

# Modeling, Analysis and Simulation of Paste Freezing in Freeze-form Extrusion Fabrication

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## Abstract

During the freeze-form extrusion fabrication process for aqueous-based pastes, the sub-zero temperature environment aids the part in maintaining its shape by freezing the water present in the paste. The paste freezes very quickly when deposited on a substrate in a freezing environment. However, as the part's height increases, the freezing time increases as the heat conduction rate to the substrate decreases. The freezing time can exceed the time required to extrude one layer of paste due to water's high latent heat, thus leaving the extruded paste in its semi-liquid state and causing the part to deform or even collapse. Therefore, dwell time is needed between layers, which may substantially increase the build time of the part. In this paper, the effects of the paste material, paste solids loading, convection coefficient, initial paste temperature, ambient temperature, total time between layers, and layer thickness on the freezing time of paste are investigated. The paste temperature and paste freezing time are computed for various process parameters via numerical simulation using the commercial code Fluent.

**Keywords:** Ceramic paste solidification; Numerical simulations

## 1. Introduction

Freeze-form Extrusion Fabrication (FEF) is a novel, environmentally friendly additive manufacturing method for fabricating ceramic parts [1-3]. In this process, aqueous-based ceramic pastes with high solids loadings up to 55 vol.% and only trace amounts of organic binder (1-4 vol.%) are used to fabricate parts in a sub-zero temperature environment. The aqueous-based colloidal paste is extruded from one or multiple extruders to fabricate a ceramic component in a layer-by-layer manner. The low-temperature environment aids the part in maintaining its shape by freezing the water present in the paste.

During the FEF process, the paste freezes very quickly when it is deposited on a substrate with a sub-zero temperature. However, as the height of the part increases, the heat conduction rate to the substrate decreases, and the freezing time increases. In some cases, the freezing time exceeds the time required to extrude one layer of paste. When the paste is not totally frozen and remains in a semi-liquid state, a large part being fabricated may deform or even collapse. Therefore, the factors affecting the paste freezing time should be investigated and adjusted in order to shorten the time required for freezing.

In a similar freeform fabrication process, the rapid freeze prototyping process [4], which uses water as the build material, the solidification time has been studied using the finite difference method [5] and finite element analysis [6,7]. In the rapid freeze prototyping process, the water is deposited in the form of droplets. In the freeze-form extrusion fabrication process, the aqueous paste consists of both water and ceramic particles, and it is deposited by continuous filament extrusion, which may have a much larger dimension than the droplets in the rapid freeze prototyping process.

In this paper, the effects of the paste material, paste solids loading, initial paste temperature, ambient temperature, convection coefficient, total time between layers, and layer thickness on the paste freezing time are investigated. The paste temperature and paste freezing time are computed for various parameters via numerical simulation using the commercial code Fluent.

## 2. Theory

### 2.1. Governing Equations

The energy governing equation is [8]

$$\frac{\partial(\rho H)}{\partial t} = \nabla \cdot (k \nabla T) + S \quad (1)$$

where  $T$  ( $^{\circ}\text{C}$ ),  $\rho$  ( $\text{kg}/\text{m}^3$ ),  $k$  ( $\text{W}/\text{m} \cdot ^{\circ}\text{C}$ ) and  $H$  ( $\text{J}/\text{kg}$ ) are the material temperature, density, conductivity and enthalpy, respectively, and  $S$  ( $\text{W}/\text{m}^3$ ) is the volumetric rate of heat generation or absorption. The enthalpy is computed by

$$H = H_{ref} + \int_{T_{ref}}^T c dT + \Delta H \quad (2)$$

where  $c$  ( $\text{J}/\text{kg} \cdot ^{\circ}\text{C}$ ) is the material specific heat, and the subscript *ref* denotes the reference condition, which is typically the absolute zero condition. The enthalpy correction, which depends upon the phase of the material, is

$$\Delta H = \beta L \quad (3)$$

where  $\beta$  is the material's liquid fraction and  $L$  ( $\text{J}/\text{kg}$ ) is the material's latent heat.

