow in the melt pool induced by surface tension gradient and fast and dynamic convection (~1 m/s) [36] in small system (sub-micron size) by high temperature gradient (Appendix 3). Additionally, non-equilibrium is considered at solid/liquid interface. Considering these assumptions, mass balance in the primary cell space, $\lambda_1/2$, at a given time can be given as:

$$\int_{0}^{x_{s}} C_{s} dx + \int_{x_{s}}^{\frac{\lambda_{1}}{2}} C_{l} dx = C_{0} \frac{\lambda_{1}}{2}$$
(35)

where C_s and C_l are solid and liquid concentration, respectively. With the assumption of a perfect mixing in liquid (see Fig. 3.3 (a)), Eq. (35) can be

$$\int_{0}^{x_{s}} C_{s} dx + C_{l} \left(\frac{\lambda_{1}}{2} - x_{s}\right) = C_{0} \frac{\lambda_{1}}{2}$$
(36)

Differentiating Eq. (36) with time,

$$\int_0^{x_s} \frac{\partial C_s}{\partial t} dx + (C_s - C_l) \frac{dx_s}{dt} + (\frac{\lambda_1}{2} - x_s) \frac{dC_l}{dt} = 0$$
(37)

The derivative $\frac{\partial C_s}{\partial t}$ in the first term becomes zero (no back diffusion in solid), and $\frac{dC_l}{dt}$ can be replaced by $\frac{CR}{m}$ where CR is cooling rate and m is liquidus slope. Then, Eq. (37) can be reorganized to:

$$\frac{dx_s}{dt} = \frac{1}{C_l(1-k)} \frac{CR}{m} \left(\frac{\lambda_1}{2} - x_s\right) \tag{38}$$

Using Euler forward treatment [37] with time step, Eq. (38) can be solved as:

$$x_{s,i+1} = x_{s,i} + \Delta t \left(\frac{1}{C_l(1-k)} \frac{CR}{m} \left(\frac{\lambda_1}{2} - x_{s,i} \right) \right)$$
(39)

where Δt is calculation time step, $x_{s,i+1}$ and $x_{s,i}$ are solid domain length for time step i+1 and i, respectively. Note that the $k = C_s/C_l$ is nonequilibrium solute partition coefficient at solid/liquid interface (see Eq. (1)).

To determine solid domain length for each time step, initial value $(x_{s,0})$ is required in Eq. (39). Under the rapid solidification condition, liquidus slope and partition coefficient change depending on solidification velocity as shown in Eqs. (1) and (2). In addition, undercooling by liquid slope change ΔT_n , curvature undercooling ΔT_r , and kinetic undercooling ΔT_K can lower the liquidus temperature. Therefore, when rapid solidification happens, equilibrium phase diagram changes to non-equilibrium phase diagram (changes in both liquidus and solidus), which is also referred as kinetic phase diagram [2], as presented in Fig. 3.4. On the other hand, when solidification starts, the constitutional undercooling ΔT_c and thermal undercooling ΔT_t can further lower the starting point of solidification without directly influence to liquidus line, which makes the starting point of solidification, point P. By applying lever rule at point P using kinetic phase diagram, fraction between solid and liquid phase at the solidification starting point P can be calculated. Since the length of entire system is a half of PDAS $\lambda_1/2$, initial solid domain length can be calculated as:

$$x_{s,0} = \frac{b}{a+b}\frac{\lambda_1}{2} \tag{40}$$

, where *a* and *b* are the length from point P to solidus line and liquidus line, respectively (Fig. 3.4). Δt in Eq. (39) is determined by sectioning solidification range, which starts at T'_m and ends at T'_e . In the present study, it was divided into 1000 equal time intervals by considering cooling rate. Then, solid fraction at each time step can be calculated using Eq. (39), and final eutectic fraction can be calculated using Eq. (34). In the present study, for the sake of simplicity, the liquidus and solidus lines are assumed to be straight for the Al-Si alloy system, which is reasonable assumption considering the phase diagram of the Al-Si system. As no back diffusion in solid and complete mixing in liquid phase are assumed in the present rapid solidification model, the solute profile in primary cell is identical to that of the Scheil cooling condition [9]. Therefore, the solute concentration inside primary cell for each time step, *i*, can be determined to be:

$$C_{s,i} = k C_{l,i} \frac{k C_0}{(1 - f_{s,i})^{1-k}}$$
(41)

Conclusively, solute profile inside solid phase can be obtained.

At the eutectic temperature T'_e , maximum solute concentration in solid is achieved (Fig. 3.4, point S), and the amount of final liquid can be determined. This remaining liquid becomes eutectic phase (Fig. 3.4, point E). In the present Al-Si system, mixture of Al fcc solution and pure Si was considered as the eutectic phase.



Figure 3.1 Schematic of meltpool formed by laser. (a) longitudinal section; (b) cross section; Solid and dashed line indicates meltpool boundary and isothermal line (T_m) respectively. Note that, solidification will occur between these two lines.



Figure 3.2 Schematics of phase diagram and solidification range by maximum solubility.


