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Microstructure design of PCM infiltrated copper composite through freeze casting method toward maximized heat absorption rate

Name of Candidate:

Christina Hoffman Master of Science, 2022

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Thesis and Abstract Approved: ____

Dr. Ronghui Ma Associate Professor Department of Mechanical Engineering University of Maryland, Baltimore County

Thesis and Abstract Approved: _

Dr. Ruey-Hung Chen Professor and Chair Department of Mechanical Engineering University of Maryland, Baltimore County

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ABSTRACT

Title of Document:	Microstructure design of PCM infiltrated copper	
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	Christina Hoffman	
	Master of Science, 2022	
Directed Dyu	Dr. Donohui Ma	
Directed By:	Dr. Konghui Ma	
	Associate Professor	
	Department of Mechanical Engineering	
	University of Maryland, Baltimore County	
	Dr. Ruey-Hung Chen	
	Professor and Chair	
	Department of Mechanical Engineering	
	University of Maryland, Baltimore County	

Thermal management of electronics is becoming increasingly difficult due to the trend of miniaturization in modern electronics. Modern electronics also pose a challenge due to pulse heating, or intermittent spikes of high heating that occur for less than one second. Studies have found that composites made of a conductive component and a phase change material (PCM) can be used to effectively mitigate overheating due to pulse heating without overdesigning the heat

sink. This is due to the conductive capacity of the conductive component in conjunction with the high thermal storage capacity of phase change materials.

A theoretical study based on phase change in homogeneous media is performed to determine the best microstructure of the composite as well as the optimal composition of the conductive component (copper). It is found that a lamellar microstructure infiltrated with PCM outperforms a disordered porous foam microstructure infiltrated with PCM for both low and high heat fluxes. It is also found that an optimal composition by volume exists for the lower heat fluxes studied and a critical composition of 30% by volume is found for the higher heat fluxes studied, above which there is no substantial decrease in the interface temperature.

Then, a numerical study at pore scale is performed to simulate simultaneous heat transfer and phase change in a unit cell of lamellar porous copper infiltrated with paraffin wax. The simulation is used to determine the effect of lamellar spacing (pore size) on the thermal management performance of the composite for different heat fluxes. This study is also performed to determine the effect of material properties, specifically thermal conductivity, on the optimal pore size. It is found that the effect of pore size is more pronounced at higher heat fluxes, showing that there is a need for application-specific microstructure design. It is also found that the effect of pore size is more pronounced for materials with higher thermal conductivities, and these materials require a smaller pore size for more efficient thermal management. For higher heat fluxes, a pore size on the order of tens to hundreds of microns is required, and a smaller pore size is not necessary to achieve better thermal management performance.

Finally, fabrication of these microstructures is investigated using the novel freeze casting technique. While this technique is well established for the fabrication of ceramic materials, it has

not been extensively studied for the fabrication of porous metals. It was found that this method can be used to produce porous cupric oxide structures with low (approximately 9 vol.%) solid loading, as well as higher (approximately 12 vol.%) solid loading with the addition of potassium hydroxide (KOH). Pore sizes were created ranging from tens of microns to hundreds of microns. It is expected that future research can lead to better control over these microstructures through manipulation of the suspension composition as well as manipulation of the freezing rate of the suspension. It is also expected that future studies can use reduction and sintering techniques to produce a pure copper lamellar microstructure.

Microstructure design of PCM infiltrated copper composite through freeze casting method toward maximized heat absorption rate

By

Christina Hoffman

Thesis submitted to the Faculty of the Graduate School of the University of Maryland, Baltimore County, in partial fulfillment of the requirements for the degree of

Master of Science

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Dedication

For my parents, thank you for always giving me the support and tools I need to be successful and accomplish whatever I set my mind to. For my family, because without their unconditional support I would not be where I am today.

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1. Introduction

1.1 Background

Modern electronics are becoming increasingly complex as technological advancements are made. Many electronic devices are becoming smaller in area and volume while having increased processing power and processing speed, which leads to higher heat fluxes produced by the device. For example, the processing power of the Samsung Galaxy increased by a factor of 5.9 between 2010 to 2012, and the Apple iPhone experienced a similar increase [1].

There is also a demand for improved battery life in devices, leading to larger batteries [1]. As battery sizes increase, the battery takes up more of the available space within the electronics that already have a reduced size. These limitations lead to a unique challenge in regulating the temperature of these devices. As electronics become more compact while simultaneously becoming more powerful, there is an increasing demand for effective small scale thermal management strategies that do not impact the size restrictions of the device. As the chip heat flux increases with increasing computing power, it is crucial to ensure that the temperature of these electronics is controlled because prolonged high temperatures can cause damage to a variety of crucial electrical components. Depending on the device and its properties, the critical temperature for the electronics ranges from 85°C to 120°C [2], above which the device could overheat and this temperature increase could cause damage to the electrical components.

Thermal management of small-scale electronics, such as portable electronics, also pose some challenges that differ from larger scale electronics. For example, portable electronics must be safe to be handled by the user. Reduced volume of the electronics also leads to a higher risk of hot spots on the outer surface of the device. If the outer surface of the device overheats above the temperatures that the user's skin can tolerate, the device then poses a health risk to the user. Current designs use 40-45°C as a maximum temperature for the surface of a device that may be in contact with the user's skin [1]. This means thermal management is crucial, not only for device longevity, but also for user safety.

There are a variety of thermal management techniques that are currently used. Table 1 shows the most promising techniques as described by Iradukunda et al [3]. A more thorough review of these different techniques is provided in the same reference [3].

Technique	Benefits	Limitations	
Heat Divers	High effective thermal	Pressure losses, entrainment	
Heat Pipes	conductivity, passive cooling	losses, dependence on	
Single-phase microchannel heat sinks (MCHS)	High surface-area-to-volume- ratio, low thermal resistance	High pressure losses, considerable temperature gradients, clogging, risk with water as cooling fluid	
Two-phase MCHS	Lower flow rates due to latent heat utilization (smaller pumps, less coolant, smaller pipes), better temperature uniformity	Two-phase flow behavior, heat transfer, and pressure losses are unpredictable	
Porous media cooling	High surface area-to-volume ratio, high effective thermal conductivity	Substantial pressure losses	
Immersion cooling	High heat transfer coefficients	High pressure loss, not as efficient other techniques	
Spray cooling	High surface-area-to-volume ratio, uniform spatial distribution of droplets, delayed film boiling	Technical uncertainties, high pressure requirements, nozzle unpredictability, clogging, nozzle erosion, corrosion, fluidic and thermal behavior not well understood	
Jet impingement cooling	Low thermal resistances, low manufacturing costs	Large temperature gradients, jet separation from the heated surface	

Table 1: Current Cooling Techniques [3]

However, the major focus of these techniques is solely on high voltage, sustained heating applications. They are not designed for pulse heating applications, which are the focus of this study. Pulse heating involves short spikes of high heat released over a sub-second interval, which occur in a variety of devices including telecommunication devices, power electronics, motors, and transformers [4]. An example of pulse heating can be seen in Figure 1, which shows the battery power consumption of an Android smartphone while the user is on YouTube.



Figure 1: Battery power consumption of YouTube on an Android smartphone [5]

This study focuses on pulse heating that occurs over a time frame of less than 1 second. Thermal management systems designed for steady state can be used for pulse heating applications but may lead to a temperature surge during the peak load if the heat sink is designed based on a time-averaged load. If a heat sink is designed to accommodate for the peak load, it is often overdesigned for the normal function of the device, which means it is often larger and heavier than it would need to be if it could be designed based on a time-averaged load.

It has been shown that transient power spikes can be mitigated by implementing phase change materials (PCMs) and utilizing the latent heat of phase change to eliminate the need to treat the

peak loads as steady-state loading [6]. It has been shown, both theoretically and experimentally, that it is possible to design an effective PCM-based heat sink using an average power level, plus a factor of safety [2]. This is done by combining a PCM with a component with a high thermal conductivity. Different types of these composites and current research regarding these materials will be discussed in Section 1.2.

1.2 Literature Review

1.2.1 Metal-PCM Composites for Thermal Management

Phase change materials have been extensively studied in the fields of thermal storage and thermal management due to their capacity to absorb a large amount of heat upon phase change. For thermal management, however, PCMs alone are not effective due to their low thermal conductivity. As previously stated, many studies have been performed to produce a composite material by incorporating a component with a high thermal conductivity into PCMs.

One method of creating this type of composite includes incorporating a phase change material in a thermally conductive foam. Studies have been performed using this type of structure (metal foams) infiltrated with a PCM to take advantage of the latent heat of phase change and enhanced thermal conductivity of the composite. Organic and inorganic (alloy) PCMs have been compared for use in this application. He et al. [7] reviews the thermal management performance for a variety of different microstructures for micro heat sinks. This review concludes that metal foams alone (without the PCM infiltration) have great potential for use in micro heat sinks, but more research must be done regarding the thermal performance of these structures. Krishnan et al. [4] compared the performance of alloy PCMs, such as gallium, with that of organic PCMs, as well as an organic PCM infiltrated in a metal foam. It was found that the organic PCM alone is not effective for thermal management, while alloy PCMs have a slight advantage in thermal conductivity, but they have a significant disadvantage in terms of weight over the PCM-foam composite [4]. While these alloy PCMs have shown potential for thermal management and these PCMs are relatively well-known, further experimental research can be done to validate the numerically simulated thermal conductivity values of these alloy PCMs [8]. For applications where size and weight are an important factor, organic PCMs are preferable. Organic PCMs are of lower cost, more readily available, and thermally and chemically stable [9].

Many studies have focused on infiltrating metallic foams with PCMs to enhance their thermal performance by increasing the effective thermal conductivity. Copper, aluminum, and nickel foams infiltrated with paraffin have been studied. It was found that copper foams can better enhance the effective thermal conductivity of the composite, can distribute heat more uniformly throughout the PCM, and are more effective when lower porosity foams with higher pore densities are used [9]. Furthermore, Sundarram et al. [10] found that, for fixed porosity metal foams, smaller pore sizes increase the surface area in contact with the PCM, therefore enhancing the thermal management capabilities. It was also found that the pore size and porosity of the foam have a greater effect at a high heating conditions and low convective cooling conditions for the materials used in this study (aluminum for the metal matrix and paraffin for the PCM). This study [10], however, is limited due to the face-centered cubic (FCC) pore morphology being studied, as seen in Figure 2. This geometry must have an open pore morphology to allow for infiltration of PCM, which means this geometry can only be used for metal compositions less than or equal to 25%. Reference [10] also only uses two heat fluxes corresponding to low and high power generation in

portable electronics. Most studies focus on commercially available copper foams that have randomly oriented porous structures, which are inefficient for conducting and distributing heat.