The convection boundary constraint is

$$-k \nabla T \cdot \vec{n} = h(T - T_0) \quad (4)$$

where  $T_0$  ( $^{\circ}\text{C}$ ) is the ambient temperature,  $h$  ( $\text{W}/\text{m}^2 \cdot ^{\circ}\text{C}$ ) is the convection coefficient, and  $\vec{n}$  is the normal vector to the boundary surface.

## 2.2. Material Properties

The paste is composed primarily of ceramic particles and water, with only trace amounts of organic binder. Therefore, the paste's properties can be estimated from the material properties of ceramic particles and water.

Typically, the solids loading (volume fraction of ceramic particles, denoted by  $v_c$ ) is known. Thus, the volume fraction of water is

$$v_w = 1 - v_c \quad (5)$$

The mass fractions of ceramic particles and water, respectively, are

$$m_c = \frac{\rho_c v_c}{\rho_c v_c + \rho_w v_w} \quad (6)$$

$$m_w = \frac{\rho_w v_w}{\rho_c v_c + \rho_w v_w} \quad (7)$$

The paste's density is

$$\rho_p = \rho_c v_c + \rho_w v_w \quad (8)$$

The paste's specific heat is

$$c_p = m_c c_c + m_w c_w \quad (9)$$

The paste's conductivity is

$$k_p = k_c v_c + k_w v_w \quad (10)$$

The paste's latent heat is

$$L_p = L_w m_w \quad (11)$$

When the paste is frozen, the properties of ice instead of water should be used in equations (9) and (10).

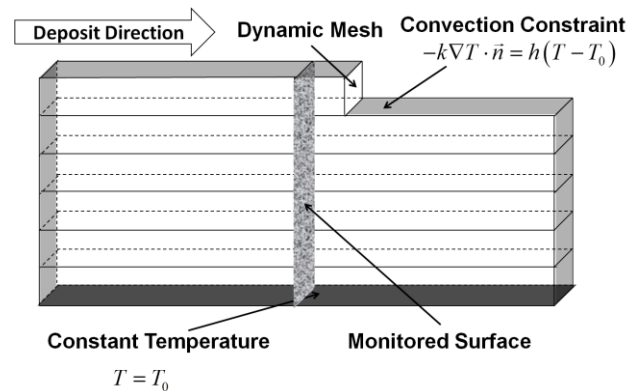
## 3. Simulation Setup

Simulations are conducted with the commercial code Fluent 12. In the simulations, dynamic meshing is applied to simulate the continuous deposition of paste. The simulation schematic with boundary conditions is shown in Figure 1. A vertical monitor surface is created inside the wall,

as the figure depicts. The maximum temperature on this monitor surface is recorded for each time step. When the newly deposited paste moves through this monitor surface, the surface's maximum temperature will increase to the initial temperature of the paste, and the time at which this occurs is recorded. When the maximum temperature of the monitor surface drops just below 0 °C, the time is also recorded. The difference between these two times is the freezing time of this layer.

The boundary conditions used in the numerical simulation are as follows:

- (1) The bottom of the first layer of paste is set to a constant temperature, which is the ambient temperature.
- (2) All other surfaces have the convection constraint shown in Figure 1.



**Figure 1. Simulation schematic.**

### 3.1. Assumptions

The following assumptions are made in the simulation:

- (1) In FEF process, a metal substrate which is much larger than the part is set in the ambient; therefore, the substrate's temperature is considered to be constant and equal to the ambient temperature.
- (2) The convection coefficient may change due to the change of air flow around the part, which is complex and difficult to predict. Thus, in order to analyze the effect of convection coefficient and simplify the simulation, the convection coefficient is considered as constant on each surface during the part building process.
- (3) When the solids loading is approximately 45%, the linear expansion rate is approximately 1.6% when phase changes. Therefore the density of the paste is considered to be constant during the paste freezing process.

(4) Water is the component which actually freezes, thus the paste freezes at the freezing temperature of water, i.e., 0 °C.

