DETERMINING THE ROLE OF POROSITY ON THE THERMAL PROPERTIES OF GRAPHITE FOAM

by

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ABSTRACT

Graphite foams have high bulk thermal conductivity and low density, making them an excellent material for heat exchanger applications. This research focused on the characterization of graphite foams under various processing conditions (different foaming pressures and particle additions), specifically studying the effects of porosity on the thermal properties. The characterization of the foams included measuring cell sizes, percent open porosity, number of cells per square inch, bulk density, Archimedes density, compression strength, thermal conductivity, thermal resistance, and permeability. Several relationships between the structure and properties were established, and a recommendation for the processing conditions of graphite foams for the use in heat exchangers was determined.
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Chapter 1: Introduction

With light weight and high thermal conductivity, graphite foam is an excellent material for thermal applications, such as: radiators, evaporative cooling systems, heat sinks, and heat exchangers. The efficiency of these cooling systems may be improved by altering the shape of the foam through various machining patterns and by altering the initial structure of the foam through changing the processing conditions, which will be the primary focus for this project.

Previous work has shown that altering the foaming pressures significantly influences the structure and, therefore, properties of the material. Also, particles or other additives can modify the structure and properties of graphite foam depending primarily upon the material type, size, and concentration of the additives. Ultimately, the properties of graphite foam can be tailored through changing the processing conditions, but to completely optimize the material for a specific application would be extremely difficult considering the large number of possibilities for particle additives alone. Combinations of different material types, sizes, and concentrations are endless. Therefore, this study focuses mainly on the relationship between structure and properties and specifically concentrates on the porosity of the foam since more research in this area was needed.

The overall goal of this project is to explore the effects of porosity on the thermal properties of graphite foam, specifically investigating the influence of pore size, overall pore percentage, number of pores per unit volume, and anisotropy on the permeability and heat transfer characteristics. By determining relationships between the porosity and thermal properties of graphite foam, valuable information for the selection of structurally modified graphite foams can be established.

This research was supported by the Tank Automotive Research Development and Engineering Center (TARDEC) of the United States Army, who is investigating the use of graphite foam for heat
exchanger applications. Through their support, this study provides an in-depth porosity analysis for graphite foam which will be beneficial for this application as well as many others. As a result, the efficiency of heat exchangers may be greatly improved, and relationships are established between porosity and thermal properties of graphite foam.
Chapter 2: Background

2.1 Introduction to Graphite Foams

Foams are a type of cellular material and are generally classified by material type (metal, ceramic, polymer, or natural) and general structure (open versus closed-cell). Open-celled foams have interconnected cells, which allow the passage of a gas or fluid through the void space from one cell to the next. Closed-celled foams do not have interconnected cell openings, so gas can be trapped inside the cell. Examples of open and closed-cell foams can be seen in Figure 1 below (1), which show a nickel-chromium open-celled foam and an aluminum closed-celled foam. Foams could also have a combination of open and closed cells within the same sample, although foams typically consist of one type of cellular structure or the other.

![Open-celled foam and Closed-celled foam](image)

Figure 1: Open-cell versus closed-cell foam (1)

2.1.1 Overview of Carbon and Graphite

Carbon is a very unique element because depending on its crystallographic structure, the material can be thermally insulating or conducting (2). Carbon is element 6 of the periodic table and has limited long-range order. Graphite is an allotropic form of carbon, commonly consisting of layers of a hexagonal array of carbon atoms although it can also exist in a rhombohedral form (3). In the hexagonal form, graphene layers are stacked parallel to each other (in an ABA stacking sequence) as seen in Figure 2. The layers exhibit long-range order, which contribute to
the high thermal conductivity of graphite (2). Due to the crystallographic nature of graphite, the thermal conductivity is two orders of magnitude higher in the (001) plane compared to the plane perpendicular to that (4).

![Planar structure of hexagonal graphite](image)

**Figure 2: Planar structure of hexagonal graphite (5)**

### 2.1.2 Foam structure

The main structural characteristics that comprise foams are ligaments (which could also be referred to as struts), cells, and nodes. These are illustrated in Figure 3 (6) and described in the following paragraphs. The size, shape, direction, anisotropy, and uniformity of these features have a significant influence on the bulk properties of the material. The ligaments and nodes together establish the framework and structural integrity of the foam, whereas the cells contribute largely to the porosity and density of the bulk material.
The ligaments of the material are a highly aligned graphitic structure as seen in Figure 4 (6). Graphene layers typically run parallel to the cell structure and can have extremely high thermal conductivities on the order of 2300 W/(mK) (5), which contribute to the high bulk thermal conductivity of the foam.

The graphite foams in this study are all open-celled structures, although the foams may contain a small fraction of closed cells. Cell shapes for graphite foams are typically ellipsoidal or spherical, and the cell sizes vary depending primarily on the processing conditions but are generally on the order of a few hundred microns.
The nodes are the junctions where graphite ligaments meet. Since the graphite is coming together from different directions, the graphite planes are disrupted, and the nodes tend to be much more isotropic compared to the ligaments (7). This is especially evident when a graphite foam optical image is viewed with cross-polarized light and a wavelength retarder, which shows graphite planes oriented in one direction as blue and perpendicular to that appears yellow. A third color, magenta, is either graphite that is between the two orientations or isotropic graphite.

2.1.3 Development of Graphite Foam

Klett has previously reported a history on the development of graphite foam (2), which is summarized in the following paragraphs. Reticulated vitreous (meaning a network resembling glass) carbon foams, also called glassy carbon foam, were developed in the 1960’s. Vitreous carbon foams are void of graphitic structure and have large openings and linear ligaments (8) as seen in Figure 5 below. These foams were created through heat treating a thermosetting organic polymer foam (specifically by carbonizing polyesters, polyurethanes, or phenolics). The production of carbon foams from alternative precursors, the raw material to create the foams, was researched in the following decade.