Figure 2: An FCC unit cell of (a) metal foam matrix and (b) phase change material infiltrated in the pores of the matrix [10]

While many studies have mainly focused on copper foams, it was also found that aluminum and nickel foams can be used to increase the effective thermal conductivity of the composite. However, aluminum has a lower melting temperature and is not effective for high temperature applications, and nickel has a relatively low thermal conductivity and is not as effective for these applications as copper and aluminum [9].

Another method of producing composite heat sinks is through the embedding of nanofibers within a PCM. A study [11] was performed where graphite nanofibers were embedded in paraffin and different fiber configurations were studied. It was found that there is an optimal fiber loading level, and the effectiveness of the composite is dependent on the style or configuration of fiber that is used. A herringbone fiber style was found to create the smallest thermal gradient throughout the PCM due to more efficient conduction. However, using these nanofibers relies on convection to effectively distribute the heat throughout the PCM.

One study [12] found that nanofibers do not maintain stable positions within the paraffin after melting and re-solidification, and most settling occurs after the first thermal cycle that the composite undergoes. This settling greatly impacts the thermal performance of the composite as the heat is not effectively distributed throughout the PCM. Some additives can be used to reduce or even eliminate this settling and enhance structural stability, but this was only tested using low solid loading (5 wt.% graphite nanofibers). Warzoha et al. [13] found that the presence of nanofibers in a PCM increases the thermal conductivity of the PCM in its solid state, but does not provide an advantage for liquid PCM [13].

To summarize, both metal foams and nanofibers embedded in PCMs usually result in a disordered matrix that distributes heat inefficiently. Because of the limited control over the matrix microstructure and limitations on the metal volume fraction that is achievable, the full potential of these composite materials is not realized, with relatively low effective thermal conductivities [14].

Theoretically, a one-dimensional structure, such as a lamellar structure, offers the highest effective thermal conductivity along the direction of the extended surface for these composites. Tamraparni et. al. [15] studied the use of a PCM-infiltrated parallel lamellar structure for thermal energy storage. The experimental study used a 3D printed AlSi12 alloy infiltrated with PCM. Figure 3 shows a diagram of the lamellar metal structure used. The results of this study identified a critical lamella spacing of 1mm, and an optimal metal composition of 60-80% by volume. However, it is also found that the critical lamella spacing is dependent on the overall thickness of the system [15].



Figure 3: Diagram of lamellar structure with 30 vol.% metal similar to the geometry used in reference [15]

Xia et. al. [16] created an interconnected lamellar structure using nanosheets of graphene oxide (GO) with a solid-solid PCM (SSPCM) in the inter-lamellar spaces. This type of PCM exhibits a change in solid crystalline structure instead of undergoing a phase change from solid to liquid. However, similar to solid-liquid PCMs, SSPCMs have low thermal conductivity values. The addition of the GO sheets effectively increases the thermal conductivity of the composite, showing that a PCM-infiltrated lamellar structure has promising potential in the fields of thermal energy storage and thermal management.

Therefore, it is proposed that infiltrating a lamellar structure with an organic PCM could mitigate peak loads without designing the heat sink to accommodate a peak load. A lamellar structure is expected to provide a more conductive matrix for the infiltrated PCM. Copper is proposed for the heat conducting matrix, as this is a common material for heat sinks due to its high thermal conductivity and high melting point. This metal-PCM composite would allow a heat sink that can be included in small scale portable electronics without impacting the size and weight constraints of the device. It is expected that this type of microstructure can be deliberately designed to obtain an effective composite material for thermal management for pulsed heating. However,

the study of heat transfer in PCM-infiltrated lamellar copper structures is limited. The relationship between the copper composition, lamellae spacing (pore size), heat flux, and thermal conductivity of the matrix remains unclear. Furthermore, well controlled fabrication of this type of structure is a challenge.

1.2.2 Fabrication of Porous Materials with Lamellar Morphology

There are multiple techniques that can be used to produce complex microstructures. As feature size decreases, it becomes more difficult to fabricate the desired microstructure. Selective laser sintering, micromachining, and freeze casting have potential to create small-scale structures that could be infiltrated with a phase change material.

3D printing of metals using selective laser sintering (SLS) is useful for creating both simple and complex metal structures. This method uses layers of metal powder that are deposited on the build plate, and certain areas are sintered using a laser to produce the desired geometry. While SLS can produce complex structures, this method has its limitations. First, the overall dimensions of the material that can be produced is limited by the build area of the machine that is used. Also, aggregation of the powder particles leads to limited feature resolution, and the layer thickness that can be achieved with this method is $20 - 150 \mu m$ while the minimum thin wall width that can be produced is approximately 0.5 mm [17]. It is expected that thin wall features on the order of tens to hundreds of microns might be necessary to provide the best advantage for thermal management. Therefore, this method is not effective for producing a bulk material with well-controlled microstructural features below 0.5 mm. Micromachining has also been found to be effective for producing micro scale heat sinks using various techniques. Mechanical micromachining, which is a subtractive manufacturing process that uses cutting tools to produce a prescribed geometry, has been found to create parts with dimensions within the range of tens of nanometers to millimeters. As conventional machining techniques are scaled down to produce smaller components [18], there are some major issues that arise with this fabrication technique. First, the cutting tools used for this technique often produce poor surface finishes and poor edge definition. Second, the tools used for these processes experience high stresses that lead to increased wear and early failure, meaning the tools must be replaced frequently [18]. This tool wear also leads to decreased dimensional accuracy. While increased wear can likely be mitigated using different tool materials and coatings, more research still needs to be done on this topic [19].

Electrochemical micromachining (ECM) uses an electrolyte bath and electrodes to cause the dissolution of the anode material, creating a duplicate shape of the tool electrode [20]. This method has been used to produce features as small as 0.5 µm. However, this method does not have well established ideal machining parameters, such as electrolyte choice and methodology for different materials. It is necessary to use optimal machining parameters to achieve precise microstructures. A great deal of research would need to be done to determine the ideal parameters for a new material [20]. Further research in this technique is also needed for tooling development, electrolyte confinement, and the development of a theoretical model to consider the transport of mass and charges, among other aspects [21].

Laser beam micromachining (LBMM) uses laser pulses to create microscale features with little to no damage on the remaining material due to the short laser pulses used. This method has been used in various industries to create structures with submicron sized features [22]. This method allows for quicker and more cost-effective fabrication of small-scale features than many other micromachining techniques. However, there are a few major disadvantages of this technique. Surface defects such as spatter and burrs are more common with this technique, and surface roughness increases with increasing laser pulse duration. Limited dimensional accuracy and thermal stresses are also major disadvantages of this technique [23].

One study [24] focuses on the combination of micromachining techniques to achieve better results than stand-alone techniques. These hybrid micromachining processes are classified as either assisted hybrid micromachining processes, where one major process is aided by the addition of energy such as vibration, or combined hybrid micromachining processes, where two processes work simultaneously to produce complex geometries. More research needs to be performed regarding these techniques including needing a more complete understanding of the mechanisms at work in combined hybrid micromachining process, development of modeling methods, and development of specialized tools and monitoring techniques. It is also necessary to develop techniques that can better produce more complex geometries [24].

The novel freeze-casting technique is expected to be useful for creating lamellar porous copper structures that can be infiltrated with PCM for utilization in small-scale thermal management applications. This technique is well-established for ceramics, and freeze-cast ceramics have been used for a variety of applications, such as biomaterials, electrodes, catalysts, and sensors. A thorough review of the use of freeze-casting for porous ceramics can be found in reference [25]. This process takes advantage of directional freezing of colloidal suspensions, and then sublimation of the solvent occurs to create a porous structure replicating the frozen solvent. Finally, the structure can be sintered to consolidate the particles, which also enhances the mechanical properties of the freeze-cast structures [26]. For this fabrication process to reach its full potential

for creating porous microstructures, the composition and freezing of the suspension must be wellcontrolled to produce the desired structure. The freezing of the suspension is the most crucial aspect, as the freezing rate determines the final porous structure obtained with this method. While this process is well-established for various ceramic materials, polymer-ceramic composites have been fabricated using this method as well, alluding to the potential versatility of this process for different types of materials. A lamellar alumina structure produced by freeze casting can be seen in Figure 4 [25].



Figure 4: Freeze-cast lamellar alumina structure [25]

Better control over lamellae spacing has been achieved using a double-sided cooling method in reference [27]. This double-sided cooling allows for better control of the temperature gradient within the suspension, which then allows for better control over the microstructural features. This setup was able to create vertically oriented lamellae along the total height of the sample, up to 40 mm, with nearly constant spacing between lamellae. This study [27] achieves average lamellae spacing ranging from $63 - 136 \mu m$, depending on the solid loading of particles and the distance from the cooled plate. Another study [28] produced highly interconnected lamellar pores with thicknesses between 210 and 600 µm using freeze casting of calcium silicate (CS). Structures were

produced using suspensions with solid loading values ranging from 10 vol.% to 25 vol.%. An example of the structure produced in this study [28] can be seen in Figure 5.



Figure 5: Porous CS structure produced by freeze casting of a suspension with 10 vol.% solid loading [28]

Different additives can also be used in ceramic slurries to further manipulate the structure produced. Reference [29] provides an overview of the effects of various additives on the final freeze-cast structure. Figure 6 shows the structural differences achieved using different additives.