### 3.2. Paste Properties

The typical materials used in the FEF process are alumina (Al<sub>2</sub>O<sub>3</sub>), zirconium carbide (ZrC) and tungsten (W). The properties of different pastes with different solids loadings are listed in Table 1.

Table 1. Properties of different pastes with different solids loadings

Solids loading and material	35%Al <sub>2</sub> O <sub>3</sub>	45%Al <sub>2</sub> O <sub>3</sub>	55%Al <sub>2</sub> O <sub>3</sub>	45%ZrC	45%W
Density (kg/m <sup>3</sup> )	2050	2350	2650	3579	9235
Thermal conductivity when not frozen (W/m·°C)	15.5	19.7	24.0	5.6	78.2
Specific heat when not frozen (J/kg·°C)	1927	1653	1441	1087	371.3
Volumetric specific heat when not frozen (J/m <sup>3</sup> ·°C)	3.95×10 <sup>6</sup>	3.88×10 <sup>6</sup>	3.82×10 <sup>6</sup>	3.89×10 <sup>6</sup>	3.43×10 <sup>6</sup>
Latent heat (J/kg)	1.06×10 <sup>5</sup>	7.82×10 <sup>4</sup>	5.67×10 <sup>4</sup>	5.13×10 <sup>4</sup>	1.99×10 <sup>4</sup>
Volumetric latent heat (J/m <sup>3</sup> )	2.17×10 <sup>8</sup>	1.84×10 <sup>8</sup>	1.50×10 <sup>8</sup>	1.84×10 <sup>8</sup>	1.84×10 <sup>8</sup>
Thermal conductivity when frozen (W/m·°C)	16.4	20.5	24.6	6.3	79.0
Specific heat when frozen (J/kg·°C)	1270	1168	1089	768.6	247.9
Volumetric specific heat when frozen (J/m <sup>3</sup> ·°C)	2.60×10 <sup>6</sup>	2.74×10 <sup>6</sup>	2.89×10 <sup>6</sup>	2.75×10 <sup>6</sup>	2.29×10 <sup>6</sup>

## 4. Results and Discussion

The seven factors considered in this study that affect the paste freezing time in the FEF process are as follows: (1) Paste material, (2) Paste solids loading, (3) Convection coefficient, (4) Initial paste temperature, (5) Ambient temperature, (6) Total time between layers (the summation of the extrusion time of the current layer and the dwell time between the current and next layers), and (7) Layer thickness.

The effects of these factors are examined via simulation using the commercial code Fluent 12. Unless otherwise noted, 45% solids loading alumina paste is used as the material, the convection condition is forced and the convection coefficient is 35 W/m<sup>2</sup>·°C, the initial paste temperature is

5 °C, the ambient temperature is -10 °C, the layer thickness and layer width are 0.58 mm, and the total time between layers is 10 s. Once the freezing time is larger than total time between layers, the paste will be in a semi-liquid state and the part being fabricated is under the risk of deforming or even collapse.

#### 4.1. Paste material

The material of the paste will change the paste's properties, i.e., thermal conductivity and specific heat. Any changes in these properties will change the heat transfer rate and, thus, the freezing time. The results of simulations with 45% solids loading pastes are shown in Figure 2. The freezing time of the ZrC paste is longer than the freezing time of the Al<sub>2</sub>O<sub>3</sub> paste, and the ZrC paste will not be totally frozen after 12 layers. This is because the ZrC paste has lower conductivity than the Al<sub>2</sub>O<sub>3</sub> paste. The freezing time of the W paste is shorter than the freezing time of the Al<sub>2</sub>O<sub>3</sub> paste because it has higher conductivity.