Figure 5: Reticulated vitreous carbon (RVC) foam (8)
One alternative precursor, called pitch is a residue from the pyrolysis (decomposition of a chemical by heat) of an organic material or tar distillation and is essentially hydrocarbons and hydrocyclic compounds (3). Pitch is a thixotropic fluid, which is a substance that is gel-like at rest but fluid when agitated, and has a high viscosity at its softening point (9). The first pitch-derived foams were developed by Bonzom et al with petroleum-derived pitch, and in the late 1990s Stiller et al at West Virginia University produced the first coal-derived pitch foams.

A specific type of pitch called mesophase pitch has a complex mixture of hydrocarbons and contains anisotropic liquid-crystalline particles (3). This raw material was used to produce graphite foams in the early 1990s by Hager et al at the Wright Patterson Air Force Base Materials Lab. Then in 1997, James Klett at the Oak Ridge National Laboratory significantly reduced the steps required to make mesophase pitch-derived graphite foams, eliminating the need for traditional blowing and stabilization steps as seen in Figure 6. Additionally, the graphite foams developed at ORNL had significantly higher bulk thermal conductivities compared to earlier graphite foams.

![Figure 6: Foam processing diagram](image)

(a) Load mold with resin

- Depressurization ("Flash")

(b) Load mold with mesophase pitch

- Proprietary blowing step, 1 (a, 1)

- Carbonization, 900°C

- Graphitization, > 2600°C

- Oxidatively Sublime

- Thermoplastic

- Decompose "Flash"

- Heat under high pressure to just above softening point

- Graphite, N, N2, H2O

- Graphitization, > 2600°C

- Decompose "Flash"

Figure 6: Foam processing diagram a: traditional blowing technique b: process developed at ORNL (10)
2.1.4 Material Processing

The processing of graphite foam takes three main steps: foaming, carbonization, and a graphitization heat treatment. The foaming process creates the general structure of the foam, whereas the purposes of the carbonization and graphitization steps are to remove the residual volatile material and increase the strength of the material, respectively (2). Each of these steps is discussed in more detail below.

The foaming process involves heating a mesophase pitch precursor above its softening point. Once the mesophase pitch precursor melts, the pressure in the furnace is raised which is referred to throughout this document as the processing pressure. The pitch decomposes and begins to release volatile gas bubbles at nucleation sites, and these bubbles grow in the upwards towards the top of the pan since that is the unrestrained direction (bubble percolation). As the temperature is raised, the viscosity of the mesophase is increased and the pitch begins to pyrolyze (polymerize), capturing the bubbles in place and creating the foam. The temperature of the furnace is again increased so that the viscosity of the pitch is raised until it is infusible so that the foam would not melt during the subsequent processing steps.

As the bubbles grow during the foaming process, passageways are created for air to flow from one cell to the next, as illustrated in Figure 7 (11). These passageways or openings between cells are called open windows. Also evident in Figure 7 is that even though the bubbles initially form a small sphere, the bubbles can take on other shapes, such as a polyhedron or ellipse as they impinge on each other (12).
After the material structure is formed, the large billet of foam undergoes a carbonization process, which is typically between 975 and 1025 °C at a very slow rate. Carbonization is a process that increases the carbon content of a material through transforming organic material in an inert atmosphere.

The final stage of processing is a graphitization heat treatment and is normally conducted above 2200 °C. It is important to note the difference between graphitization and graphitization heat treatment. Graphitization is a solid-state transformation of thermodynamically unstable non-graphitic carbon into graphite by means of a heat treatment, and the graphitized carbon exhibits long-range 3D crystallographic order. A graphitization heat treatment, however, does not include any information on the degree of graphitization or the extent to which the graphite exhibits long-range order. The term graphitization is often incorrectly used when referring to the heat treatment without confirming the crystallographic structure through X-ray diffraction studies. Previous research on the graphite foams produced at ORNL have shown through transmission electron microscopy (TEM) and X-ray diffraction that the graphite crystals within the foams are highly aligned and exhibit long-range order, but the graphitization heat
treatment results in a foam structure that is only partially graphitic with small crystalline regions dispersed among other non-crystalline region (2).

The carbonization and graphitization heat treatment rates strongly influence the defects present in the final material. The strain energies and stresses generated during the heat treatments can cause microcracks, lattice damages, and delamination of the graphite planes (5). With increased carbonization and graphitization heat treatment rates, the crystal structure is more likely to become disrupted, significantly hindering the final material properties (13).

### 2.1.5 Influence of Particle Additives

Various additives can also be used during the foaming process to significantly alter the structure and properties of the foam. Nucleating agents, which aid the formation of bubbles along the liquid-solid interface, are defined as a finely dispersed solid phase throughout a liquid system and can vary by material type, size, concentration, or shape (12). The nucleating agents reduce the surface tension between the liquid mesophase pitch precursor and the solid particle or additive.

Figure 8 shows a schematic of how a solid particle interacts with a polymer, which in the case of the graphite foam is the mesophase pitch, and the gaseous bubbles that begin to form. Because the surface energies of various particles can vary widely, the wetting angle between the mesophase pitch and solid particle can be significantly different for various additives. Ultimately, the nucleating agents can control the number density and size distribution of the pores within the final foam structure (14).

**Figure 8: Particle interaction with gas and polymer (11)**
The Gibbs free energy is the barrier needed to overcome for nucleation to occur and has the strongest impact on the resulting foam structure (14). With particle additions in the mesosphase pitch, the Gibbs free energy is more heterogeneous and is lowered according to the equations below:

\[ \Delta G_{\text{heterogeneous}}^* = \Delta G_{\text{homogeneous}}^* f(\theta) \quad \text{Equation 1 (11)} \]

\[ f(\theta) = \frac{(2 + \cos \theta)(1 - \cos \theta)^2}{4} \quad \text{Equation 2 (11)} \]

Where: \( \Delta G_{\text{heterogeneous}}^* \) = heterogeneous Gibbs free energy

\( \Delta G_{\text{homogeneous}}^* \) = homogeneous Gibbs free energy

\( f(\theta) \) = is the heterogeneity factor

The heterogeneity factor, \( f(\theta) \), accounts for the reduction in surface tension between the liquid mesophase and the solid particle. This factor determines the extent to which the heterogeneous Gibbs free energy is lowered compared to homogeneous nucleation, and the effect is shown graphically in Figure 9 below.