Figure 3.3 The schematics of primary cell formation when solidification occurs. (a) Cell array in the middle of solidification, and 1-D scheme of mushy zone; (b) Solidification process by cooling. The process starts at T'_m and ends at T'_e . Note that when T'_e is reached, remaining liquid transforms to eutectic.



Figure 3.4 Schematics of equilibrium and non-equilibrium (kinetic) phase diagram by rapid solidification velocity. ΔT_n , ΔT_r , ΔT_K declines liquidus slope and ΔT_c , ΔT_t lowers starting point (point P) of solidification. Figure at right top shows solid and liquid fraction at point P. C_s' and C_e' indicates modified maximum solubility and eutectic composition respectively.

uidus slope, and tip radius				
Parameters	Va Al-12Si	ılue AlSi10Mg	Units	Ref.
Equilibrium partition coefficient (k_e)	0.1	212		
Equilibrium liquidus slope (m_e)	-7.	328	K/Si wt%	[31]
Gibbs-Thomson coefficient (Г)	7×	10-7	m·K	
Bulk diffusive speed (V_D)	0	8	m/s	[66]
Interface diffusive speed (V_{DI})	0	00	m/s	[ננ]
Diffusion activation energy (Q)	30	000	J/mol	[20]
Pre-exponential factor (D_0)	1.34	$\times 10^{-7}$	$m^{2/s}$	[nc]
Latent Heat (Qs)	47801	41227	J/100g	[29, 32]
Speed of sound (v_s)	εņ	40	m/s	[2]
Heat Capacity (c_p)	605.285	625.825	J/100g	[29, 32]

Table 3.1 Parameters and thermal properties for Al-12Si and AlSi10Mg used to determine partition coefficient, ÷ , , liquidı

Chapter 4. Experimental

This chapter focuses on experiments held for the evaluation of the present solidification model. Al-12Si single track experiments were performed in the present study because our model doesn't consider heat coarsening effect by multiple layer formation. Experimental design is shown to form single track and post-processing was done to observe microstructure using Scanning electron microscope (SEM) and Transmission electron microscope. Afterwards, using ImageJ, line intercept method, and point scan, PDAS, primary cell fraction, and average solute concentration inside primary cell was measured. Each part will be specifically explained in this chapter.

4.1 Powder Selection

Various factors should be considered to choose the alloy for this study:

- For verification of the model, simplest case should be utilized. Thus, binary alloy should be selected.
- 2) For SLM, specialized metal powder is required. Hence, the alloy that is chosen should be able to be made as metal powder.
- Even though, powder can be made, it might be hard to get. Therefore, the alloy should be one of the commercial alloys used in AM foundry.

In this regard, Al-12Si binary alloy was chosen for single track fabrication. Al-12Si SLM powder was fabricated by MK company, Korea. Exact composition of alloy powder was Al-12.235 Si-0.065 Fe in wt.% analyzed by ICP method. Size distribution of the powder used in the present SLM experiment is summarized in Table 4.1.

4.2 Single Track Experiment and Post-Processing

For SLM experiment, MetalSys 250 was employed (Fig. 4.1). Maximum power available is 400W and maximum scanning speed available is 0.9 m/s. Prior to single track formation, as can be seen in Fig. 4.2, Al-12Si blocks with height of 3 mm were made on the substrate to prevent mixing of Al-Si alloy with substrate Al alloy (for present study, A6061). Process condition for Al-12Si block substrate is summarized in Table 4.2. To verify model for various conditions, two different laser powers (200 W and 250 W) and three different scanning speeds (0.4, 0.6, and 0.8 m/s) were chosen for single track scanning. Exact process conditions and label for each sample are shown in Table 4.3. Conditions are chosen based on process window, which are conditions for single track to be successfully formed, of Al-Si alloys [38] and limit of MetalSys 250. For each processing condition, four single tracks were fabricated on Al-12Si block to check the reproducibility of experimental results.

After single tracks were fabricated, post-processing was done before microstructure observation. Samples were cut by using macro and micro cutter. Then, cross-sections of single track samples were taken vertical to the single track direction. Each sample was mounted in epoxy resin and ground by SiC paper with grit sizes from 400 to 4000. Then, mirror-finished polishing was done by using 1 μ m diamond suspension. Polishing was done using MetPrep 3 Grinder/Polisher and exact polishing conditions are shown

in Table 4.4. Afterward, for a clearer observation, samples were etched for 20 s with Keller's reagent (HNO3 2.5 vol%, HCl 1.5 vol%, HF 1 vol%). Generally, etching time is about 10 s, however, it wasn't adequate to measure only primary cell by image analysis (Fig. 4.3 (a)). Therefore, for present study it was intentionally taken a bit longer than conventional cases to distinguish primary cell and eutectic region more clearly. As shown in Fig. 4.3 (b), it is much easier to verify the fraction of primary cells when etching time was 20 s than 10 s. Note that, if etching time becomes longer, sample will burn and less accurate measurement will be done due to decline of primary cell amount.