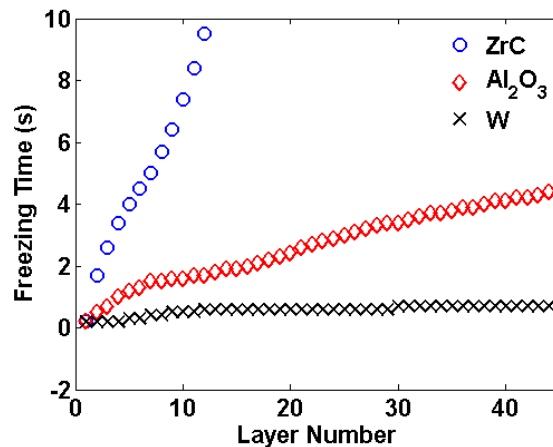
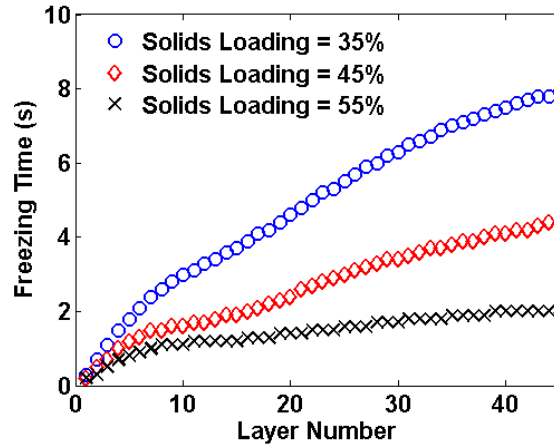


Figure 2. Paste freezing time with different paste material under forced convection.

#### 4.2. Paste solids loading

Any change in the paste solids loading also will change the thermal conductivity and specific heat of the paste, as well as the paste's latent heat. These changes will alter the energy contained in the paste and the heat transfer rate, thus affecting the freezing time. The results of simulations for Al<sub>2</sub>O<sub>3</sub> pastes with different solids loadings are shown in Figure 3. As the solids loading increases, the latent heat decreases, and, thus, the freezing time decreases. If the solids loading increases by 10% (from 35% to 45% or from 45% to 55%), the freezing time of the paste will decrease by approximately 50% after 20 layers.

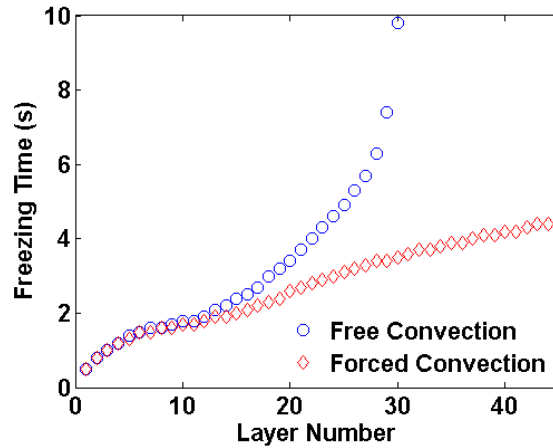


**Figure 3. Paste freezing time with different paste solids loadings under forced convection.**

### 4.3. Convection coefficient

A change in the convection coefficient will change the heat transfer rate between the paste and its surroundings, which affects the paste freezing time. When the convection coefficient increases, the paste freezing time decreases. The convection coefficient can be changed by using a fan to blow cool air over the extruded paste. When the fan is off, the convection condition is free convection, and the convection coefficient is  $6.7 \text{ W/m}^2 \cdot ^\circ\text{C}$ . When the fan is on, the convection condition changes to forced convection, and the convection coefficient is  $35 \text{ W/m}^2 \cdot ^\circ\text{C}$  in this study. The results of simulations with the two different convection conditions are shown in Figure 4.