Figure 9: Heterogeneous nucleation has a lower Gibbs free energy (11)
2.2 *Macroscopic Material Structure*

The structure of graphite foams is very complex and difficult to accurately model due to the randomness and variety of the cell sizes and configurations. Cell sizes, shapes, and amounts may vary depending on the specific location being analyzed. The bottom portion of graphite foam is reported to have a slightly lower percent porosity compared to the middle or top portion of the sample due to gravity during the foaming process (15). Additional factors that may cause a density gradient within the foam rely on the viscosity of the mesophase pitch precursor (5), (8).

The macroscopic orientations of the planes and directions for a bulk piece of graphite foam can be seen in Figure 10 below. The z direction is the foaming direction since the x and y planes are constrained by the pan, thus restricting growth. The orientations seen below for both the planes and directions are used throughout this document.

![Figure 10: Macroscopic directions and planes](image)

2.2.1 *Density*

The bulk density of a material is quite simply the mass per unit volume. Graphite foams have low bulk densities, typically ranging from 0.2 to 0.6 g/cm$^3$ (8). The true (also referred to as apparent or absolute) density is the mass per unit volume of material, which excludes all voids or pores. A common way to measure the bulk density of a porous material is based on Archimedes’ principle, which states that a body submerged in a fluid will be buoyed up by a force equal to the
weight of the fluid it displaces. Equation 3 shows how this principle can obtain the bulk density of a material.

\[
\rho_{\text{bulk}} = \frac{m_{\text{dry}}}{m_{\text{wet}} - m_{\text{suspended}} + m_{\text{wire}}} \quad \text{Equation 3}
\]

Relative density is a ratio of the bulk density to the density of the solid material. This is a common calculation for foams and is related to the porosity as seen in Equation 4.

\[
R = \frac{\rho_{\text{b}}}{\rho_{\text{s}}} = 1 - \frac{P}{100} \quad \text{Equation 4}
\]

### 2.2.2 Pore Geometry

With open celled foams, diameters can be measured for both the overall cell size and the cell windows, which connect one cell to another on the opposite side. Also, ligament thicknesses can be measured from one cell wall to the wall of a neighboring cell. Examples of the cell diameter, window diameter, and ligament thickness can be seen in Figure 11 (16) below, which is graphite foam with five weight percent alumina powder.

![Figure 11: Scanning Electron Microscope image of graphite foam showing structural features](image)
A wide range of cell sizes have been reported for graphite foams, but the values are typically on the order of 100 microns (17). One of the major influences on the resulting cell size is the processing pressure. The growth of the pores is confined due to the processing pressure (9) because a higher pressure requires a higher temperature for gas evolution of the mesophase pitch, resulting in smaller pore sizes (5).

Other factors that strongly affect the cell sizes are the properties of the mesophase pitch precursor, specifically the viscosity, melting temperature, and pyrolysis temperature (5). A higher viscosity mesophase pitch inhibits molecular mobility and restricts the growth of the bubbles during the foaming process (8). The resulting foam has thicker cell walls and a higher density (9).

2.2.3 Porosity

As noted earlier, there are two major classifications for porosity: open and closed. Closed porosity may also be referred to as internal porosity and is the ratio of the volume of void space within the material that is not accessible from the exterior, to the bulk volume (18). Open porosity, which can also be called apparent or interconnected porosity, is the ratio of the volume of void space within the material that is accessible from the exterior, to the bulk volume (18). The total porosity of a material is the sum of the open and closed porosity.

For the graphite foams in this study, a majority of the porosity is open, although there is a small percentage of closed porosity within the material. Also notable is the porosity embedded within the graphite ligaments, which is not as obvious as the open and closed porosity of the cells, but still contributes to the overall porosity of the graphite foam. The percent of open porosity can be measured based on Archimedes principle using Equation 5, which is slightly different than the bulk density equation mentioned earlier (Equation 3).
\[
\text{open porosity} = \frac{\text{mass}_{\text{wet}} - \text{mass}_{\text{dry}}}{\text{mass}_{\text{wet}} - \text{mass}_{\text{suspended}} + \text{mass}_{\text{wet}}} \quad \text{Equation 5}
\]

2.2.4 Anisotropy of Cell Shapes

Foams typically have cells that are elongated in the foaming direction due to the gas bubbles expanding in the direction with the minimal local stress. This is schematically illustrated in Figure 12, which shows the cell structure of foam parallel and perpendicular to the foaming direction (19). Typically, cells normal to the direction of foaming defines the z plane. The cells are generally elongated in the foaming direction, so the cells appear ellipsoidal when viewed in the x-y plane and spherical when viewed in the z plane.

![Figure 12: Anisotropy of cell structure (19)](image)

This anisotropy is evident in the Scanning Electron Microscope (SEM) images of graphite foam in Figure 13 (foam with five weight percent tungsten particles studied as part of Mueller’s senior design project) (16), which are of the same sample but in two different planes. The image on the left side consists of cells that appear to be spherical, but those cells are actually ellipsoids cut perpendicular to the elongated direction. The image on the right clearly shows that the cells are ellipsoids, and the z-direction is shown by the arrow drawn.
2.3 Structure-Property Relationships

2.3.1 Thermal Conductivity

Thermal conductivity, typically expressed in Watts per meter-Kelvin, is a property used to describe its ability to transfer heat under steady state conditions. High thermal conductivity materials are generally very good conductors of heat, whereas materials with very low thermal conductivity are insulators. The thermal conductivity of graphite foam is typically calculated by first measuring the thermal diffusivity and density of the material, and then using Equation 6 below:

\[ \alpha = \frac{k}{\rho \cdot C_p} \]

Equation 6

where:
- \( k \) is the bulk thermal conductivity of the foam (W/mK)
- \( \alpha \) is the measured thermal diffusivity (m\(^2\)/s)
- \( \rho \) is the bulk density (g/cm\(^3\))
- \( C_p \) is the specific heat, and for graphite foam equals 840 J/kg\(^\circ\)C

The thermal diffusivity is a measure of the rate at which heat accumulates and flows through a material, so the higher the thermal diffusivity, the faster a temperature passes from one
side of a material to the opposite side. The units for this property are a length squared per unit time, and the thermal diffusivity for graphite foam is typically expressed in cm²/second.