4.3 Microstructure Observation and Measurement – SEM

To observe microstructure, and measure PDAS and primary cell fraction, field emission scanning electron microscope (FE-SEM; JSM-7800F Prime, JEOL) was used. Secondary electron images were taken for observation of microstructures inside the single tracks. Images were taken near the melt pool center for model verification. For PDAS measurement, line intercept method was utilized on five different images (size of 17.18 μ m × 13.86 μ m): total twenty straight lines were drawn on various positions of each sample and averaged. Primary cell fraction was measured using image analysis with ImageJ program. To measure only primary cell fraction, eutectic Al was erased by hand (Fig. 4.4). To reduce statistical error, ten SEM pictures (each size of 8.59 μ m × 6.43 μ m) were taken and averaged.

4.4 Microstructure Observation and Measurement – TEM

In case of SLM microstructures, size of primary cell is usually sub-micron. Thus, to observe a precise microstructure and measure average solute concentration inside primary cells, transmission electron microscope (TEM) was utilized. Prior to observation, Field Ion Beam (FIB) machine (Helios 650, FEI, USA) was used to prepare TEM samples. Single track part was collected and put on Cu grid. To confirm the variation of the microstructure by solidification condition, two samples were chosen for TEM samples: 250 W, 0.4 m/s (c1) and 250 W, 0.8 m/s (c3). After making TEM samples, microstructure observation by TEM-EDS mapping and TEM-EDS quantitative analysis was held using Cs-TEM (JEM-ARM200F, Cold FEG, JEOL Ltd, Japan). For quantitative analysis, randomly selected ten sections for each sample were measured and the results were averaged to get the solute composition inside the primary cells.



Figure 4.1 MetalSys 250 from POSTECH



Figure 4.2 Schematics of samples prepared in the present SLM experiments: Al-12 single tracks on pre-Al-12Si blocks on A6061 substrate, and Al-12Si single tracks are formed on Al-12Si blocks



Figure 4.3 Microstructure observation by etching time; (a) 10 s, (b) 20 s



Figure 4.4 Measuring primary cell fraction using image analysis; (a) Original SEM image, (b) After threshold (c) After erasing eutectic Al by hand.

D90	52.7
D50	31.4
D10	17.4
Percentage	Size (um)

Table 4.1 Size distribution of Al-Si SLM powder

Table 4.2 Al-12Si block process condition

Rotation Angle	(0)	67
Hatch Spacing	(md)	150
Layer	Thickness (µm)	40
Scanning Speed	(mm/s)	500
Power	(W)	320

Label	Power (W)	Speed (m/s)
b1		0.4
b2	200	0.6
b3		0.8
c1		0.4
c2	250	0.6
c3		0.8

Table 4.3 Labels and process conditions for single track fabrication

Table 4.4 Polishing condition for Al alloys

Grit Size	Rotating direction	Sample RPM	Platen RPM
400	Same	130	110
2000	Same	130	110
4000	Same	130	110
1 µm	Opposite	150	110

Chapter 5. Results and Discussion

This chapter shows experimental results and discusses about validity of presented model by comparing with empirical results. First, both macrostructure and microstructure of SLM product is observed and analyzed. Then, by using the analyzed data and a single fitting parameter A, PDAS model and microsegregation model are compared respectively. By using PDAS model, empirical relationship between fitting parameter A and initial concentration is derived for a wider application. Also, the results are compared with conventional equations. Moreover, for additional practical applications, relationship for n, which correlates cooling rate and PDAS, and initial concentration is determined by using presented model. With microsegregation model, modified eutectic point is predicted too.

5.1 Microstructures of Single Track SLM

As shown in Fig. 5.1 (a), six single track samples were prepared on A6061 substrate. In order to mimic the real SLM process, six Al-12Si blocks (~ 3mm) was made first on Al6061 substrate, and four single tracks with the same SLM processing condition were formed on top of each Al-12Si block. The examples of SEM microstructure images of the single tracks are shown in Fig. 5.1 (b) to (d). Brighter part corresponds to eutectic Si and darker part is primary Al. Morphology of melt pool center (MPC) is cellular structure, which is consistent with well-known results from the previous study [20]. Melt pool boundary (MPB) of the single track (rather small area between single track and substrate) could be easily identified by sudden changes in microstructure: Coarse columnar dendrite structure and more eutectic Si

formation, consistent with the previous study [20]. The morphology difference between MPC and MPB should be due to the large difference in cooling rate (CR) and solidification velocity (V) at MPC and MPB region. In some cases, partial disintegration was observed in the heat affected zone (HAZ) of Al-12Si block side. However, no heat affected zone (HAZ) was observed inside the single track.

Fig. 5.2 displays the microstructures of all single track samples prepared in the present study. Regardless the power (200W and 250W), both cell size and PDAS decreases with increasing scanning velocity. On the other hand, primary cell fraction increases with increasing scanning velocity. All experimental results for the PDAS and phase fraction are summarized in Table 5.1. The energy density (laser power/laser scanning speed) of the present SLM condition is varied from 0.25 to 0.625 J/m.

Fig. 5.3 shows SEM, TEM and TEM-EDS mapping images of the single track fabricated with 250 W and 0.8 m/s scanning speed (c3 sample). Eutectic microstructure is well captured in SEM-BSE image (Fig. 5.3 (a)). In addition, precipitates are exhibited inside the primary Al cells. TEM-EDS mapping (Fig. 5.3 (c)) shows that these precipitates are Si particles. As well known, solute trapping by rapid interface movement can cause excess amount of Si in Al cell during the solidification, which could lead the exsolution of Si particles after the solidification.