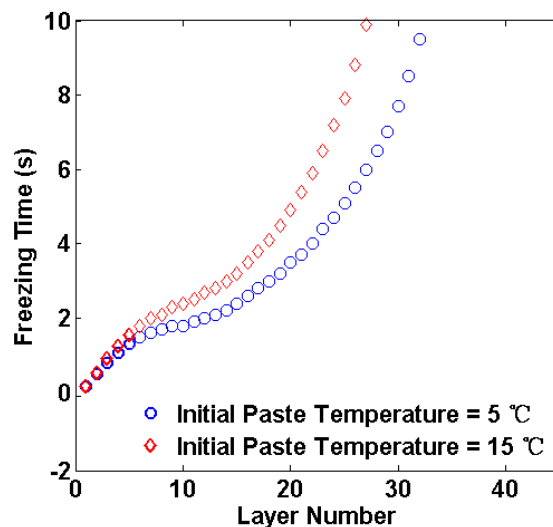
Under free convection conditions, the paste freezing time increases exponentially after approximately 15 layers, and the paste will not be totally frozen after 30 layers. In this case, a large part being built will deform or even collapse. Under forced convection conditions, the paste freezing time is shorter than the total time between layers, and it increases more slowly with respect to time; therefore, the part will not collapse during the fabrication process regardless of how tall it is. At the beginning of the extrusion process, the freezing times under both free and forced convection conditions are very similar. This is because when the paste layers are close to the substrate, conduction will dominate, and the effect of the convection condition will not be significant. When the part's height increases, convection will dominate, and the effect of the convection condition will become significant.



**Figure 4. Paste freezing time under free and forced convection.**

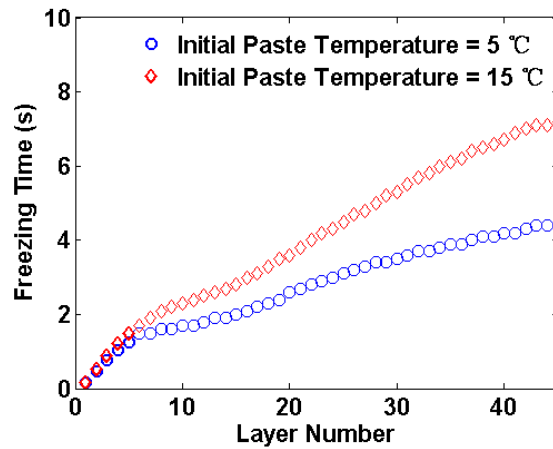
#### 4.4. Initial paste temperature

The increase in the initial paste temperature will increase the energy carried by the paste. However, it will also increase the temperature difference between the ambient and the paste; thus, the paste's heat transfer rate to the ambient will increase. The results of simulations with different initial paste temperatures are shown in Figures 5 and 6. As the initial paste temperature increases, the increase in freezing time is approximately proportional to the number of layers. The freezing times under the free and forced convection conditions are very similar at the beginning of the extrusion process. However, as the part's height increases, the freezing time for free convection eventually will increase exponentially, while the freezing time for forced convection will eventually level out. If the initial paste temperature increases by 10 °C (from 5 °C to 15 °C), the freezing time will increase by more than 60% after 25 layers.



**Figure 5. Paste freezing time with different initial paste temperatures under free convection.**

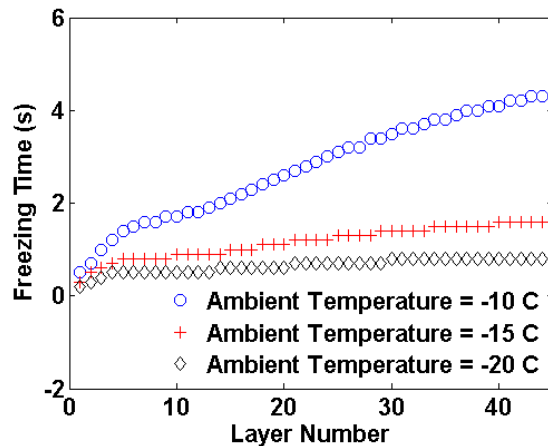




**Figure 6. Paste freezing time with different initial paste temperatures under forced convection.**

#### 4.5. Ambient temperature

The change in ambient temperature will modify the temperature difference between the ambient and the extruded paste. When the ambient temperature decreases, the paste freezing time will decrease. The results of simulations with different ambient temperatures are shown in Figure 7. When the ambient temperature decreases from  $-10\text{ °C}$  to  $-15\text{ °C}$ , the freezing time decreases substantially. When the ambient temperature decreases from  $-15\text{ °C}$  to  $-20\text{ °C}$ , the freezing time does not decrease nearly as much.