The graphite ligaments are an important attribute for the thermal conductivity of the foam. The individual ligaments have thermal conductivities up to 2300 W/(m-K), however the bulk thermal conductivities are significantly lower and are up to 180 W/(m-K) in the z-plane (5). The bulk density of the material strongly influences the resulting thermal conductivity. As seen in Figure 14, thermal conductivity increases with increasing density. This can be rationalized because with an increased density, more solid graphite is present which transmits the heat more effectively than air.

![Graph showing thermal conductivity vs. density](image)

**Figure 14: Thermal conductivity increases with increasing density (5)**

The graphitic planes can be disrupted through the addition of particles to the mesophase pitch precursor, resulting in a considerable decrease in thermal conductivity. As seen in Figure 15 (6), foams with carbon particle additions of six weight percent or more resulted in a substantial decrease in thermal conductivity.
Figure 15: Increased amount of carbon particle additives resulted in lower thermal conductivity

Another major influence for the bulk thermal conductivity of graphite foam is the anisotropy. Figure 16 shows that thermal conductivities in the z-direction (parallel to the foaming direction) are significantly higher compared to thermal conductivities in the x and y directions. There are two major reasons for the z direction thermal conductivity being so much higher: elongation of the ligaments and orientation of the graphitic crystals in the z direction.

Figure 16: Anisotropy effects on thermal conductivity (5)
As discussed earlier, the ligaments are elongated in the z direction due to the ellipsoidal pore structure, so the thermal conduction along the graphite planes is less complicated. The path for heat flowing through the graphite ligaments is less tortuous route compared to the x and y directions as illustrated in Figure 17, which shows an idealized model of hexagonal pores and the flow of heat through the material. The path for the z direction is more straightforward, which would allow for faster heat transfer through the material.

![Figure 17: Illustration of flow paths in different planes of an idealized model](image)

The crystallographic nature of the graphite also causes anisotropy of the thermal conductivity (20). The preferred orientation of the mesophase crystals is parallel to the cell walls during the foaming process due to biaxial extension (13), (9), (8). After the graphitization heat treatment, the oriented mesophase domains create highly aligned graphitic planes, which significantly contribute to the thermal conductivity of the foam. A mesophase pitch with a lower viscosity results in better re-orientation of the mesophase domains parallel to the ligaments, which translates to better alignment of the graphitic crystals and higher thermal conductivity (8).
2.3.2 Permeability

Permeability describes the ease at which a gas or fluid passes through a material. For a given inlet face velocity or speed of a gas or fluid entering one side of the material, a lower pressure drop measured across the substance indicates higher permeability. The process for measuring the permeability is discussed in detail in the procedure section.

Because cell windows allow a gas or fluid to flow through graphite foam, the permeability is hindered not only by small pore sizes but small window sizes between the cells as well. (21). The larger the size of the cell windows and the higher the quantity, the more easily a fluid can transfer through the material. The quantity and size of open windows are extremely important for graphite foam in order to increase the permeability through the material and dissipate heat away from a system.

Figure 12 (6) shows that open porosity increases with an increasing concentration of particle additions to the mesophase pitch precursor, which results in more permeable foams. Another way to obtain more open and permeable graphite foams is through changing the processing pressures during the foaming procedure. Lower processing pressures have resulted in more open and permeable foams (22).
2.3.3 Heat Transfer Coefficient and Thermal Resistance

The heat transfer coefficient (HTC) is a measure of the quantity of heat that passes between a fluid and solid. The HTC can be calculated as seen in Equation 7.

\[
Q = h_{loc} A \Delta T \quad \text{Equation 7 (23)}
\]

Where: \( Q \) = the overall heat transfer per unit area of material

\( h_{loc} \) = the localized heat transfer coefficient

\( A \) = the overall surface area of heat transfer

\( \Delta T \) = the temperature difference between the surface and the fluid

Since the surface area is extremely difficult to measure in graphite foams, an effective HTC replaces the localized HTC, so the equation changes slightly to Equation 8:

\[
Q = h_{eff} \Delta T \quad \text{Equation 8}
\]

The temperature difference is the driving force for heat transfer and is calculated as shown in Equation 9.
\[ \Delta T = \frac{T_e - T_i}{\ln \left( \frac{T_h - T_i}{T_h - T_e} \right)} \]  
\text{Equation 9 (23)}

Where: 
\( T_i \) = the inlet fluid temperature
\( T_e \) = the exit fluid temperature
\( T_h \) = the temperature of the hot source

More porous foams with larger cell diameters have improved heat transfer capabilities due to the increased surface area of the material (15). The large surface area available in graphite foam contributes to the high heat transfer coefficients of foam-based heat exchangers, which can be up to two orders of magnitude higher compared to conventional heat exchangers (24). With a higher heat transfer coefficient, heat exchangers could be significantly lighter and smaller by using the graphite foam.

The thermal resistance is a measure of a materials ability to prevent heat from flowing through it and is the temperature difference along a heat flow path dived by the power dissipated along that path. The thermal resistance can easily be calculated from the HTC and the area of the hot source because the thermal resistance is equal to the thermal impedance divided by the area of the hot source, and the thermal impedance is simply the inverse of the HTC (25).

2.4 Three Dimensional Modeling
2.4.1 Theoretical Modeling

Theoretical 3-D models have been developed for graphite foam, however a major problem with theoretical models is the creation of a homogeneous, isotropic model for a heterogeneous, anisotropic material. Several important aspects are lacking in these idealized models, most of which neglect the non-uniformity of cell sizes, anisotropy of thermal transport, and variety of cell shapes. Some models, however, account for the differences in cell shapes by
including a pore shape factor, but this factor is only accurately known for low porosity foams (17).