Figure 6: Structural differences produced by different additives in freeze casting process (a) 10 wt.% sucralose with pH = 2.5, (b) 4 wt.% ethanol, (c) 4 wt.% sodium chloride, (d) 4 wt.% sucrose, (e)-(h) detailed views of (a)-(d), respectively; scale bars: (a) 50 μ m, (b) 100 μ m, (c) 100 μ m, (d) 50 μ m, (e) 50 μ m, (f) 100 μ m, (g) 100 μ m, (h) 100 μ m [29]

Many studies have reported that well-controlled lamellar structures can be achieved using freeze casting for aluminum oxide (alumina, Al₂O₃). The mechanisms behind this type of directional solidification for alumina are described in reference [30]. The effect of freezing velocity, i.e. the speed of the advancing solidification front, on freeze-cast alumina structures is discussed in reference [31], where it is shown that decreased freezing velocities and instability created by the presence of particles cause a transition from a planar solidification front to a more complex morphology such as cellular or lamellar.

This transition of ice structure can also be seen in situ in references [32] and [33]. It is shown that a freeze-cast alumina structure begins with planar ice growth. Then randomly oriented pore growth occurs, followed by vertical lamellar ice crystals. However, the companion paper [33] shows that a lamellar structure can be achieved along the whole height of the sample if steady-state freezing is achieved. Samples with lamellar alumina structures produced in references [32] and [33] can be seen in Figure 7 and Figure 8, respectively.



Figure 7: (a) Vertical cross section of freezecast alumina sample where the dashed line in the lower left corner indicates the copper freezing substrate, (b)-(e) horizontal cross sections of freeze cast sample; scale bars: (a) $250 \mu m$, (b)-(e) $150 \mu m$ [32]



Figure 8: (a) Vertical cross section of freezecast alumina sample obtained via steady-state freezing, (b)-(e) horizontal cross sections of freeze cast sample; scale bars: (a) 300 μm, (b)-(e) 150 μm [33]

While freeze-casting is well established for ceramics, there are few studies that focus on freezecasting of porous metals. Two studies have reported an isotropic porous structure obtained by freeze-casting and reduction sintering of metals [34, 35]. Reference [34] produces an interconnected porous copper structure via freeze casting. Structures with solid loading values ranging from 20 vol.% to 40 vol.% were produced using cupric oxide (CuO) and then the structures were reduced to pure copper (Cu) metal and sintered, where the freeze-cast porous structure was preserved after reduction and sintering. Three samples from this study can be seen in Figure 9.



Figure 9: Porous copper structures produced by freeze casting with solid loading = (a) 20 vol.%, (b) 30 vol.%, and (c) 40 vol.% [34]

Reference [35] focuses on freeze casting of titanium alloy (Ti-6Al-4V) scaffolds. An interconnected pore structure was produced for porosities ranging from 34 – 65%. An example of the structure produced in this study can be seen in Figure 10. Also, a composite structure was created by infiltrating the porous Ti-6Al-4V structure with a polymer, poly(methyl methacrylate) (PMMA) to create a lightweight composite with enhanced mechanical properties. While some residual porosity exists after infiltration possibly due to air bubbles, this composite provides a feasibility study for the infiltration of a freeze-cast porous metal structure [35].



Figure 10: Freeze-cast Ti-6Al-4V scaffolds for solid loading = (a) 20 vol.%, (b) 5 vol.% and the difference in structure produced by freezing rate = (c) 1°C/min, and (d) 10°C/min [35]

However, a lamellar porous structure was not obtained in either reference [34] or [35]. A lamellar copper pore structure was obtained by freeze casting in reference [36], with ~80% well-aligned and interconnected pores. Interestingly, the structure produced in this study differs from the ceramic structure produced in reference [32]. As opposed to planar ice growth closer to the freezing substrate, reference [36] exhibits planar ice growth at the top of the sample, furthest from the freezing substrate. Much of the sample, however, exhibits a lamellar structure before this planar ice growth begins, as seen in Figure 11. It is expected that further study will lead to better control over the pore structure with potential for future manipulation of the structure formed by this process. This study [36] also found that higher solid loading can be achieved by adjusting the pH of the slurry using potassium hydroxide (KOH), and the best dispersion was obtained with pH values of 10 and 11 [36].



Figure 11: Lamellar copper structure produced with a solid loading of 15 vol.% [36]

One other study has achieved a lamellar copper structure via freeze casting for use in a lithiumion battery [37]. This study produced a lamellar structure made of pure copper using the freeze casting technique, followed by reduction to and sintering that was then coated with tin to produce an anode for a lithium-ion battery. Pores on the order of tens of microns were fabricated using freeze-casting, which can be seen in Figure 16. This study [37] focuses primarily on the use of the tin-plated copper for use in a lithium ion battery, so the effects of freezing temperature, freezing rate, and suspension composition on the copper structure are not explored. Research is still limited regarding the freeze casting of porous metals to produce a well-controlled lamellar structure


Figure 12: Lamellar copper structure produced with a solid loading of 13.4 vol.% for use in lithium-ion batteries [37]

It is proposed that the novel freeze casting method can be used to effectively create a wellcontrolled and predictable copper microstructure with pores ranging from tens to hundreds of microns that can be infiltrated with a phase change material. It is also expected that this method can be used to produce bulk material while maintaining a well-controlled microstructure.

1.3 Needs and Challenges

An effective PCM-infiltrated lamellar copper structure in bulk with a controllable microstructure has not yet been created. The major challenge is the fabrication of such a small-scale structure in a bulk material. Freeze-casting is proposed for the fabrication of a lamellar copper structure, however very few studies have achieved the desired structure using cupric oxide (CuO) for freeze-casting, as discussed in Section 1.2. Cupric oxide has a density approximately 60% higher than alumina, which creates a challenge in freeze casting, as cupric oxide particles are more

likely to settle than alumina. This suggests that nano-sized CuO particles are required to create the slurry used for freeze-casting. However, nano-sized particles are more prone to aggregation, making it more difficult to produce a well-dispersed slurry. These challenges will be addressed throughout this study.

1.4 Research Goals and Tasks

It is proposed that a lamellar copper structure can be effective for the thermal management of pulse heating applications and the lamellar copper structure in bulk can be created using the freeze casting method. Cupric oxide will be used for freeze casting, and ultimately this structure will be reduced to pure copper in future studies. Numerical and theoretical studies will be performed for a lamellar structure made of copper, with pores infiltrated with an organic phase change material (paraffin wax) to utilize the latent heat of the phase change process for thermal management. The goals of this study are to (1) show that lamellar structures infiltrated with PCM outperform unoriented porous metal foams for a range of heat fluxes and porosities, (2) show that a lamellar spacing on the order of tens to hundreds of microns is necessary to achieve the best thermal management outcome, and (3) show that it is possible to fabricate this structure using the novel freeze-casting technique. The specific research tasks that will be performed are as follows:

 Modeling of heat transfer for lamellar and unoriented foam structures infiltrated with PCM using two different modeling approaches. For both morphologies, simulations are performed to compare the structures at different copper compositions and heat fluxes. Pore scale simulations are also performed to determine the optimal lamellae spacing for various heat fluxes.

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- 2. Creation of well-dispersed cupric oxide colloidal suspensions (slurries) and freeze casting to fabricate a lamellar structure. Copper is a well-established material for heat sink applications. However, copper particles are prone to oxidation in the slurry. Therefore, cupric oxide will be used for freeze-casting.
- 3. Characterization of the microstructure produced by freeze casting. It is necessary to understand the properties of the microstructure so future studies can make correlations between the freezing profile and the resulting microstructure. This will allow future control over the microstructure properties such as lamellae thickness and lamellae spacing.

2. Design of Composite Microstructure Using Numerical and Theoretical Studies

The goal of the numerical and theoretical studies is to show that the composition, pore morphology (foam vs lamellar), and pore size of porous copper composites infiltrated with phase change materials can be optimized to achieve better thermal management performance and a lower interface temperature.

First, a one-dimensional theoretical model for transient heat transfer with phase change is used to (1) compare the effect of a disordered foam-like structure with a lamellar structure on heat dissipation from a heated surface in a PCM-copper composite, and (2) determine the optimal volume fraction of copper (copper composition) for a given heat flux value. This model considers the material as a homogeneous medium with effective properties calculated based on the composition of the material.

Then, a two-dimensional pore scale model is developed to study transient heat transfer with phase change in a unit cell of a lamellar porous copper structure infiltrated with paraffin. This model is used to numerically simulate the lamellae and the phase change material as two separate entities with their own respective material properties. The goals of the numerical study are to (1) determine the effect of pore size (spacing between lamellae) for different copper compositions and heat flux values, and (2) demonstrate the effect of thermal conductivity on the optimal pore size using two different types of metal, copper and stainless steel.

Some microporosity may exist within the lamellae after the freeze casting process possibly due to aggregation of particles which can leading to insufficient particle packing. However, it is expected that this will be minimized by the sintering process in which the packed particles are densified under elevated temperatures. The effect of the microporosity on heat transfer performance will be explored in future research. Therefore, only the macroporosity, which is the spacing between the lamellae, will be considered in the theoretical and numerical studies. These two different types of porosity can be seen in Figure 13. This macroporosity will be referred to as "pore spacing" in the future.



Figure 13: (a) Macroporosity (spacing between lamellae) in freeze-cast sample; magnification = 10x, (b) Microporosity (within lamellae) in freeze-cast sample; magnification = 50x

2.1 Theoretical Study

2.1.1 Problem Setup

The one-dimensional theoretical model is developed for heat dissipation from a heated surface in a PCM-copper composite, as shown in Figure 14. This theoretical model considers a semiinfinite phase change material with a single melting temperature T_m . Initially, the PCM is in solid phase at T_m . At t > 0, its boundary is subject to a heat flux decaying with time as $q = q_0 t^{-1/2}$ where q_0 is the heat flux constant. In this special case, the boundary temperature T_0 is maintained at a constant value above the melting temperature as a result of the decreasing heat flux. Therefore, the value of T_0 indicates how efficiently the composite dissipates heat from the boundary [38]. This model is used to compare the performance of porous copper with a disordered foam-like structure for various copper compositions and heat flux values.



Figure 14: Diagram of semi-infinite homogeneous material subject to a decreasing heat flux at the interface

The theoretical model assumes the PCM-infiltrated porous copper as a semi-infinite homogeneous medium, shown in Figure 14, where effective values of thermal conductivity, density, and specific heat are used to describe heat transfer and phase change in the composite material. This assumption is valid when the pore size is sufficiently small that the local thermodynamic equilibrium between the metal and embedded PCM exists. The calculation of the effective properties is discussed in Section 2.1.2.