5.2 PDAS Model

As mentioned in section 3.2, PDAS can be calculated in the present study

using Eq. (10) which includes the influence of undercooling, tip radius and solidification parameters. The only empirical fitting parameter is A that influences to eutectic undercooling (see Eq. (26)). In order to optimize A parameter as a function of composition and validate the present PDAS prediction model, the present experimental data as well as previous experimental data available in literature were used:

(i) Present single-track data of Al-12Si

(ii) SLM data (SEM images) of AlSi10Mg (Al-10wt.%Si-0.35wt.%Mg) by Narra [38]

(iii) SLM data (SEM images) by Kimura et al.[39] for Al-xSi alloys where x = 4.07, 7.13, 10.38, and 12.47 wt.%

(iv) solidification of Al-1wt.%Si alloy by Sarreal et al. [40].

It should be noted that a small amount of Mg (0.35 wt.%) in the AlSiMg alloy by Narra [38] was ignored and treated as a binary Al-10Si alloy, and the growth direction of the cell was re-evaluated [38] to obtain more accurate PDAS values from the microstructure images. Sarreal et al. [40] performed the solidification study of Al-1wt.%Si alloy under various solidification velocities (up to 0.15 m/s). Among their results, the data obtained at 0.15 m/s solidification velocity was used in the present study because this solidification condition is similar to SLM process condition. To calculate PDAS for different Al-Si alloys, all parameters used for the present model are listed in Table 5 [2, 29-33, 38, 39, 41-43].

All PDAS results in the present study for Al-12Si alloy and the previous study by Narra [38] for Al-10Si alloy are plotted in Fig. 5.4 and shown

Table 5.2 & 5.3. The PDAS for both alloys increases with increasing energy density of SLM process. The PDAS of the Al-Si alloys can be calculated using the present model described in section 3.2. In order to reproduce these PDAS results shown in the figure, a specific *A* parameter in Eq. (26) was required: A = 130 for Al-10Si and 223 for Al-12Si. That is, for the given alloy, one constant parameter *A* can be sufficient to predict the PDAS of the cells fabricated in a wide range of SLM operation condition and *A* parameter is independent of solidification velocity.

All the experimental data from the previous studies [39, 40] and the present study were used in the calculation of *A* parameter for each specific Al-Si alloy. The optimized *A* parameters are plotted in Fig. 5.5 and shown in Table 5.4 as a function of Si content in the Al-Si alloy. *A* value for pure Al was assumed to be zero because of no eutectic undercooling expected for pure Al. The optimized function of *A* as a function of Si content is:

$$A = 71.24 \ \sqrt{C_0(wt.\%Si)} \tag{42}$$

where $C_0(wt.\%Si)$ is initial concentration of Si in the Al-Si alloy. Note that, this relationship is valid only for hypo-eutectic binary Al-Si alloys. The results by Narra [38] for AlSi10Mg were not taken into account in the optimization of *A* parameter above because 0.35%Mg can induce further complexity like ternary eutectic formation.

The predicted PDAS results from the present model is plotted in Fig. 5.6 and shown in Table 5.5. In comparison, the predictions from the previous conventional model by Kurz and Fisher [9] were plotted together. In the previous model, Kurz and Fisher proposed a relationship in which the PDAS is related to the square root of the dendrite tip radius:

$$\lambda_1 \approx \frac{4.3(\Delta_v D_L \Gamma)^{0.25}}{k^{0.25} V^{0.25} G^{0.5}}$$
(43)

This model was for example adopted in the study by Hekmatjou et al. [17] to explain the microstructure of Al alloy by laser welding. As shown in Fig. 5.6, the conventional model predicts well the trend of PDAS with solute content and energy density. However, the absolute PDAS values predicted by the conventional model are about twice larger than the experimental data. On the other hand, the present model can reproduce the PDAS accurately within the experimental error range.

For the given alloy, PDAS value decreases with increasing solidification velocity. Therefore, the PDAS can vary with cooling rate (CR). When solidification velocity exceeds absolute stability, planar microstructure is formed [9]. Therefore, PDAS can be assumed to be zero when CR is infinity (inverse number is 0). The PDAS values for Al-10Si alloy and Al-12Si alloy (both experimental results and predicted results from the present model) are plotted in Fig. 5.7 with CR^{-n} where n is constant. It should be noted that this is consistent with a semi-empirical relationship proposed by Matyja et al. [44] According to Sneha et al. [38], CR is inversely proportional to melt pool area. Thus, PDAS is proportional to energy density as shown in Fig. 5.4. Hence, it could be said that PDAS is simply related to cooling rate or melt pool size for a given alloy. As shown in Fig. 5.7, however, *n* value varies with composition. This means that PDAS is not simply varied by CR,

but depends on G, V, and composition (eutectic undercooling). Therefore, it is difficult to find the simplified universal relationship between PDAS and CR for Al-Si alloy from experiments. The present model can be used for the prediction of PDAS of Al-Si alloys under any SLM operation condition. Based on the present simulation results, the following relationship between n and initial concentration in Al-Si alloy can be predicted for more practical applications:

$$n = 0.0067C_0(wt. \% Si) + 0.2677 \tag{44}$$

Eq. (44) was derived by determining *n* for various concentration (2, 4.07, 5, 7.13, 9, 10.38, 12.235, 12.47 wt.%) and process conditions (same as AlSi10Mg process conditions). Plotted results for each composition and plot between *n* and C_0 are displayed in Fig. 5.8 & Fig. 5.9. Also, exact values of n by composition are shown in Table 5.6. These results show that n is affected by change of C_0 . This is due to change of solidification range by different C_0 . As C_0 declines, solidification range becomes wider. With a wider range, change of cooling rate will affect solidification process more, which is related to PDAS. Thus, as C_0 decreases, cooling rate will influence solidification more, which makes *n* smaller.

5.3 Microsegregation Model

Primary cell fractions f_c for the Al-12Si alloy in the present study are plotted in Fig. 5.10 and shown in Table 5.7. According to the present experimental results, f_c increased with increasing scanning speed which is

proportional to solidification velocity V. At the same scanning speed, however, no significant variation in f_c was observed with laser power. Laser power has less influence to the solidification temperature range, while solidification velocity can directly influence to the liquidus and eutectic undercooling. In the present study, primary cell fraction f_c is calculated using Eq. (34) based on PDAS and solid domain length. Although the f_c values from the present model are about 3-5 % lower than the experimental data, the trend of f_c is well predicted. The small deviation of model results from experimental data may result from an extraordinary properties of Al-Si alloy: tilted coupled zone [22] and different eutectic formation mechanism [45]. As these are beyond the scope of this study, no further investigation has been made here.

Solute profile inside primary cell or dendrite is determined by the microstructure evolution during solidification process. In the present microsegregation model explained in section 3.3, Scheil solidification was assumed due to very short solidification time and the solute trapping and various undercoolings are let to influence to the solute content in primary cells. Unfortunately, it was difficult to determine the solute profile due to the Si precipitate formation in primary cells, as shown in Fig. 5.3 (a) and (c), resulting from high supersaturation of Si. Instead, average solute concentrations in the cells were measured and compared with the predicted results for the verification of the present model. Two samples (c1 and c3) were analyzed using TEM-EDS analysis and their results are summarized in Figure 5.11 and Table 5.8. The average Si concentrations inside the cell were 3.10 ± 0.25 wt.% for c1 sample and 3.24 ± 0.14 wt.% for c3 sample, which exceed the equilibrium maximum Si solubility (1.65 wt.%). The

predicted average concentrations from the present model are 2.40 and 2.95 wt.% for c1 and c3 sample, respectively, and the maximum concentrations at the eutectic undercooling are 3.03 wt.% (at 701.21 K) and 3.66 wt.% (at 633.79 K) for c1 and c3 sample, respectively.

Even though the Si concentration predicted in the present model is less than the experimental data, the trend is well captured in the model. As explained in above, this difference could be originated from the 3-5 % inaccuracy in the primary cell fraction f_c prediction. However, considering that there has been no model to estimate the solute concentration in the primary cell for AM process, the present microsegregation model can still provide important microstructure information such as f_c and solute profile for AM process. The previous study by Pierantoni [22] examined the microstructure for Al-15.5~26Si alloy after laser remelting and reported more than 20 wt.% of Si in eutectic composition, which is consistent with eutectic compositions (21.89 wt.% for c1 and 23.63 wt.% for c3) by the present model. In summary, the present microsegregation model is valid and accurate enough to provide reasonable solute profile in primary cells and eutectic composition for SLM process.

47



Figure 5.1 Marco and microstructure of single track samples. (a) Macrostructure of each samples after single track is formed. Red box indicates single track. Note that, four single tracks are successfully fabricated for almost all cases; (b) Closer view of single track cross section by SEM. Orange and blue box each indicates meltpool center (MPC) and meltpool boundary (MPB); (c) microstructure of MPC; (d) microstructure of MPB and heat affected zone (HAZ).



Figure 5.2 SEM image of microstructure by process conditions. (a) b1; (b) b2; (c) b3; (d) c1; (e) c2; (f) c3; Eutectic part is a brighter zone and primary cell part is darker zone. As scanning speed increases, cell spacing decreases. On the contrary, primary cell fraction increases.





(a)



Figure 5.4 The comparison of experiment and model PDAS value. (a) AlSi10Mg; (b) Al-12Si; Note that, Al-12Si shows better agreement with model compared to AlSi10Mg.



Figure 5.5 Optimized A parameter as a function of Si content of hypoeutectic Al-Si binary alloys.



Figure 5.6 PDAS comparison plot between experiment, present model, and conventional model. (a) Al-xSi (x=4.07, 7.13, 10.38, 12.47); (b) Al-12.235Si.



Figure 5.7 Plot showing relationship between cooling rate and PDAS for each sample. (a) AlSi10Mg, (b) Al-12Si; Blue line denotes linear trend line.



Blue line denotes linear trend line.



Figure 5.9 Relationship between *n* value and Si composition.



Figure 5.10 Primary cell fraction comparison between experiment and model result for different scanning speed and power. (a) 250W; (b) 200W; Note that, experiment results are consistently higher than modeling result.