Based on theoretical models, thermal transport studies have been conducted to predict the resulting properties of graphite foam. The common method for composite analysis using the rule-of-mixtures does not apply to graphite foam. This approach, using the volumes of air and graphite, is not correct due to the non-uniformity and tortuous heat flow path through the graphite ligaments (26). Other calculations and models have been developed to account for the anisotropy of the matrix through the use of a “conduction parameter” which considers the influence of pore shape and volume fraction on the bulk thermal conduction (26). Due to the non-uniformity and anisotropy of cells within graphite foam, a theoretical model is extremely difficult to create and may not accurately represent the true material structure or resulting properties.

2.4.2 Serial Sectioning

Based upon the Cavalieri method (27), which estimates an object’s volume through the evaluation of thin slices spaced equally apart, serial sectioning reconstructs those slices into a three dimensional object. The serial sectioning process yields an unbiased estimate of the object’s volume, but the method may not be very precise unless the shape of the object is fully known beforehand (27). Precise information is not known between the slices, so the shorter the distance between the slices, the more accurate the three dimensional model will be.

A 3D model of graphite foam was created at the Air Force Research Laboratory (AFRL) using automated serial sectioning and light microscopy (21). The graphite foam was infiltrated with an epoxy resin, and images were taken at specific depths. Successive images were then rendered together to create a 3D model using as seen in Figure 19. Finally, the thermal and
mechanical properties of the model were explored using finite element modeling and were consistent with experimental results (21).

![Three-dimensional model of AFRL graphite foam](image)

**Figure 19: Three-dimensional model of AFRL graphite foam (21)**

### 2.4.3 Photogrammetry

Photogrammetry is a term used to describe spatial measurements through images (28). At least two or more images are needed because a single image lacks depth information. These images are taken at different perspectives, which are generally the positive and negative of the same tilting angle to create what stereo-pair or stereoscopic images. With the different perspectives and laws of projection, a three dimensional object can be created through matching the homologous points between the two images and accounting for the tilt angle (28). This three-dimensional object is generally referred to as a Digital Elevation Model (DEM), and the depth information is calculated through Equation 10 below:

\[
h = \frac{d_1 \cos \theta_2 - d_2 \cos \theta_1}{\sin(\theta_2 - \theta_1)} \quad \text{Equation 10 (29)}
\]

Where: \( \theta_1 \) and \( \theta_2 \): the tilt angles

\( d_1 \) and \( d_2 \): disparity (distance between homologous points at different tilt angles)

\( h \): height or depth

A Scanning Electron Microscope (SEM) is a commonly used tool for photogrammetry due to its high resolution, a large depth of field, and a wide range of magnifications to capture
the images (28). A major limitation to the SEM for photogrammetry, however, is that the current maximum working distance is restricted to 10 mm. Due to this restriction and the large cell size of graphite foam, the magnification was too high and only allowed a few pores to be visible. Although photogrammetry may be an excellent technique for materials with pore sizes in the nanometer range, it is not currently a feasible technique to obtain a significant amount of information for materials with large cell sizes like graphite foam.

2.4.4. Stereology

Stereology is essentially the deduction of a three-dimensional structure based upon only two dimensions. More specifically, stereology is a statistical technique to find the number of particles of a particular size and shape within a given volume based upon the number of observations within a random cutting plane (30). The main purpose of stereology is to obtain quantitative information from microscopic images (31). Unlike theoretical modeling, serial sectioning, or photogrammetry, the goal of stereology is not to generate or recreate a three-dimensional structure of a material, but rather to apply information from two dimensional sections to infer three dimensional structural features.

According to Howard and Reed, stereology is fundamentally statistical in its nature, relying on sampling design and theory (32). Similar to how a survey of a sample of people may statistically infer information about the larger population, a sample of a material may provide information about the larger bulk material. Two very important considerations for this to be correct are that the sample size must be large enough to accurately representative the larger population and the sampling must be random.

In stereology, “particles” is a loosely defined term that can be used to describe any discrete physical object in the bulk material such as: crystalline grains in a metal, reinforcements
in composites, cells in biological tissue, pores in foam, etc. (31). Several different particle systems exist, which depend upon the homogeneity of both particle sizes as well as shapes throughout the material. A monodispersal system contains particles of the same size and shape, a polydispersal system has particles of the same shape but with a variety of sizes, and a multidispersal system includes both varied shapes and sizes (30). With the random sampling of a multidispersal system, other factors emerge. As seen in Figure 20, it is highly unlikely that the random cutting plane would pass through the true center of a particle, and in some cases the random cutting plane may not pass through the particle at all.

2.4.5 Summary of 3D Modeling

Three-dimensional modeling of graphite foams is extremely complicated due to the heterogeneity, anisotropy, and size of the cells. Thus far, the best method seems to create a three-dimensional model seems to be serial sectioning. Although the original intent for this project was to include either photogrammetric or stereological analysis, the photogrammetry is not a feasible option due to the large cells sizes of the graphite foams in this study, and the stereology is too complex for the scope of this research.
Chapter 3: Procedure

3.1 Material Processing

Graphite foam samples were processed by the Carbon Materials Technology group at Oak Ridge National Laboratory. A mesophase pitch supplied by Koppers™ was used as the precursor to make the foam, and a total of eight bulk pieces of foam were produced with the foam processing specifications listed in Table 1. Four different pressures with and without the additions of five weight percent particle additives were used during the foaming process in order to significantly alter the structure of the foam.

<table>
<thead>
<tr>
<th>Pressure (MPa)</th>
<th>Pressure (psi)</th>
<th>Particles (weight percent)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.689</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>0.689</td>
<td>100</td>
<td>5%</td>
</tr>
<tr>
<td>1.379</td>
<td>200</td>
<td>0</td>
</tr>
<tr>
<td>1.379</td>
<td>200</td>
<td>5%</td>
</tr>
<tr>
<td>2.068</td>
<td>300</td>
<td>0</td>
</tr>
<tr>
<td>2.068</td>
<td>300</td>
<td>5%</td>
</tr>
<tr>
<td>2.758</td>
<td>400</td>
<td>0</td>
</tr>
<tr>
<td>2.758</td>
<td>400</td>
<td>5%</td>
</tr>
</tbody>
</table>

For the foams with the addition of five weight percent particles, the mesophase pitch was mixed with the particles in ethanol and ball-milled to ensure thorough mixing. Afterwards, the liquid mixture was poured into a glass container and the ethanol evaporated. The mesophase pitch with particles was then placed in an aluminum pan along with another pan of just the
mesophase pitch and processed at one of the pressures listed in Table 1. The same procedure was repeated for each processing pressure.