2.1.2 Mathematical Model – Homogeneous Medium Model

When a phase change material, initially maintained in solid phase at the melting temperature T_m , is exposed to heating, the material starts melting. The heat transfer within the melted PCM can be expressed by Eq. 1:

$$\left(\rho c_p\right)_l \frac{\partial T_l}{\partial t} = \frac{\partial T}{\partial z} \left(k_l \frac{\partial T_l}{\partial z} T_l\right)$$
 Eq. 1

where ρ is the density, c_p is the specific heat, T is the temperature, t is the time, and k is the thermal conductivity. The subscript l denotes the liquid phase. The energy conservation at the interface can be described by Eq. 2:

$$k_s \nabla T_s - k_l \nabla T_l = \rho L_W \frac{\partial z_m(t)}{\partial t}; \quad T_l = T_s = T_m$$
 Eq. 2

where L_W is the latent heat of the phase change material, $z_m(t)$ is the location of the solid-liquid interface, and the subscript *s* denotes the solid phase. In the solid phase, the temperature is maintained at $T = T_m$.

Eq. 1 and Eq. 2 can be rewritten for a composite with the melting temperature T_m and effective properties based on the composition of the material. The heat transfer within the melted composite can be described by Eq. 3:

$$\left(\rho c_p\right)_{l,eff} \frac{\partial T_l}{\partial t} = \frac{\partial T}{\partial z} \left(k_{l,eff} \frac{\partial T_l}{\partial z} T_l\right)$$
 Eq. 3

where the subscript eff refers to the effective properties of the melted composite. Then the energy conservation at the solid/liquid interface for this composite can be described by Eq. 4:

$$k_{s,eff} \nabla T_s - k_{l,eff} \nabla T_l = \rho_{eff} L_{eff} \frac{\partial z_m(t)}{\partial t}; \quad T_l = T_s = T_m$$
 Eq. 4

As the temperature gradient in the solid phase is zero, the complete mathematical formulation of this problem can be given by Eq. 5.

$$\left(\rho c_p\right)_{eff} \frac{\partial T_l}{\partial t} = \frac{\partial T}{\partial z} \left(k_{eff} \frac{\partial T_l}{\partial z} T_l\right) \quad 0 < z < z_m(t), \quad t > 0$$

$$T = T_m \quad z > z_m(t)$$

$$F_m = T_m \quad z > z_m(t)$$

$$T_l(z,t) = T_m$$
 and $-k_{eff} \frac{\partial T_l}{\partial z} = \rho_{eff} L_{eff} \frac{\partial z_m(t)}{\partial t}$ $z = z_m(t), t > 0$

The interface temperature relative to the melting temperature of the material, which is $u_l = T_l(x, t) - T_m$, can be derived and is given in Eq. 6 [38].

$$u_l = \frac{q_o}{k_{eff}} \cdot \sqrt{\pi \alpha_{eff}} \cdot \operatorname{erf}(\lambda)$$
 Eq. 6

where
$$\alpha_{eff} = \frac{k_{eff}}{\rho_{eff} \cdot c_{p,eff}}$$
 Eq. 7

where k_{eff} is the effective thermal conductivity, α_{eff} is the effective thermal diffusivity given by Eq. 7, erf is the error function, and λ is the solution to the transcendental equation in Eq. 8 shown below.

$$\frac{\sqrt{\pi}}{Ste} \cdot \lambda \cdot \operatorname{erf}(\lambda) = e^{-\lambda^2}$$
 Eq. 8

where *Ste* is the Stefan number defined by Eq. 9.

$$Ste = \frac{c_{p,eff} \cdot u_l}{L}$$
 Eq. 9

These equations (Eq. 6 and Eq. 8) are solved simultaneously in MATLAB to obtain the interface temperature u_l .

The effective properties for this model are calculated based on the composition of the material. The properties of pure copper (subscript Cu) and pure paraffin wax (subscript W) are shown in Table 2. Although paraffin melts over a range of temperatures, for this model it is assumed that melting occurs at a representative temperature of T = 321 K.

Property	Units	Copper (Cu)	Paraffin Wax (W)
Density (p)	kg/m ³	8978	800
Thermal Conductivity (k)	W/mK	387.6	0.2
Specific Heat (c_p)	J/kgK	381	2200
Latent Heat (L)	J/kg	-	200 x 10 ³
Solidus Temperature (T^s)	K	-	321
Liquidus Temperature (T^l)	K	-	335

Table 2: Thermophysical Properties of Copper and Paraffin

Using the properties of the pure materials, the effective properties of the composite can be computed [14]. The effective density of the composite is calculated using Eq. 10.

$$\rho_{eff} = \Phi \rho_{Cu} + (1 - \Phi) \rho_W$$
 Eq. 10

where Φ is the volume fraction of copper in the composite, ρ_{Cu} is the density of copper, and ρ_W is the density of the paraffin. The mass composition of copper in the composite is calculated using the following equation, Eq. 11.

$$\delta = \Phi\left(\frac{\rho_{Cu}}{\rho_{eff}}\right)$$
 Eq. 11

The effective specific heat of the composite is calculated using Eq. 12.

$$c_{p,eff} = \delta c_{p,Cu} + (1 - \delta) c_{p,W}$$
 Eq. 12

where $c_{p,Cu}$ is the specific heat of the copper, and $c_{p,W}$ is the specific heat of the paraffin. The effective latent heat of the composite is calculated using Eq. 13.

$$L_{eff} = (1 - \delta)L_W$$
 Eq. 13

where L_W is the latent heat of the paraffin. The effective thermal conductivity for a disordered foam is calculated using the theoretical upper limit of the effective thermal conductivity for an isotropic porous material. Eq. 14 is used to calculate this value [14]:

$$k_{eff,max} = k_{Cu} \frac{2k_{Cu}\Phi + k_W(3 - 2\Phi)}{k_{Cu}(3 - \Phi) + k_W\Phi}$$
 Eq. 14

where $k_{eff,max}$ is the theoretical upper limit of the effective thermal conductivity for an isotropic porous material, k_{Cu} is the thermal conductivity of copper, and k_W is the thermal conductivity of paraffin.

Lamellar structures are anisotropic and heat flow is assumed to be in parallel along the direction of the extended surface. The effective thermal conductivity for two materials in parallel ($k_{eff,f}$) is calculated using Eq. 15 [14].

$$k_{eff,f} = \Phi k_{Cu} + (1 - \Phi)k_W$$
 Eq. 15

There are some limitations for the homogeneous medium model used in this study for both the foam and lamellar morphologies. First, the assumption of local thermodynamic equilibrium is only valid for small pore sizes. Also, this theoretical solution is only valid with a decreasing heat flux proportional to $t^{-1/2}$.

The interface temperature relative to the material's melting temperature u_l is calculated for various heat fluxes and copper compositions using MATLAB.

2.1.3 Results of Theoretical Study

First, the interface temperature for the two different morphologies, disordered foam and a lamellar structure, is calculated for decaying heat fluxes described by $q = q_0 t^{-1/2}$, with q_0 ranging from 100 kWs^{1/2}/m² to 1 MWs^{1/2}/m² to assess the effect of copper morphology on the interface temperature. Copper compositions ranging from 10% to 90% are studied to determine if

there is an optimal copper composition and identify the optimal value, if it exists. Figure 15 shows the results from the theoretical study.



Figure 15: Boundary temperature vs. copper composition (by volume) for $q_0 =$ (a) 100 kWs^{1/2}/m² (b) 500 kWs^{1/2}/m² (c) 750 kWs^{1/2}/m² and (d) 1 MWs^{1/2}/m²

The results in Figure 15 clearly show that the lamellar structure outperforms the porous foam structures for all compositions, with a greater difference occurring for the lower compositions at higher heat fluxes. For example, at 10% copper with a heat flux of 1 MW/m^2 , the interface

temperature for a lamellar structure is approximately 40°C lower than the interface temperature for a foam structure. Therefore, future studies will proceed with a lamellar structure.

To explain the better performance of the lamellar structure, the effective thermal conductivities for the two different morphologies are compared for copper compositions ranging from 10 to 90%, as shown in Figure 16. This figure shows that a lamellar structure with the extended surface in parallel to heat flux has a higher theoretical value for the effective thermal conductivity for all copper composition values. These morphologies also have the largest difference in thermal conductivity values between 50% and 60% copper. For both 50% and 60% copper composition, the effective conductivity of the lamellar structure is higher than the theoretical upper limit of the effective thermal conductivity for the porous foam by approximately 39 W/mK.



Figure 16: Effective thermal conductivity vs copper composition foam and lamellar morphologies

For the lower heat fluxes studied ($q_0 = 100 \text{ kWs}^{1/2}/\text{m}^2$ and 500 kWs^{1/2}/m²), an optimal copper composition can be clearly seen. This optimal composition occurs due to the competition between the energy storage and conduction in the composite material. Increasing the fraction of copper will enhance the thermal conductivity but reduce the energy storage capacity of the phase change material. The optimal composition for these heat fluxes occurs between 50% and 60% copper.

At the higher heat fluxes studied ($q_0 = 750 \text{ kWs}^{1/2}/\text{m}^2$ and 1 MWs $^{1/2}/\text{m}^2$), it is clear that the more copper in the composite, the lower the interface temperature, as shown in Figure 15. However, a greater copper composition causes increased weight, which is not ideal for applications such as portable electronics where weight needs to be minimized. There seems to be a critical copper composition after which the temperature continues to decrease, but at a very slow rate. This critical composition occurs between 30% and 50% copper. Further increasing the copper fraction does not demonstrate substantial improvement in thermal management. Based on these results, future studies will proceed with both 30% and 50% metal composition.

2.2 Numerical Study

2.2.1 Problem Setup

The effect of lamellar spacing for various heat flux values is studied using a pore scale model. Based on the previous theoretical study, 30% and 50% metal compositions are used in this numerical study. Figure 17 shows the problem setup that consists of the heating element made of aluminum, thin heat spreaders made of copper, and a lamellar copper structure infiltrated with paraffin wax. The copper spreader between the heating element and the PCM-copper composite ensures that the heat is evenly distributed over the interface between the heating element and the lamellar composite structure. The composite is then sealed with another thin copper spreader on the top, which evenly distributes the cooling effect of the convection.