Figure 5.11 Comparison of average concentration inside primary cell between experiment and model values for c1 and c3.

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Table 5.2 The comparison of PDAS between single track experiment result of AlSi10Mg [38] and modeling result using A=130

Power	Speed	Energy Density	Experiment	Model
(M)	(m/s)	(J/m)	(hm)	(mn)
370	0.4	0.925	0.480±0.038	0.459
300	0.8	0.375	0.351 ± 0.048	0.320
370	1.4	0.264	0.271 ± 0.021	0.291
200	1.4	0.143	0.229 ± 0.023	0.217

Table 5.3 The comparison of PDAS between single track experiment result of Al-12Si and modeling result using A=233

			Energy Density	Experiment	Model
Label	Power (W)	Speed (m/s)	(J/m)	(mu)	(mn)
b1	200	0.4	0.5	0.440±0.032	0.432
b2	200	0.6	0.333	0.391 ± 0.029	0.384
b3	200	0.8	0.25	0.346±0.042	0.349
c1	250	0.4	0.625	0.481 ± 0.044	0.481
c2	250	9.0	0.417	0.422 ± 0.062	0.428
c3	250	0.8	0.313	0.388 ± 0.040	0.388

Composition (wt%)	<i>A</i> (K⋅s ^{0.5} /m ^{0.5})	Reference
0	0	Pure Al
1	66.41	[40]
4.07	141	
7.13	187	[39]
10.38	234	
12.235	233	This work
12.47	265	[39]

 Table 5.4 Optimized A parameters for various Al-Si alloys

	Concentration	Domos	Curred	Experiment	Present model	Conventional
Sample		LOWEL	naade	PDAS	PDAS	model
	(w1/0)	(, ,)	(s/III)	(mn)	(mm)	PDAS (µm)
Al-4Si	4.07	250	1.2	0.579	0.584	0.865
Al-7Si	7.13	250	1.6	0.459	0.464	0.741
Al-10Si	10.38	300	2	0.400	0.394	0.656
		200	0.4	0.440	0.459	1.023
		200	0.6	0.391	0.410	0.882
:00110	300 01	200	0.8	0.347	0.372	0.779
IC71-IW	CC7.71	250	0.4	0.481	0.511	1.139
		250	0.6	0.422	0.456	0.982
		250	0.8	0.388	0.414	0.867
Al-12Si	12.47	250	1.8	0.323	0.308	0.560

Table 5.5 PDAS comparison between experimental, model, and conventional model

Si composition (wt%)	n
2	0.28
4.07	0.298
5	0.303
7.13	0.313
9	0.326
10.38	0.334
12.24	0.35
12.47	0.355

Table 5.6 *n* value by Si composition.

Table 5.7 The comparison of experiment and model primary cellfractions.

Sample	Experiment (%)	Model (%)			
b1	57.020 ± 1.491	51.581			
b2	57.992 ± 1.434	55.260			
b3	61.218 ± 2.084	57.880			
c1	56.935 ± 1.396	51.558			
c2	57.969 ± 0.901	55.258			
c3	$\boldsymbol{61.079 \pm 3.668}$	57.798			
		Average Concentration	(wt%)	2.39	2.95
------------------------	------------	-----------------------	-------	-----------------	-----------------
serve clear difference	Model	Maximum Solubility	(wt%)	3.03	3.66
c3 were adopted to ol		Eutectic Point		701.21K, 21.89%	633.79K, 23.63%
1 model. Sample c1 and	Experiment	average concentration	(wt%)	3.10 ± 0.25	3.24 ± 0.14
experiment and		Sample		cl	c3

Table 5.8 Modified eutectic point, maximum solubility, and average concentration inside primary cell for

Chapter 6. Conclusions

This chapter summarizes the developed rapid solidification model presented in this study. Also, original contributions to knowledge are listed. Finally, possible future works are suggested related to the model.

6.1 Summary

A rapid solidification model which predicts the microstructure evolution during additive manufacturing process was developed in the present study by integrating both conventional and rapid solidification theories. Primary dendrite arm spacing, primary cell fraction, eutectic fraction, and solute profile in primary cells can be calculated from the present model. To evaluate the accuracy of the model, single track SLM experiments of Al-12Si alloy were also performed under various solidification conditions. The model predictions were compared with the present experimental data and literature data on Al-Si alloys. Moreover, equation for practical application was suggested using the model.

(1) Using a single semi-empirical parameter (A), model PDAS value matched well with single track experimental data in all velocity range. This proved that presented PDAS model is reasonable and semi-empirical parameter is only dependent to initial concentration. Equation for A by concentration was derived by optimizing A values from other and this study. Due to this equation, presented model can be applied to various compositions. Additionally, compared to conventional model,

estimated PDAS values were much closer to experimental results (error: nearly 100 % to less than 8 %). This shows that developed model is better than conventional one.