Following the foaming process, each sample was carbonized in an atmosphere of nitrogen at 1000°C and a rate of 0.2°C/min. The final processing step was graphitization, which occurred at 2800°C in an atmosphere of argon and nitrogen.

### 3.2 Optical Microscopy

For each block of foam, samples were cut using a diamond saw in planes parallel (z) and perpendicular (x-y) to the foaming direction. All of the samples were taken from the center area of the foam except for the 1.379 MPa (200 psi) sample, which had two samples cut in the z direction directly above and below each other so a comparison between the top half and bottom half could be made. After the foams were cut, each sample was infiltrated with an epoxy resin and placed in a vacuum chamber to eliminate a large number of air bubbles trapped within the cells. Standard grinding and polishing techniques were used to finish preparing the samples.

Images were acquired with a Leica DMI5000M microscope and the Leica Application Suite 3.0.0 software program. Due to the significantly large cell sizes in graphite foams, an automated stage was used with a multistep function to collected adjacent images by moving a specific distance horizontally and vertically and then merging neighboring images together. For each sample, a total of forty-nine images were collected using a 7 x 7 grid before they were automatically combined into one large image. To accomplish this, the four corners of the foam sample were selected and each position was saved along with the depth of focus for each location. During the image collection, a predictive focus feature was used to estimate the depth of the stage based upon the location and the depth of stage saved for each of the corners. The final, merged images for each sample can be seen in Appendix A.
3.2.1 Measurement of Cell Sizes

After the optical images were collected, ImagePro® Plus version 6.2 was used for the measurement of cell sizes. A majority of the cells were either spherical or ellipsoidal in shape and both the longest and shortest distances were measured as seen in Figure 21 below.

![Image of cell sizes measurement](image1.jpg)

Figure 21: Measurement of cell sizes in the 2.068 MPa (300 psi) x-y plane sample

Although most of the cell sizes were easily measured, a major difficulty was the measurement of uniquely shaped cells. Several examples of abnormal shaped cells are seen in Figure 22 below, many of which appear to be caused by cells nearly growing together or shortly thereafter.

![Examples of abnormal shaped cells](image2.jpg)

Figure 22: Examples of abnormal shaped cells
Another problem measuring the cell sizes was the lack of ligament walls surrounding the cells, particularly in the foams with lower processing pressures. The most difficult sample to measure was the 0.689 MPa (100 psi) with particles in the z plane, which is shown below in Figure 23. The lack of ligament walls causes a slight bias towards smaller cells since those are more likely to be measurable.

![Figure 23: Openness of foam causes a large number of pores to be immeasurable- 0.689 MPa (100 psi) with particles; z plane](image)

3.2.2 Measurement of percent porosity

ImagePro® Plus was used to measure the percent porosity of the foams from the optical images. To accomplish this, the number of pixels for the ligaments were measured for each sample and subtracted from the total number of pixels. Then, the number of pixels for the pores was divided by the total number of pixels for each image as seen in Equation 11.

\[
\text{Percent Porosity} = \frac{\text{total # of pixels within image} - \text{# of pixels in ligaments}}{\text{total # of pixels within image}}
\]

Equation 11

To measure the number of pixels for the ligaments, the intensity range had to be adjusted within the count/size command. It was very important to select a consistent histogram range for each sample in order to obtain repeatable data. For all of the foam samples analyzed, the
intensity range selected was 115-255. Next, the ‘filled’ option was selected within the outline style and the count command was selected, which results in image with the ligaments highlighted as seen in Figure 24. Viewing the statistics showed the sum of the number of pixels within the ligaments; this was then used along with the total number of pixels within the image to calculate the percent porosity.

![Figure 24: Ligaments highlighted for the 1.379 MPa (200 psi) sample in the z plane](image)

### 3.3 Scanning Electron Microscopy (SEM)

Samples were cut from each block of foam and in both the x-y and z-planes and viewed in a Hitachi S3400N microscope. Unlike the optical microscope, the SEM images could not automatically be combined to generate one larger image. Therefore, images were taken at the lowest magnification setting in order to obtain as large of an image as possible.

### 3.3.1 Measurement of open windows

The open windows were measured from the SEM images, again using the ImagePro® Plus software. The freeform area of interest (AOI) and magic wand tools were used to automatically select the open windows. The freeform AOI function allowed for any area to be selected, regardless of shape, and the magic wand function automatically traced an area based upon the
differences in gray-scale colors, similar to a ‘find edges’ function. An example of selecting and filling an open window with the freeform AOI magic wand tool is shown in Figure 25 below.

![Open pores were individually selected with the freeform AOI and magic wand tools then filled (Figure 25)](image)

Figure 25: An open pore selected and filled in the 0.689 MPa (100 psi) z plane sample

Figure 26 below shows the initial 0.689 MPa (100 psi) z plane image and the completed image ready for measurement. Similar to the measurement of percent porosity, the percent open porosity was completed using the count/size command to measure the total number of pixels within the open pores. The total number of pixels within the open pores was then divided by the total number of pixels in the entire image to obtain the percent open porosity. All of the SEM images used to analyze the percent porosity (both before and after the open pores were highlighted) can be found in Appendix B.

![0.689 MPa (100 psi) z plane sample before and after the selection of open pores (Figure 26)](image)

Figure 26: The 0.689 MPa (100 psi) z plane sample before and after the selection of open pores

### 3.4 Bulk Density

The bulk density was measured on cylindrical samples that were later used for testing the thermal conductivity of the foam. The height and diameter of each sample was measured with calipers and the bulk density was calculated by simply using Equation 12:
\[ \text{density} = \frac{\text{mass}}{\text{volume}} \]  

Equation 12

3.5 Compression Tests

Cylindrical samples were cut with a drill press using a 2 cm diameter cutting tool and then were sanded to approximately 2.6 cm in height. The masses of each sample were recorded as well as the diameter and height dimensions in order to calculate the bulk density. The dimensions of the sample were entered into a Labview® program for running compression tests, and the foam specimen was placed between the two metal platforms. Samples were crushed at a velocity of 0.00423 cm/s (0.1 in/min) to 20% reduction in height and the maximum stresses achieved were recorded.