Figure 17: Diagram of proposed lamellar structure (50% metal copper)

As the lamellar structure is two-dimensional following a repeated pattern, a unit cell consisting of one half fin and one half pore space is used to examine the heat transfer performance of the whole structure, as shown in Figure 18. Only one unit cell is used in this simulation, as the fin and pore spaces are symmetric. The aluminum heat source has a height of 0.4 mm, the copper spreaders at the top and bottom each have a height of 0.1 mm, and the lamella has a height of 3 mm.

It is assumed that the external boundary of the heater is perfectly insulated. The left and right sides of the unit cell are symmetric boundaries. At the top end of the lamella, a convection heat flux is applied using a convection heat transfer coefficient of $h = 15 \text{ W/m}^2\text{K}$ and an external temperature of 293K. The system is also initially at room temperature (293K).



Figure 18: Pore scale model morphology for 50% copper

It is assumed that the phase change of the paraffin occurs over a range of temperatures, approximately 321K to 335K [10]. Between these temperatures, liquid and solid paraffin coexist until the paraffin is above 335K, when it is completely in the solid phase.

This model also studies the effect of material properties by comparing the performance of copper and 304 stainless steel in the pore scale model. The material properties for copper and stainless steel can be seen in Table 3.

Property	Units	Copper (Cu)	304 Stainless Steel
Density (p)	kg/m ³	8978	8000
Thermal Conductivity (k)	W/mK	387.6	16.2
Specific Heat (c_p)	J/kgK	381	500

Table 3: Material properties of Copper and Stainless Steel

2.2.2 Mathematical Model – Pore Scale Model

In the numerical study, a pore scale model is developed to study the heat transfer and phase change of paraffin embedded in a lamellar copper structure shown in Figure 18. Interface resistance between paraffin and copper is not considered. It is necessary to calculate the Grashof number, defined as the ratio of buoyant force to viscous force, to determine the effect of free convection on heat transfer within the melted paraffin. This value can be calculated using Eq. 16.

$$Gr = \frac{g\beta(T_s - T_{\infty})L_c^3}{\nu^2}$$
 Eq. 16

where *g* is gravitational acceleration, β is the coefficient of thermal expansion, T_s is the surface temperature, T_{∞} is the temperature of the fluid at a distance from the surface, L_c is the characteristic length over which the convection would occur, and ν is the kinematic viscosity of the flow. The value of *Gr* is calculated for the pore size in the range of 600 µm – 4 mm. The gravitational acceleration is equal to 9.81 m/s². The surface temperature is $T_s = 361.1$ K, which is defined as the maximum temperature of the heat source when the system is subjected to a steady state heat flux of 1 MW/m² at t = 0.5 s (as seen in Figure 21(a)), while T_{∞} is defined as the liquidus temperature of the paraffin (335K). The characteristic length is the height of the lamella in the unit cell, which is 3 mm. The thermal expansion coefficient (β) is 0.00011 (1/K) [39]. The kinematic viscosity can be calculated using Eq. 17.

$$\nu = \frac{\mu}{\rho}$$
 Eq. 17

where μ is the dynamic viscosity and ρ is the density. The dynamic viscosity is 0.0269 kg/m [39], and the density is 800 kg/m³. This creates a kinematic viscosity of 3.36x10⁻⁵ m²/s. Inserting these values into Eq. 16, the resulting Grashof number is 2.26×10^{-5} , which is sufficiently low (<10³) for free convection in the melted paraffin to be negligible.

The transient heat conduction in the multi-component system is expressed by Eq. 18 [10].

$$\nabla \cdot (k_i \nabla T) + \dot{q}_i = (\rho c_p)_i \frac{\partial T}{\partial t}$$
 Eq. 18

where \dot{q} is the volumetric heat generation rate, and the subscript *i* represents different material, such as metal and paraffin in both the liquid and solid phase. The heat generation \dot{q}_i is only a nonzero value in the heating element. The latent heat absorbed/released over the phase change of paraffin wax is accounted for using the enthalpy approach, which uses a temperature-dependent specific heat. The piecewise function describing this specific heat is shown in Eq. 19.

$$c_{p,W*} = \begin{cases} c_{p,W,s} & T \le T^{s} \\ c_{p,W} + \frac{L_{W}}{T^{l} - T^{s}} & T^{s} < T < T^{l} \\ c_{p,W,l} & T \ge T^{l} \end{cases}$$
 Eq. 19

where $c_{p,W,s}$ and $c_{p,W,l}$ are the specific heats of the solid and liquid PCM, respectively. In this function, T^s is the solidus temperature, the temperature below which the paraffin is completely solid. T^l is the liquidus temperature, the temperature above which the paraffin is completely liquid. Between T^l and T^s , there exists both solid and liquid paraffin, as it is in the process of melting. In this case, the specific heat of the paraffin in solid form is equal to that of the liquid form $(c_{p,W,s}$ and $c_{p,W,l})$ [10]. However, the specific heat within the melting range is represented by a step function due to the effect of the latent heat of phase change. This function produces sharp interfaces that could lead to numerical instability at the liquidus and solidus temperatures of the paraffin. Therefore, a sinusoidal smoothing function is used to reduce the numerical instability that occurs within the simulation. Eq. 20 shows the specific heat of paraffin with the smoothing function implemented.

$$c_{p,W*} = \begin{cases} c_{p,W,s} & T \leq T^s \\ c_{p,W} + \left[\frac{\pi}{2} \left(\frac{L_W}{T^l - T^s} - c_{p,W} \right) \sin \left(\pi \left(\frac{T - T^s}{T^l - T^s} \right) \right) \right] & T^s < T < T^l \\ c_{p,W,l} & T \geq T^l \end{cases}$$
Eq. 20

Figure 19 shows the specific heat of paraffin both with and without the smoothing function implemented. Despite the different functional form, the difference in the latent heat is less than 4%. Beyond the defined bounds (273K < T < 800K), the specific heat is extrapolated using a constant function based on the endpoints of the piecewise function.



Figure 19: Temperature-dependent specific heat of paraffin wax with and without smoothing function

The boundary conditions used in this model are as given by Eq. 21-Eq. 23:

At the left and right boundary of the unit cell shown in Figure 18, the symmetric boundary condition is applied, leading to Eq. 21.

$$-k\frac{\partial T}{\partial x} = 0$$
 Eq. 21

At y = 0, the bottom boundary of the heating element, it is assumed to be perfectly insulated, which is given by Eq. 22.

$$\frac{\partial T}{\partial y} = 0$$
 Eq. 22

The top surface of `the top spreader (y = 3.6mm) is exposed to the surroundings at 273K with a convection heat transfer coefficient of h = 15W/m²K. Thus, the boundary condition is given by Eq. 23.

$$-k\frac{\partial T}{\partial y} = h(T - T_{\infty})$$
 Eq. 23

This study is performed using a finite volume with a commercially available software, COMSOL Multiphysics 5.6.

2.2.3 Results of Numerical Study

2.2.3.1 Effect of Pore Size on the Fraction of Melted Paraffin

Pore size is a parameter that determines the contact area between the conducting material and the embedded paraffin. A smaller pore size results in larger contact area but poses more challenges in fabrication. Understanding the effect of the pore size on the thermal response of the PCM-metal composite to various heat fluxes is important for designing the microstructures of porous metals. In this numerical study, the pore size varies over a large range, from 20 μ m to 4 mm, and the applied steady state heat flux ranges from 100 kW/m² to 1 MW/m². The copper compositions are 30% and 50%, as these are the volume fractions of copper that were found to be the critical compositions for optimal thermal management performance in the previous theoretical study. Besides copper, the effect of pore size for stainless steel is also investigated for one steady state heat flux, to determine if the thermal conductivity of the conductive material impacts the optimal pore size. To qualitatively show the effect of pore size on the thermal response of the composite, multiple unit cells (as shown in Figure 18) were stacked together to show one whole copper lamellae and two whole pore spaces, as seen in Figure 20.



Figure 20: Multiple unit cells stacked together to show one whole copper lamellae and two whole pore spaces, 30% copper, pore size = 600 microns

Figure 21 shows the field plot for a 30% copper structure with a pore size of (a) 600 microns and (b) 150 microns subjected to a steady state heat flux of 1 MW/m² for t = 0.5 s. Multiple unit cells are combined to see the full temperature distribution in the pore spaces and lamellae. It can be seen that the temperature of the copper structure in Figure 21(a) has a higher temperature than the infiltrated paraffin. Clearly, the incorporated copper (the red and orange regions) serves as the "hot bridge" to conduct and distribute heat. In paraffin, only the layer of material in contact with copper exhibits an elevated temperature (the yellow and green regions) while the core remains cold (the blue colored regions). This is because, as the paraffin wax in contact with the copper melts, it creates a kind of insulating layer that resists the heat penetration into the wax, and some of the wax stays in solid phase (the blue-colored regions). The latent heat of this solid wax is then not used to absorb heat and it can be referred to as "inaccessible latent heat." In comparison, the smaller pore size in Figure 21(b) shows a lower temperature in the heating element, demonstrating a better cooling effect. On the other side, the lowest temperature in the paraffin is higher in the smaller pore size than in the larger pore size and is within the melting temperature range of the paraffin, as shown by the difference in the minimum temperature for the two different cases shown in Figure 21.



Figure 21: (a) The field plot for a 30% copper lamellar structure with a pore size of 600 microns and (b) the field plot for a 30% copper lamellar structure with a pore size of 150 microns, subject to a heat flux of 1 MW/m² at t = 0.5 s. The temperature is in Kelvin

Figure 22 shows two isothermal contours in the paraffin. The red line represents the liquidus temperature (321K) and the blue line represents the solidus temperature (335K). In Figure 22(a), the area between the two curves is the partially melted, "mushy" region of paraffin. Inside the blue line, the paraffin is completely solid and the area outside of the red line, closest to the lamellae and spreaders, is the paraffin that is completely melted. Although it is difficult to see, only the red line is visible in Figure 22(b), demonstrating that with the smaller pore size, all of the paraffin is either within or above the melting temperature range of 321K - 335K. In both Figure 22(a) and (b), the paraffin closest to the heat source, below the red line, is in the liquid phase.