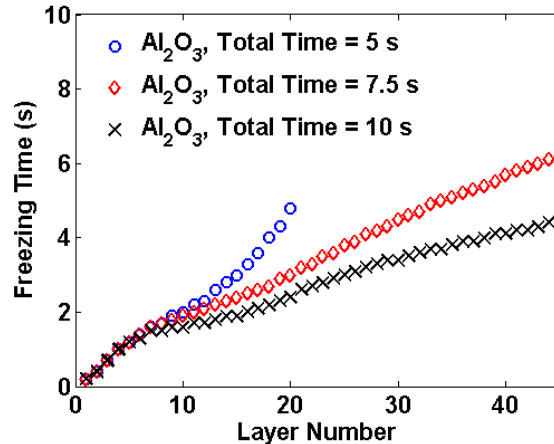


**Figure 7. Paste freezing time with different ambient temperatures under forced convection.**

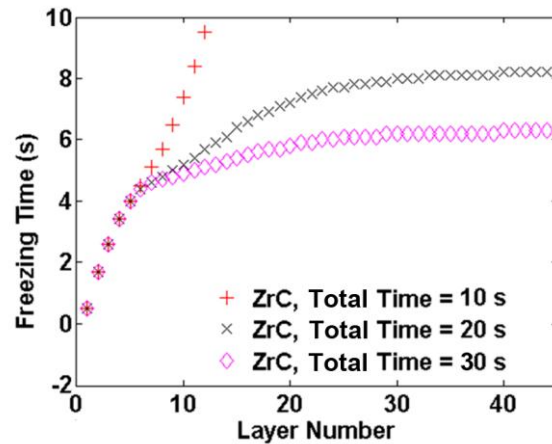
#### 4.6. Total time between layers

The total time between layers refers to the summation of the extrusion time of the current layer and the dwell time between layers. When the paste freezing time is shorter than the extrusion time, the dwell time is not required. However, if the freezing time is longer than the extrusion time, dwell time is necessary. When the dwell time between layers increases, the extruded paste will become colder, which will increase the temperature difference between the extruded and newly deposited pastes; therefore, the freezing time of next layer will decrease. However, the increase in dwell time also will increase the part's total build time. The results of simulations with different total times between layers are depicted in Figures 8 and 9.

Figure 8 shows that when the total time between layers is 5 s, the freezing time of alumina paste will increase quickly after the 12<sup>th</sup> layer, and the paste will not be totally frozen after the 20<sup>th</sup> layer. When the total time between layers is 7.5 s, the freezing time will increase more slowly, and the paste can still be frozen until the 45<sup>th</sup> layer. When the total time is 10 s, the freezing time is even shorter; however, the part building time will be much longer. Similar to alumina paste, Figure 9 shows that when the total time between layers is 10 s, the ZrC paste will not be totally frozen after the 12<sup>th</sup> layer. When the total time between layers is 20 s, the paste can be totally frozen until the 45<sup>th</sup> layer. When the total time between layers is 30 s, the freezing time of the ZrC paste is shorter; however, the part building time will be much longer.