- (2) For practical purposes, relationship between PDAS and cooling rate was determined using our model. Linear relationship between model value and CR^{-n} was observed, and this result is consistent with preliminary study. However, *n* value changed with alloy's composition. Therefore, additional relationship between *n* and initial concentration was derived for prediction in every hypo-eutectic Al-Si binary alloys.
- (3) Experiment results denoted that as scanning velocity increases, primary cell fraction increased. On the other hand, cell fraction didn't show critical difference by change of laser power. These trends were well predicted by our microsegregation model. Even though, model values were uniformly 3~5% lower than empirical data, its estimation was reasonable. Difference between model and experiment value is thought to be caused by extraordinary properties of Al-Si alloys. Presented model is suitable for SLM, but with additional consideration, it would show a better result.
- (4) By precipitation of Si particles inside primary cell, average concentration was measured to verify solute profile model. Average concentration was revealed by using TEM-EDS. Experiment result showed that Si wt% in the cell was much higher than maximum solubility, and this phenomenon was well determined by the model.

Additionally, average concentration increased as scanning velocity increased, and the model also showed consistent result in both trend and absolute value. Modified eutectic point was predicted, and by comparing it with other experiment results, the range was reasonable. In conclusion, our microsegregation model predicts solute profile rationally.

6.2 Original Contribution to Knowledge

The original contributions of the present study to knowledge are as below:

- 1. A new integrated PDAS model for SLM was presented without using small Peclet number assumption in the Kurz and Fisher model.
- PDAS, primary cell fraction, and average solute concentration inside Al-12Si single track microstructure were measured experimentally for various process conditions, which was never done before.
- 3. Undercooling effect by initial composition was verified for rapid solidification cases, and the equation for the effect was improved based on present experiment and literature data.
- By determining equation for n value using the model, universal equation between PDAS and CR was improved for Al-Si binary alloys.
- Microsegregation model that could predict both phase fraction and solute profile inside primary cell of SLM product was developed for the first time.

6.3 Future Works

This work provides a rigid rapid solidification model that could be applied to SLM produced Al-Si binary alloys. With additional experiments and investigation, the model could be developed and extended to other cases as shown follow:

- Microsegregation model can be improved by considering eutectic morphology of Al-Si alloys.
- 2. If powder fabrication is available, the model's validity could be verified for other binary alloys, such as Al-Mg, Ni-Nb etc.
- 3. With extra experiments for various composition of AlSiMg alloys and by gearing the model for ternary cases, the model could also be applied for ternary alloys. Moreover, with this clue, the model could be expanded to higher order alloys, which are related to industrial alloy, such as Ti64, SLS316 etc.
- 4. By using present model and mechanical property model, mechanical property can be predicted.

Appendix

Appendix 1. Review of Rosenthal Equation

As mentioned in section 3.1, Rosenthal equation is utilized for calculating thermal distribution formed by moving heat source, and it is widely adopted for SLM cases. However, there are some strict assumptions [28]:

- 1) Heat source is a point source.
- 2) Heat transfer is governed purely by conduction.
- 3) Latent heat due to phase change is not included.
- 4) Deposition of powder doesn't affect melt pool size.

Assumptions 1) ~ 3) are basic assumptions made by Rosenthal and assumption 4) is an additional one to apply the equation to SLM cases. Several researchers showed that existence of powder bed doesn't affect the shape and size of a melt pool significantly [46-48], which shows validity of assumption 4).

Moreover, with rigorous assumptions 1) ~ 3) remaining, both melt pool dimension and solidification parameters are accurately predicted. With no keyhole effect, melt pool dimension of AlSi10Mg is well demonstrated [49] (Fig. A.1). In case of solidification parameter, Umberto S. B. et al., showed that cooling rate estimated by Rosenthal equation is similar with empirical measurements and computational methods that consider additional phenomenon other than conduction [27]. Also, Patcharapit P. et al.,

demonstrated that thermal gradient predicted by Rosenthal equation and Finite Element method, which considers radiation, show similar values [28]. With accurate estimation of cooling rate and thermal gradient, solidification velocity can also be well predicted due to relationship between solidification parameters ($CR = G \cdot V$).

Conclusively, even with strict assumptions, Rosenthal equation is reasonable to estimate melt pool dimension and solidification parameters for SLM.

Appendix 2. Effect of Thermal Diffusivity

In case of KGT model, as shown in section 2.1, stability function for concentration (ξ_c) is considered. However, for a precise application, thermal stability function (ξ_T) should also be taken into account.

$$\xi_T = 1 - \left[1 + \left(\frac{2\pi}{P_T}\right)^2\right]^{-\frac{1}{2}} \tag{A1}$$

For SLM cases, solidification velocity is between 0.1 ~ 1.0 m/s, dendrite tip radius is in the scale of 10^{-8} m, and for Al – Si alloys, thermal diffusivity (α) is in the scale of 10^{-5} m²/s. As a result, thermal Peclet number (P_T) is between $10^{-3} \sim 10^{-2}$, which makes ξ_T almost unity (Eq. (A1)). This shows that when calculating dendrite tip radius, effect of thermal diffusion is negligible.

However, in case of solute diffusion, diffusivity in liquid is 10000 smaller

than thermal diffusivity. Thus, concentration Peclet number becomes 10000 larger than thermal Peclet number, which makes concentration stability function not negligible. Conclusively, in present study, only effect of solute diffusion is considered in KGT model.