Figure 22: (a) Isothermal contours for a 30% copper lamellar structure with a pore size of 600 microns and (b) isothermal contours for a 30% copper lamellar structure with a pore size of 150 microns at t = 0.5s, showing the upper and lower limits of the melting range for paraffin

To calculate the percentage of each phase in both Figure 22(a) and (b), the temperature at each node of the mesh in the paraffin is determined to find the percentages of solid, "mushy", and liquid paraffin. The number of nodes in each phase is then divided by the total number of nodes and then rounded to the closest whole number to determine the percentage of each phase. The solid paraffin is any node at a temperature below 321K, the partially melted paraffin is any node with a temperature satisfying $321K \le T \le 335K$, and the liquid paraffin is any node at a temperature above 335K. This approach of phase breakdown is valid as all mesh elements in this study are created to have the same volume.

For the case with the larger pore size (600 microns) shown in Figure 22(a), the phase breakdown of the paraffin is as follows: approximately 44% solid, 34% partially melted, and 22% liquid. For the case with the smaller pore size (150 microns) shown in Figure 22(b), the phase breakdown is as follows: 0% solid, approximately 89% "mushy", and 11% liquid. In the structure with the larger

pore size, the larger portion of solid paraffin contributes to the higher maximum temperature because less latent heat is utilized to cool the heat source. Clearly, a smaller pore size, or the size of the spacing between lamellae, increases the contact area, per volume of paraffin, enlarges the volume of melted or partially melted paraffin, and ultimately yields a lower temperature in the heating element than the larger pore size.

2.2.3.2 Effect of Pore Size on Thermal Response to Various Heat Fluxes

The optimal thermal management performance calls for the full utilization of the latent heat associated with the phase change of paraffin. That is, it is desirable to have as much melted paraffin as possible. The results of the above Section 2.2.3.1 illustrate that the morphology and structural parameters can be optimized to create the most efficient structure for thermal management to utilize both the conductive potential of the metal in conjunction with the thermal storage capabilities of the paraffin. It is necessary to determine how the pore size affects the extent to which paraffin melts in the unit cell for various heat fluxes.

Numerical simulations of transient heat transfer and phase change in the unit cell, shown in Figure 18, have been performed with a pore size ranging from 20 µm to 4 mm and two different steady state heat fluxes: 1kW/m² and 500 kW/m². The volumetric heat generation rate in the heating element is applied corresponding to the applied heat flux. The variation of the temperature with time at a point in the middle of the heating element is used to show the thermal response of the PCM-copper composite to the imposed heat flux for t > 0.

Shown in Figure 23 is the transient thermal response of the composite with various pore sizes at a copper composition of 30% to an interface heat flux of 1 kW/m². The heating duration is 5000 s to allow the system to reach a steady-state temperature.



Figure 23: Transient thermal response at the center of the heat source, 30% copper, heat flux = 1 kW/m^2

The thermal response shows three distinctive stages for all pore sizes studied. Stage 1 occurs from the initial temperature, 293K to the lower limit of the melting range of the paraffin, 321K while heating occurs. Stage 2 occurs over the melting range of paraffin, 321K to 335K, where phase change occurs. Within this temperature range, the rate of temperature increase slows down as the paraffin melts. Stage 3 occurs above 335K where phase change is complete and heating continues. During this stage, the graph takes on a shape similar to an error function as the system reaches steady state at approximately 360K for this applied heat flux.

While most of the pore sizes in Figure 23 create a very similar thermal response, the 2.4 mm and 4 mm pores reach the melting temperature slightly sooner than the smaller pore sizes and remain in the melting temperature range for less time, which is in agreement with the study performed in reference [10]. However, this is difficult to see in the graph as there is not a large difference in temperature between the pore sizes at this heat flux. Clearly the pore size does not substantially change the thermal response of the composite to the heat flux of 1 kW/m^2 .

A similar study is performed using a volumetric heat generation corresponding to a heat flux of 500 kW/m^2 applied at the interface. A smaller time frame is studied to view the effect of phase change on the temperature of the heat source. The results of this study can be seen in Figure 24.



Figure 24: Transient thermal response at the center of the heat source showing the effect of phase change, 30% copper, heat flux = 500 kW/m^2

Interestingly, the three stages exhibited in Figure 23 can only be seen for pore sizes smaller than 600 microns. For pore sizes of 600 microns and larger, the graph takes on a more linear shape, rather than showing a distinctive range where phase change occurs. This can be explained by the large temperature difference in the paraffin at larger pore sizes, as shown in Figure 21. Due to the limited contact area per unit volume between the lamellae, and a larger portion of the paraffin remains in the solid phase and the utilization of latent heat is delayed compared to the smaller pore size. Complete melting of paraffin takes a longer time as pore size increases because of this limited contact area, so there is no distinctive phase change shown in the thermal response for the pore sizes larger than 600 microns. The results in Figure 24 also show that the temperature increases at a slower rate for the smaller pore sizes for the same reason. After approximately 0.1 s, there is a noticeable temperature difference between the largest pore size and the smallest pore size is approximately 18K. The temperature difference between these pore sizes continues to increase, and at t = 2 s, the temperature difference is approximately 67K.

2.2.3.3 Effect of Pore Size on Time Taken to Reach the Safety Threshold

In many studies of thermal management of electronic devices, 85° C is considered a threshold for safe and reliable operation [2]. Above this temperature, the risk of damaging the electronics increases dramatically. Therefore, protracted time to reach this threshold is favorable. In this study, simulation is performed to investigate the effect of pore size on the time taken to reach this temperature when the PCM-copper composite is subjected to heat fluxes ranging from 100kW/m² to 1 MW/m². Both 30% and 50% copper compositions are employed in this study. In addition, the effect of pore size in a lamellar stainless steel structure is studied at a heat flux of 500 kW/m^2 for comparison.

For the convenience of comparing the effect of pore size at various heat fluxes, the time taken to reach 85°C is normalized by dividing the time for each pore size by the time for the largest pore size at each heat flux, which is 4mm (4000 μ m). Figure 25 shows the results for a 30% copper lamellar structure, while Figure 26 shows the results for a 50% copper lamellar structure.



Figure 25: Normalized time taken for the center of the heat source to reach 85°C for 30% metal at various heat flux values



Figure 26: Normalized time taken for the center of the heat source to reach 85°C for 50% metal at various heat flux values

From these results, a few conclusions can be drawn. First, it is clear that the stainless steel microstructure is less sensitive to pore size compared to copper. It is believed that this is due to the lower thermal conductivity of stainless steel leading to a lower volume of melted paraffin for the same volumetric contact area. It can also be concluded that the effect of pore size becomes more pronounced as heat flux increases. At higher heat fluxes, a smaller pore size increases the volume of melted paraffin due to a larger contact area, leading to better thermal management performance, as discussed in the results shown in Figure 22. However, pore sizes smaller than the optimal pore size for each heat flux do not show a remarkably better performance. For example, for a heat flux of 500 kW/m^2 , no substantial improvement is observed when the pore size is smaller than 150 µm. Therefore, fabrication on the order of tens to hundreds of microns will be pursued, as fabrication becomes more difficult as pore size decreases. This result clearly shows that

application-specific microstructure design is necessary based on the dependence that the critical pore size has on the applied heat flux.

A mesh dependence study is performed using a copper composition of 30% and a pore size of 150 μ m. This is done using the unit cell shown in Figure 18. The simulation is performed for 2 seconds with a heat flux of 500 kW/m², and the temperature distribution along the centerline of the paraffin (the right boundary of the unit cell in Figure 18) at t = 2 s is plotted for various uniform mesh element sizes, ranging from 1 μ m to 100 μ m. The results for this study can be seen in Figure 27.



Figure 27: Mesh dependence study for a pore size of 150 microns with a heat flux of 500 kW/m^2

Based on the results of the mesh dependence study, the temperature distribution in the paraffin is not greatly impacted by mesh element sizes below $100 \,\mu\text{m}$. Therefore, in this particular study, a maximum mesh element size of 7.5 μm and a minimum mesh element size of 2.5 μm are used.

Based on the theoretical and numerical results obtained in these studies, fabrication of a copper lamellar structure with pore sizes on the order of tens to hundreds of microns will be pursued using the novel freeze casting technique.

3. Freeze Casting

3.1 Freeze Casting Overview

The novel freeze casting technique is being investigated for the creation of lamellar copper structures in this study. Due to its ability to create anisotropic, interconnected three-dimensional porous structures that are tunable for a specific application, freeze casting has been employed to create various porous materials. This method has been used to create ceramics, polymers, and some metals used for a wide range of applications, such as biomaterials, insulators, separation filters, gas distributors, catalyst supports, biosensors, etc. However, as previously stated, very few studies have achieved a freeze-cast lamellar copper structure [36, 37]. Figure 28 shows the freeze casting process.



Figure 28: (a) A well dispersed slurry is prepared and introduced to a freezing substrate, (b) solvent crystals begin to directionally form and reject the nanoparticles; the nanoparticles begin to accumulate in the inter-dendritic spaces, (c) the solvent crystals are fully formed and the final structure is obtained, (e) the solvent crystals are sublimed to create the final porous structure

First, as shown in Figure 28(a), a well-dispersed liquid suspension of powder is prepared in a mold. The base of this mold is introduced to a cold surface, where the top and sides of the mold are insulated. This creates a temperature gradient within the suspension only in the vertical direction, leading to unidirectional solidification of the solvent. This directional freezing leads to the formation of elongated, aligned solvent crystals, which can be seen in Figure 28(b). As solidification occurs, the particles are rejected by the growing solidification front and accumulate in the inter-dendritic space. Once the sample is completely frozen, which can be seen in Figure 28(c), the sample is then dried in a vacuum at below-freezing temperatures to sublime the solvent crystals to create a porous structure. The interconnected pores created by this process replicate the solvent crystals, as shown in Figure 28(d). This diagram also shows spaces between individual particles, independent of the well-aligned dendrites, which is the microporosity that was previously discussed. It is expected that the sintering process will minimize any microporosity that results from the freeze casting process, which will be explored in future studies. For this process, water is widely used as an environmentally friendly, abundant solvent that favors the formation of lamellar porous structures.