**Figure 8. Alumina paste freezing time with different total times between layers under forced convection.**

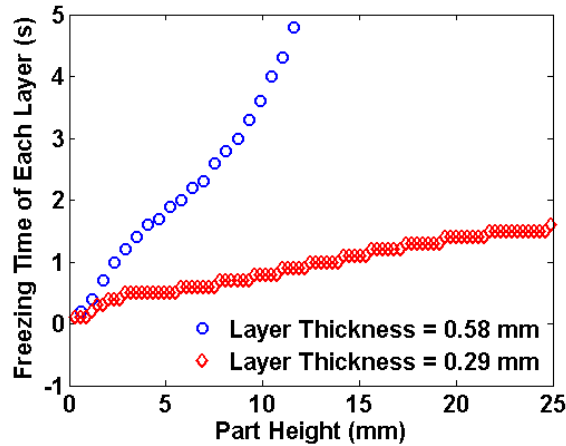


**Figure 9. Zirconium carbide paste freezing time with different total times between layers under forced convection.**

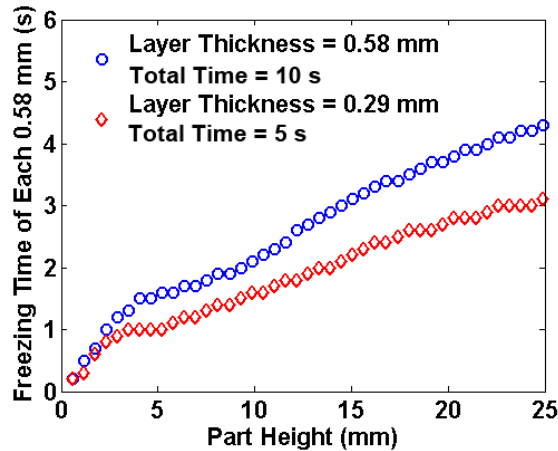
#### 4.7. Layer thickness

Here we consider that the nozzle diameter is fixed, and the table and extrusion speeds are tuned to ensure a constant width of extruded paste; therefore, a change in the layer thickness will alter the ratio between the volume and the surface of the extruded paste exposed to the ambient, thus also altering the ratio between the energy contained in the paste and the heat transfer rate. When the layer thickness decreases, the paste freezing time decreases; however, building the part will require many more layers. In this case, if the table speed is limited, the part building time will increase significantly; if the table speed can be increased, the total time between layers can be reduced to keep the part building time constant. The results of simulations with variations in layer thickness and total time between layers are shown in Figures 10 and 11.

Figure 10 shows that when the total time between layers is kept constant, as the layer thickness decreases, the freezing time of the paste decreases substantially. However, in this case, the part building time will double. In the case shown in Figure 11, when using a layer thickness of 0.58 mm, the total time between layers is 10 s; when using a 0.29 mm layer thickness, the total time between layers is 5 s. Therefore, the part building time is kept constant. In this case, the freezing time for every 0.58 mm still decreases; however, the magnitude of this reduction is relatively small.



**Figure 10. Paste freezing time with different layer thicknesses under forced convection and when total time between layers is constant.**



**Figure 11. Paste freezing time with different layer thicknesses under forced convection and when part building time is constant.**

## 5. Summary and Conclusions

A series of numerical simulations were conducted to study the seven factors affecting the freezing time of aqueous-based ceramic paste. The effects of these seven factors are: (1) When the solids loading is 45 vol.%, the freezing time of zirconium carbide paste is longer than the freezing time of alumina paste because it has lower conductivity, and the freezing time of tungsten paste is shorter than the freezing time of alumina paste because it has higher conductivity. (2) As the solids loading increases, the freezing time will decrease because the latent heat and specific heat will decrease. (3) As the convection coefficient increases due to forced convection, the freezing time will not change substantially for the initial layers where conduction is dominant; however, the freezing time will decrease significantly where convection is dominant. (4) As the initial paste temperature increases, the freezing time will increase because the energy contained in the paste will increase. (5) As the ambient temperature decreases,

the freezing time will decrease because the heat transfer rate will increase. (6) As the total time between layers increases, the freezing time will decrease because the temperature gradient and heat transfer rate will increase; however, the total part building time also will increase. (7) As the layer thickness decreases, the freezing time will decrease because the ratio between the energy contained in the paste and the heat transfer rate will increase; however, the total part building time may increase.

When planning the FEF process, proper parameters should be used for the equipment setup and fabrication process. To shorten the freezing time and the total part building time in the FEF process, the initial paste temperature and the ambient temperature should be decreased while the convection coefficient should be increased. Properly adjusting the layer thickness and the total time between layers can shorten the freezing time; however, the overall influence of these factors on the total part building time and dimensional accuracy of the built part may not be positive and should be investigated further in future research.

## 6. Acknowledgment

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