3.6 Archimedes Density

Archimedes density, also called immersion density, was performed on four samples for each processing condition to obtain the bulk density of the foams. First, a sample was weighed while it was completely dry and then placed in a beaker with ethyl alcohol and a vacuum was pulled for several minutes to ensure the open pores would be filled with the ethanol. Next, the beaker was placed on a stand over a balance, and the temperature of the ethanol and its corresponding density which was looked up on a chart were recorded. A wire was hung so it was below the ethanol’s surface but not touching any sides of the beaker, and the wire weight was recorded. The foam sample was lifted onto the wire with tweezers and the suspended weight was recorded. Lastly, the sample was removed from the ethanol, quickly blotted, and weighed to obtain the wet weight. After all the measurements were recorded, the Archimedes densities, percent open porosities, closed densities, and percent theoretical densities were calculated using the following equations:
3.7 Thermal Conductivity

To obtain the thermal conductivity of the foam, first the bulk density was determined as described earlier. Next, the thermal diffusivity was found through using a xenon flash diffusivity system in the High Temperature Materials Laboratory (HTML) at ORNL, which is illustrated in Figure 27.

In this method, liquid nitrogen was inserted into the chamber to create an extremely cool environment. Next, the sample was mounted onto the chamber and turned to face the xenon flash lamp. The length of the sample was entered into the computer and the test began. When the xenon lamp flashed, a pulse of heat lasting less than 1 millisecond was discharged and traveled through the foam. The temperature change was measured between the front and back faces of the
material by an Indium Antimonide (InSb) infrared detector. Three measurements of the thermal diffusivity were taken for each sample.

After the bulk density and thermal diffusivity were measured, the bulk thermal conductivity was measured using the equation below:

\[ \alpha = \frac{k}{\rho c_p} \]  

**Equation 17**

where:

- \( k \) is the bulk thermal conductivity of the foam (W/mK)
- \( \alpha \) is the measured thermal diffusivity (m²/s)
- \( \rho \) is the bulk density (g/cm³)
- \( C_p \) is the specific heat, and for graphite foam equals 840 J/kg°C

### 3.8 Permeability and Heat Transfer

Both the permeability and heat transfer capabilities were tested in the same device at ORNL. A 5.08 cm x 5.08 cm x 0.66 cm (2” x 2” x 0.26”) sample of foam was cut in the z plane for the testing rig, and two samples were cut for each processing condition to explore two different methods of attachment: brazing and soldering.

#### 3.8.1 Methods of Attachment

The first method of attachment that was explored was brazing. The foam samples were coated with TN700 and placed onto 5.08 cm x 5.08 cm (2” x 2”) copper plates. The TN700 powder was supplied by Material Resources International and was mixed with a braze-binder gel to create a paste. The samples were then placed in a furnace and backfilled twice with Argon to pull a vacuum.

Soldering the samples to the copper plates was also examined. First the 5.08 cm x 5.08 cm x 0.66 cm (2” x 2” x 0.26”) pieces of graphite foam were electrolessly copper plated using a technique developed by Poquette et. al. (33). Through this process, the graphite foam is placed in
a chemical bath (consisting of copper sulfate pentahydrate, EDTA, sodium hydroxide, and formaldehyde) for several minutes until the material is coated with a copper layer. After the samples were rinsed and dried, a 50-50 lead-tin soldering paste was brushed onto one side of the foam as well as the top of a copper block. The foam was then placed on top of the copper block and heated on a hot plate until the soldering paste melted.

### 3.8.2 Equipment Set-up

Figure 28 shows a schematic of the heat transfer equipment for testing the permeability and thermal resistance of the foams. All the materials seen in the figure were machined from phenolic resin. An o-ring was placed along the bottom plate of phenolic and vacuum grease was put around the exposed surface of the o-ring. Then the top phenolic part was aligned with the bottom and tightly sealed using nuts and bolts around the perimeter. A heater was placed in the top phenolic piece and tightly screwed in place. Permatex® High Temperature RTV silicone was placed between the outer edges of the heater and the phenolic to provide a tight seal and minimize the potential for air leaks.
A graphite foam sample was placed in the circular opening of the top phenolic rectangular piece with compressible foam underneath. The purpose of the compressible foam was to prevent air leaks underneath the graphite foam or around the sides of the material. After the sample was in place, ThermalCote® thermal paste was spread on the top of the copper plate as well as the bottom of the heater block.

Next, the cylindrical phenolic pieces were aligned with the bottom pieces and pressed downwards into the system. The heat block and the copper plate, which contacted the graphite foam, were tightly screwed together. A thermocouple used to measure the temperature of the foam top was inserted within a hole of the heater block that extended through most of the copper block. Another thermocouple was taped to the top of the heater block. Finally, the lid was tightly sealed on the system, and the test was ready for data collection.
3.8.3 Permeability and Heat Transfer Testing

As seen in Figure 28, the air flows into the system through the foam and out on the opposite side, with pressure taps directly before and after the air flows through the foam. The amount of air initially flowing into the system can be controlled by turning a valve to the desired air flow rate, which is termed face velocity. The pressure drop between the air flow in and out of the foam is a measure of the permeability, and the lower the pressure drop, the more permeable the foam. For the samples studied in this project, the face velocities were increased from 0 to 13.25 m/s (0-300 Ipm) in increments of 0.95 m/s (20 Ipm) and the pressure drops were recorded.

The heater was turned on to a power setting of approximately 100 Watts and the air flow was adjusted to 7.1 m/s (150 Ipm). After the temperatures reached steady state, readings of the pressure drop, current, voltage, air inlet temperature, heat temperature, foam top temperature, and air outlet temperature were recorded. These readings were used to calculate the heat transfer coefficient and thermal resistance as described in Chapter 2 section 3.3. The air flow was then adjusted to 9.46 m/s (200 Ipm) and 11.83 m/s (250 Ipm) and readings were taken after the system reached steady state.