3.2 Objective

The objective of this experimental study is to use freeze casting to create a lamellar porous structure of cupric oxide that could ultimately, in future studies, be reduced to a pure copper porous structure and infiltrated with a phase change material (PCM) to form a composite for thermal management. The tasks that will be performed are as follows: (1) Prepare stable aqueous suspensions of cupric oxide particles of different concentrations, (2) Create a lamellar microstructure using freeze casting and (3) Characterize the microstructure using optical

microscopy. It is expected that the solid loading of the suspension can be increased by manipulating the pH value as shown in reference [36]. It is also expected that the pore thickness can be controlled by manipulating the freezing rate of the slurry, as discussed in reference [30]. Once the samples are freeze dried, epoxy infiltration will be used to facilitate cross-sectional cutting of the samples and optical microscopy will be used to view the microstructure.

3.3 Materials and Methods

3.3.1 Preparation of Aqueous Suspensions of Cupric Oxide Nanoparticles

Formation of lamellar structures by freeze casting requires a stable and well dispersed suspension of particles, which is also termed slurry in the literature of freeze casting. It is important to ensure the slurries are stable so that aggregation and sedimentation do not occur. With aggregation of particles, the ice front may not be able to push them into the space between ice crystals, and a lamellar morphology will not be formed. In addition, sedimentation can lead to a dense and isotropic microstructure at the bottom of the sample, rather than a lamellar microstructure along the length of the whole sample [35].

Aqueous slurries are prepared by dispersing cupric oxide nanoparticles (80 nm in diameter) in deionized water. Two sets of samples with different solid loadings are prepared. The first set uses approximately 9 vol.% cupric oxide powder (Sigma Aldrich, St. Louis, MO). 2 wt.% (relative to the CuO powder) polyvinyl alcohol (PVA) (Sigma Aldrich, St. Louis, MO) is used as a binder in the slurry, while 2 wt.% (relative to the CuO powder) polyvinylpyrrolidone (PVP) (Sigma Aldrich,

St. Louis, MO) is used as a dispersant to stabilize the slurry, mitigating sedimentation and aggregation of the CuO particles.

For the second set of samples, approximately 12 vol.% of CuO particles of the same size are dispersed in deionized water. Besides 2 wt.% (with respect to the CuO powder) PVP and PVA, an increased pH value is necessary to achieve higher solid loading, with optimal dispersion occurring for slurries with pH values of 10 and 11 [36]. To increase the pH value for these slurries, potassium hydroxide (KOH) is also added to the slurry, along with the PVA and PVP.

The slurry used for freeze casting is created in a two-step process. For both compositions, 2 wt.% each of PVA and PVP (0.124 g each) are added to a beaker and dissolved in 3mL of deionized water at approximately 90°C. The cupric oxide (CuO) powder for each composition is added to 8 mL of deionized water and stirred by hand. Then, both the PVA/PVP solution and the aqueous cupric oxide solution are allowed to cool in an ice bath, followed by degassing in a vacuum chamber for approximately 5 minutes. Then the PVA/PVP solution is carefully added to the aqueous cupric oxide. Sonication is then used to create homogeneous and stable slurries, and the slurry is degassed in a vacuum chamber once more to remove any residual air bubbles for approximately 10-15 minutes. This process produces approximately 11 mL of slurry that can be used to make multiple samples.

The slurry is then transferred into molds made of polypropylene test tubes with a diameter of 13 mm and a height of 35 mm. To facilitate unidirectional freezing, the round bottom of the test tubes is sectioned and sealed with a copper plate, as seen in Figure 29. Before adding the slurry to the mold, a thin layer of ice is allowed to freeze at the bottom of the mold to provide thermal
resistance that is expected to facilitate particle rejection by the growing ice crystals due to the decreased freezing rate at the onset of freezing.



Figure 29: Mold used for freeze casting method

For the second set of samples, KOH solution (Cole-Parmer, Vernon Hills, IL) is added to the PVA/PVP solution to achieve a pH of approximately 11 in the final slurry with a solid loading of approximately 12 vol.%. The rest of the protocol to prepare the higher solid loading slurry is the same as that with the lower solid loading.

3.3.2 Freeze Casting Process

After sonication and degassing, the samples are cooled to just above the freezing point and then frozen in a precooled freeze dryer (Harvest Right, North Salt Lake, Utah). The first set of samples (9 vol.% CuO, without KOH) are placed in a freeze dryer precooled to approximately -5°C and the samples are held at this temperature for 2 minutes, then the temperature is ramped at a rate of approximately -1°C/min to approximately -15°C where this temperature is held for 2 minutes, and

finally the temperature is ramped at the same rate to -25°C, which is held constant for 1 hour 20 minutes. This freezing profile can be seen in Figure 30(a). Once the samples are completely frozen, they are removed from the freezer, taken out of the molds, and placed back in the freeze dryer at approximately -25°C under near vacuum conditions for 72 hours to sublime the ice.



Figure 30: Freezing profiles for (a) first set of samples with approximately 9 vol.% CuO and (b) second set of samples with approximately 12 vol.% CuO

For the freezing of the second set of samples, the samples are placed in the freeze dryer which is precooled to approximately -5°C and the samples are held at this temperature for 2 minutes, then the temperature is ramped at a rate of approximately -1°C/min to approximately -15°C where the temperature is held for 2 minutes, and finally the temperature is ramped at the same rate to approximately -29°C, which is held constant for 1 hour 20 minutes. This freezing profile can be seen in Figure 30(b). Once the samples are completely frozen, they are removed from the freezer, taken out of the molds, and placed back in the freeze dryer at approximately -29°C under vacuum conditions for 72 hours to sublime the ice.

3.4 Microstructure Characterization

As the samples produced by this freeze casting are very brittle and delicate, some postprocessing is necessary to view the microstructure, which involves infiltrating the samples with epoxy resin (West System, Bay City, MI). The epoxied samples are degassed to ensure that the epoxy has completely filled the pores in the microstructure. It should be noted that when degassing the epoxied samples, the air bubbles within the sample expand and can cause the fragile structure to break.

Once the epoxy is fully cured, the samples are polished, first using a very rough grit sandpaper to remove material so the interior microstructure can be seen. Then, increasingly fine grits of sandpaper are used to polish the sample until the scratches are removed from the surface and the sample can be viewed clearly under the microscope. However, since this is an anisotropic structure, there is a specific direction in which the sample should be polished, which is difficult to determine visually. This direction is determined by cutting a thin horizontal cross section from the top of the sample using a diamond wheel saw (South Bay Technology Inc., San Clemente CA). A diagram of the cut plane can be seen in Figure 31.



Figure 31: Diagram showing the cut plane of the sample used to determine polishing direction

Once the top slice of the sample is removed, optical microscopy (Cascade Microtech, Beaverton, OR) is used to view the top cross section, which can then be used to determine which direction the sample should be polished. An example of the microscopic image of the top slice can be seen in Figure 32.



Figure 32: Microscopic image of top slice of sample used to determine polishing direction

Figure 33 shows a diagram of the polishing process, where the sample is polished, and the microstructure can be viewed under a microscope. Images are taken using optical microscopy and a digital microscope camera (Amscope Microscopes, Irvine CA) and the pore sizes are measured using the Amscope software.



Figure 33: Diagram of polishing process

3.5 Summary of Microstructure Fabrication Using Freeze Casting Technique

Aqueous cupric oxide colloidal suspensions are prepared using a polymeric dispersant (PVP). The pH value is adjusted to approximately 11 for suspensions with a higher solid loading. The freeze casting process uses a prescribed freezing profile based on the composition of the suspension with the goal of producing the desired lamellar structure. Once the samples are freeze cast, they are infiltrated with epoxy and polished to allow for the characterization of the microstructure using optical microscopy.

4. Experimental Results

4.1 Microstructure Characterization

Four samples are generated using the freeze casting method with two different solid loading values and are then infiltrated with epoxy and polished so that the internal structure could be viewed via optical microscopy. Two samples are produced for each value of solid loading.

4.1.1 Lower Solid Loading (9 vol.%)

Two different samples, shown in Figure 34 and Figure 35 (samples 1 and 2), are produced in the first set of samples with approximately 9 vol.% solid loading.

The first sample, as shown in Figure 34, shows a lamellar structure throughout much of the sample. At the top of the sample, shown in Figure 34(a), a well-aligned lamellar structure with pore sizes on the order of hundreds of microns can be seen. Shown in Figure 34(b), a tilted lamellar structure is observed as the ice growth transitions from planar to dendritic. The bottom of the sample closest to the freezing substrate, shown in Figure 34(c), exhibits an amorphous structure. This is believed to be caused by the fast freezing rate that occurs in this region of the sample. A fast freezing rate causes the particles to be encapsulated by the ice crystals rather than being rejected from the growing ice dendrites, which would pack the particles into the inter-dendritic spaces. Particle rejection by the non-planar ice front is what leads to a lamellar structure, while the encapsulation of particles leads to an amorphous structure.



Figure 34: Freeze cast sample #1 produced with lower solid loading (approx. 9 vol.%) (a) well oriented lamellar structure observed at the top of the sample (b) tilted lamellar structure observed in the center of the sample and (c) amorphous structure observed at the bottom of the sample, closest to the freezing substrate, scale bar = 1 mm

The sample in Figure 35 shows a similar structure to the sample shown in Figure 34 along the height of the sample. The same well-oriented lamellar structure can be seen at the top of the sample in Figure 35(a). However, the middle section of this sample exhibits a more randomly oriented porous structure rather than a tilted lamellar structure, as seen in Figure 35(b). Again, this is caused by the transition from planar ice growth to dendritic ice growth, however it is not known why these two samples exhibit different transitional structures. The cause of these different transitional

structures will be explored in future studies. At the bottom of the sample, an amorphous structure is also observed, shown in Figure 35(c).