Appendix 3. Scheil Cooling Assumptions

In section 3.3, Scheil cooling assumptions were adopted to estimate microsegregation inside primary cell. Hence, validity of these assumptions for SLM cases should be confirmed. For SLM, cooling rate is in the range of 10^7 K/s and solidification range is over 100 K. Thus, solidification will be completed within 10^{-5} s. Utilizing diffusivity in Table 3.1, diffusivity of Si in fcc Al at temperature between $350 \sim 750$ °C (available solidification range considering various process conditions) is in the scale of 10^{-9} m²/s. Adopting these values and diffusion distance equation,

$$x = \sqrt{Dt} \tag{A2}$$

where x is diffusion distance, t is diffusion time, and D is diffusivity of Si in fcc Al, diffusion distance of Si will be 10^{-7} m. Considering that system's length is ~ 1 µm and diffusion direction is random, diffusion of Si inside fcc Al can be ignored, which makes assumption (i) in section 3.3 reasonable. However, more accurate result can be estimated by taking back diffusion into account, which can be done in future work.

Additionally, assumption related to mixing inside liquid should be

considered. As mentioned in section 3.3, fast and dynamic convection (~1 m/s) occurs during SLM and total solidification time is 10^{-5} s. Thus, during solidification, liquid will move about 10 µm, and with total system's length in micron scale, liquid will circulate in the whole system at least once. Therefore, it is reasonable to assume perfect mixing inside the melt pool.

Nevertheless, by using equation of liquid composition inside the melt pool [50],

$$C_{L}(u) = \begin{cases} C_{0} + (C_{L}^{*} - C_{0}) \frac{E_{i}(P_{C}u)}{E_{i}(P_{C})}, & V < V_{D} \\ C_{0}, & V \ge V_{D} \end{cases}$$
(A3)

where, u is position, $C_L(u)$ is liquid composition by position, C_L^* is liquid composition on the interface, and $E_i(x)$ is exponential integral function, microsegregation model can be applied without adopting perfect mixing assumption. Conclusively, the model can be extended to slower cooling rate cases where perfect mixing of liquid is not applicable.

Appendix 4. Solidification Velocity vs Undercooling

For verification of undercooling model, many researchers drew growth velocity (solidification velocity, V) vs undercooling plot for experiment and model [51-53]. For both cases, when large undercooling occurs (> 100 K), solidification velocity becomes 1 m/s scale. However, in author's knowledge, there is no published work that shows V vs undercooling plot for Al-Si alloys. Therefore, using present model, V vs undercooling plots have been

demonstrated for Al-10Si and Al-12Si (Fig. A.2). As shown in Fig. A.2, about 250 K undercooling is required for rapid growth (~ 1 m/s) for both Al-10Si and Al-12Si. Compared to other researches, larger undercooling is required to reach specific solidification velocity for Al-Si alloys due to alloy difference. Nevertheless, trend by undercooling is similar in SLM process condition range ($V \sim 1$ m/s).



Figure A.1 Melt pool dimension by (a) SLM experiment by Tang Ming [49] and (b) Rosenthal equation. Matlab was utilized to display the melt pool (Red line).



Figure A.2 *V* vs undercooling plot for Al-Si alloys; Al-10Si (Black line & square), Al-12Si (Red line & triangle)

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요약 (국문 초록)

적층 제조를 위한 급속 응고 모델 개발 및 Al-Si 합금에서의 응용

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금속 분말을 활용한 적층 제조 기술은 현재 많이 각광을 받고 있는만큼 그 물성의 예측에도 많은 관심을 기울이고 있다. 이를 위해서는, 제조 조건과 합금의 조성에 따라 미세구조가 어떻게 형성되는지를 예측해야 한다. 따라서, 본 연구에서는 다양한 응고 이론과 CALculation of PHAse Diagram (CALPHAD) 계산을 기반으로 적층 제조, 그 중에서 선택적 레이저 용융법에 적용될 수 있는 급속 응고 모델을 개발했다. 개 발된 모델은 Rosenthal equation을 통해 계산한 응고 인자들과 한 개의 피팅 파라미터를 통해 primary dendrite arm spacing (PDAS), 일차상 분율, 그리고 용질 분포를 예측할 수 있다. 모델의 유효성을 확인하기 위하여 Al-12Si single track 실험을 했고, 그 외에도 다른 다양한 문헌 자료들을 사용했다. PDAS 모델의 경우 기존의 모델보다 예측 값이 훨씬 정확함을 확인했으며, 더 다양한 경우에 모델을 적용하기 위해 아공정 Al-Si 합금에 대해 피팅 파라미터와 초기 농도 사이의 실험 관계식도 알아냈다. 추가적으로, 더 높은 활용도를 위해 모델 결과값으로 PDAS와 냉각 속도 간의 관계식을 유도했다. 그 뿐만 아니라. 본 연구에서 처음 으로 만들어진 급속 응고에 적용 가능한 미세 편석 모델을 통해 일차상

81

내부의 용질 농도 및 상분율을 정확하게 예측할 수 있었다.

Keywords : 급속 응고, 선택적 레이저 용융법, PDAS, 일차상 분율, 용질 분포, Al-Si 합금