Figure 35: Freeze cast sample #2 produced with lower solid loading (approx. 9 vol.%) (a) well oriented lamellar structure observed at the top of the sample (b) randomly oriented porous structure observed in the center of the sample and (c) amorphous structure observed at the bottom of the sample, closest to the freezing substrate, scale bar = 1 mm

4.1.2 Higher Solid Loading (12 vol.%)

The samples shown in Figure 36 and Figure 37 (samples 3 and 4) are produced in the second set of samples with higher solid loading (approximately 12 vol.%) made possible by the addition

of KOH. It is believed that the top center of the sample shown in Figure 36 was damaged by the epoxy infiltration process, so no structure can be observed there. The dark spaces seen in this area are believed to be caused by epoxy that began to cure before being added to the mold for infiltration of the sample. This damage only occurred to this portion of the sample because this epoxy was only added to the top to completely cover the top of the sample in the mold after previous epoxy had settled to the bottom of the mold and infiltrated the majority of the sample.

However, the side of the sample close to the mold surface at the top of the sample can still be observed, as it was not damaged by the epoxy infiltration process. This area shows a lamellar structure with large, inconsistent pore sizes, ranging from approximately 150 to 800 μ m, as seen in Figure 36(a). In the center of the sample, a very densely packed porous structure is observed, where a lamellar structure is seen in the center of the sample closest to the mold surface, as seen in Figure 36(b). This densely packed center of the sample could be caused by insufficient insulation, causing faster freezing at the sides of the sample compared to the center. This would cause the displacement of particles from the sides to the center, ultimately causing a higher solid loading in the center of the sample. Closest to the freezing substrate, this sample shows a very fine lamellar microstructure with pore spacing on the order of tens of microns, as seen in Figure 36(c). This sample shows an uneven surface at the bottom caused by breakage when transferring the green sample into the mold for epoxy infiltration.

Damage believed to be caused by epoxy infiltration



Figure 36: Freeze cast sample #3 produced with higher solid loading (approx. 12 vol.%) (a) lamellar structure observed at the top of the sample close to mold surface, (b) lamellar structure observed at the center of the sample close to the mold surface, and (c) fine lamellar structure observed at the bottom of the sample, closest to the freezing substrate

Interestingly, the sample in Figure 37 shows a different structure from the previous sample made with the same batch of slurry. This sample shows a dense porous microstructure at the top and bottom of the sample, as shown in Figure 37(a) and Figure 37(c), respectively. An amorphous structure is observed in the center of the sample, but a similar lamellar structure is observed along the sides close to the mold surface, as seen in Figure 37(b).

One major difference between these two samples is that the sample in Figure 36 shows a lamellar structure at the bottom of the sample rather than an amorphous structure. It is possible that this discrepancy occurred due to the melting of the layer of ice at the bottom of the mold before the samples were placed in the freezer. It is also important to note that a small portion of the sample that was broken off during the process of transferring the sample into the epoxy mold and could not be characterized. Nevertheless, more research should be done to understand the formation of these structural differences.



Figure 37: Freeze cast sample #4 produced with higher solid loading (approx. 12 vol.%) (a) dense porous structure observed at the top of the sample close to the mold surface (b) lamellar structure observed in the center of the sample close to the mold surface, and (c) dense porous structure observed at the bottom of the sample closest to the freezing substrate

It is also important to note that throughout all of the samples shown in Figure 34 - Figure 37, black dots can be seen in the images. This is caused by air bubbles in the sample where the epoxy did not properly infiltrate. Therefore the structure in those areas is not preserved and can not be characterized. Epoxy infiltration also does not allow for future use of a sample. For example, after the sample is infiltrated with epoxy for the microstructure characterization process, it then can not be used for paraffin infiltration. Due to these limitations of epoxy infiltration, it is important to find a more effective method of microstructure characterization in future research.

4.2 Summary of Microstructure Characterization of Freeze Cast Samples

It has been shown that freeze casting can be used to create a lamellar microstructure with pore spacing on the order of hundreds of microns. However, the samples exhibit distinctively different pore morphologies along the height of the samples. An amorphous morphology has been observed near the bottom in most of the samples, which could be explained by the rapid freezing at the beginning of the freezing stage. With a well-controlled freezing rate, it is likely that this structure can be improved to obtain the desired pore morphology, sizes, and orientation. Higher solid loading has also been achieved with the addition of KOH, with finer pore spacing on the order of tens of microns, and a much denser porous structure.

5. Conclusions and Future Work

5.1 Conclusion

Both theoretical and numerical studies have been performed to demonstrate that porous copper with a lamellar morphology and a tunable pore size in the range of tens to hundreds of microns are desirable for thermal management of transient heat load in electronic systems. Then, an experimental study was performed to demonstrate the feasibility of freeze casting to produce a lamellar structure using aqueous suspensions of cupric oxide particles.

5.1.1 Conclusion of Theoretical Study

The theoretical study demonstrated that a lamellar copper morphology outperforms random porous copper foams for all copper compositions and all heat fluxes. This is explained by the fact that the effective thermal conductivity of the lamellar structure is higher than that of a foam structure. This study also demonstrated that an optimal composition exists for lower heat fluxes, while a critical composition exists for higher heat fluxes, due to the competition between the energy storage and conduction. At compositions higher than this critical composition, the thermal management performance does not improve significantly. The optimal composition for the lower heat fluxes is between 50% and 60%, while the critical composition for the higher heat fluxes is between 30% and 50%.

5.1.2 Conclusion of Numerical Study

The numerical study showed the effect of pore size for both 30% and 50% copper by volume. It was demonstrated that a smaller pore size produces greater contact area per unit volume between the copper structure and the infiltrated PCM, leading to a greater percentage of melted or partially melted PCM. This increases the latent heat utilized to mitigate the temperature, thus yielding a better thermal management performance. The thermal response of the PCM-copper composite showed that smaller pore sizes lead to a slower temperature increase in the heat source. At low heat fluxes, the difference in thermal performance for different pore sizes is negligible, but for larger heat fluxes, the smaller pore sizes show a distinct advantage.

The study of the time taken to reach the safety threshold demonstrated the dependence of critical pore size on the thermal conductivity of the porous structure as well as heat flux. The effect of pore size becomes more pronounced for higher metal thermal conductivity as well as higher heat fluxes, demonstrating the importance of application-specific microstructure design. Higher heat fluxes require a smaller pore size to slow the rate at which the heat source temperature increases. This study also demonstrated that an optimal pore size exists, below which the structure does not exhibit a remarkably slower temperature increase of the heat source. For the heat fluxes in this study ranging from 100kW/m² to 1MW/m², a pore size on the order of tens to hundreds of microns improves the thermal performance of this structure, and smaller pore sizes are not necessary.

5.1.3 Conclusion of Experimental Study

The experimental study shows that a portion of the freeze cast samples, mostly near the top, exhibits a lamellar structure with pore sizes ranging from tens to hundreds of microns. A lamellar

structure with higher solid loading (and thus a greater copper composition) can be achieved using potassium hydroxide (KOH) to increase the pH of the slurry and act as an additional dispersant. It is expected that the composition of the slurry and the parameters of this technique can be improved to create a more consistent and controllable structure.

5.2 Future Work

5.2.1 Determining Optimal Composition

It will be necessary to determine the optimal composition, such as PVA, PVP, pH value, and solid loading for the desired microstructure. The viscosity of the slurries with various pH values, various amounts of PVA, and various amounts of PVP will be measured to obtain the optimal composition for future samples. The lowest viscosity value correlates to the slurry with the best particle dispersion, and therefore the optimal composition. The pore size obtained by freeze casting is expected to be controllable by controlling the freezing rate of the slurry.

5.2.2 Freezing Rate Measurements

Future work for this study also includes freezing rate measurements to produce more predictable and controllable copper lamellar structures using freeze casting. The setup shown in Figure 38 can be used to determine the freezing rate of the slurry. A copper rod is placed in an insulating container filled with a dry ice and ethanol bath. A heating coil is wrapped around the copper rod and connected to a PID controller to maintain a desired temperature of the rod to initiate directional freezing and create a temperature gradient throughout the sample. The sample is placed on the top of the copper rod.

This setup also utilizes an infrared camera fixed at a certain distance from the sample to observe the freezing interface. A thermocouple is connected to the base of the sample to monitor the temperature of the sample base. This experiment can first be done with deionized water as a calibration step, as the freezing interface of water can be easily measured visually, and the exact freezing temperature is known. For the slurry freezing rate experiment, a long thin probe inserted vertically into the slurry will be used to determine the freezing interface of the sample, as it is impossible to determine visually. The effect of the needle diameter on the freezing of the slurry is negligible, as the diameter of the needle is less than one twentieth of that of the tube, and the probe is kept cool at a temperature of 0°C between measurements.



Figure 38: Freezing rate experiment setup

Calibration is performed with four thermocouples inserted in the sidewall of the polypropylene tube at regular intervals. As previously stated, this calibration is performed using deionized water, which has a freezing temperature of exactly 0°C. At regular time intervals, an infrared image will

be taken, the freezing interface of the sample will be measured, and the temperature of each thermocouple will be recorded. If an offset exists between the infrared temperature reading and the thermocouple readings, this offset will be used to correct the temperature measured by the IR camera for future experiments. Thus, the temperature measured by the IR camera can be approximated to be that of the slurry after calibration using the thermocouple measurement.

5.2.3 Reduction and sintering

It is also necessary to pursue reduction and sintering of the green bodies to produce stronger materials made of pure copper that can be directly characterized, without requiring any postprocessing techniques, such as the epoxy infiltration used in this study. Reduction is crucial to create a pure copper structure and must be investigated in future work.

5.2.4 Other future work

Once the reduction-sintering process is established, the samples must be infiltrated with a phase change material, which is currently intended to be paraffin wax, followed by experimental studies to verify the performance of these composite materials.

It is also possible to pursue less intrusive techniques for viewing the internal structure of the samples that will not damage them in the process. For example, microCT can be pursued where the microstructure of the sample can be viewed. This will give crucial information regarding the three-dimensional microstructure before and after sintering, and if the microstructure can be maintained after sintering.

Future work also includes investigating ball milling rather than sonication to be able to create larger batches of well-dispersed slurries at once. There are a few issues that must be addressed before ball milling can be used. First, ball milling parameters must be established such that minimal foam is formed. Ball milling also produces waste heat that may contribute to the formation of foams. Creating a sufficiently cold environment may be productive in limiting the amount of foam that forms during ball milling. However, different parameters must be explored to determine the optimal ball milling settings to produce the least foam possible while still creating well dispersed, stable slurries.

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