3.8.4 Solutions to Air Leaks

Several changes were made to the system after not obtaining repeatable permeability data. It was suspected that air was leaking around the circumference of the cylindrical phenolic insert, so a gasket was placed around the outer surface using Weldwood® contact cement, which dried over a weekend. Although the gasket significantly improved the repeatability of the permeability, there was still concern that air was somehow leaking around the foam. This concern increased when it was noticed that tightening the bolts on the phenolic lid decreased the pressure drop of the system (meaning increasing permeability), which was counterintuitive to
what was expected. It was finally realized that tightening the bolts actually lifted up part of the
phenolic piece below it. To solve this problem, a C-clamp was used to tightly seal the cylindrical
insert with the rectangular phenolic piece. After using the C-clamp, the permeability data was
very repeatable.
Chapter 4: Results and Discussion

4.1 Optical Microscopy

Measurements of cell sizes and percent porosity were taken for the 0.689, 1.379, and 2.068 MPa (100, 200, and 300 psi) samples both with and without particle additions and in the x-y and z planes. The images for the 2.758 MPa (400 psi) samples were unable to be collected since the automated stage for the microscope had to be machined. Other microscopes either did not have the low magnification necessary to view a large area of cells or the resolution was not high enough to collect accurate measurements of cell sizes.

4.1.1 Cell Sizes

Tables 2 and 3 below summarize the average cell sizes and their standard deviations as well as the anisotropy ratios for the x-y and z planes, respectively. The lower processing pressure foams have larger cell sizes in both the major and minor axes. Additionally, the anisotropy ratio is higher in the x-y plane compared to the z plane due to the elongated pores parallel to the foaming direction.

<table>
<thead>
<tr>
<th>Processing Pressure (MPa)</th>
<th>Processing Pressure (psi)</th>
<th>Particles (weight percent)</th>
<th>Average minor axis (microns)</th>
<th>Standard deviation (microns)</th>
<th>Average major axis (microns)</th>
<th>Standard deviation (microns)</th>
<th>Anisotropy Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.068</td>
<td>300</td>
<td>0%</td>
<td>622</td>
<td>262</td>
<td>756</td>
<td>303</td>
<td>1.25</td>
</tr>
<tr>
<td>1.379</td>
<td>200</td>
<td>0%</td>
<td>649</td>
<td>244</td>
<td>955</td>
<td>363</td>
<td>1.50</td>
</tr>
<tr>
<td>0.689</td>
<td>100</td>
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<td>1006</td>
<td>458</td>
<td>1329</td>
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<td>1.35</td>
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<td>608</td>
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<td>955</td>
<td>386</td>
<td>1209</td>
<td>468</td>
<td>1.29</td>
</tr>
</tbody>
</table>
Table 3: Average cell sizes (z plane)

<table>
<thead>
<tr>
<th>Processing Pressure (MPa)</th>
<th>Processing Pressure (psi)</th>
<th>Particles (weight percent)</th>
<th>Average minor axis (microns)</th>
<th>Standard deviation (microns)</th>
<th>Average major axis (microns)</th>
<th>Standard deviation (microns)</th>
<th>Anisotropy Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.068</td>
<td>300</td>
<td>0%</td>
<td>559</td>
<td>250</td>
<td>662</td>
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<td>1.22</td>
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<td>665</td>
<td>263</td>
<td>811</td>
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<td>1.24</td>
</tr>
<tr>
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<td>100</td>
<td>0%</td>
<td>1118</td>
<td>552</td>
<td>1353</td>
<td>601</td>
<td>1.27</td>
</tr>
<tr>
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<td>300</td>
<td>5%</td>
<td>575</td>
<td>224</td>
<td>666</td>
<td>240</td>
<td>1.19</td>
</tr>
<tr>
<td>1.379</td>
<td>200</td>
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<td>560</td>
<td>274</td>
<td>694</td>
<td>324</td>
<td>1.26</td>
</tr>
<tr>
<td>0.689</td>
<td>100</td>
<td>5%</td>
<td>884</td>
<td>439</td>
<td>1147</td>
<td>509</td>
<td>1.23</td>
</tr>
</tbody>
</table>

The number of cells measured in both the x-y and z planes for each sample is summarized in Table 4. Also, an estimate of the number of cells per square inch was calculated from the number of cells measured relative to the total dimensional area of the image and converted to square inches. For example, the first row in Table 4 was calculated by the following:

\[
\frac{\text{Number of cells measured}}{\text{Total image area (pixels)}^2} \times \frac{1.3^2 \text{ (pixels)}^2}{\text{ (microns)}^2} \times \frac{25,400^2 \text{ (microns)}^2}{\text{ (inches)}^2}
\]

\[
\frac{496}{383533056 \text{ (pixels)}^2} \times \frac{1.3^2 \text{ (pixels)}^2}{\text{ (microns)}^2} \times \frac{25,400^2 \text{ (microns)}^2}{\text{ (inches)}^2} = 1410 \frac{\text{cells}}{\text{in}^2}
\]

For all of the samples, the number of cells per square inch was higher in the z plane compared to the x-y plane, with exception of the 0.689 MPa (100 psi) with particles foam. This is most likely due to a large number of pores in the z plane of that sample being immeasurable due to the large amount of disruption of the graphite ligaments as explained in Figure 23 on section 2.1 in the procedure chapter. A higher number of cells per square inch in the z plane compared to the x-y plane can be explained by the cells having an elongated structure in the x-y plane. Additionally, the higher processing pressures had a higher number of cells per unit area.
This is rationalized because the higher processing pressures most restricted the growth of the pores, which resulted in smaller cell sizes.

<table>
<thead>
<tr>
<th>Processing Pressure (MPa)</th>
<th>Processing Pressure (psi)</th>
<th>Particles (weight percent)</th>
<th>Viewing Plane</th>
<th>Number of cells measured</th>
<th>Calculated number of cells per square inch</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.068</td>
<td>300</td>
<td>0%</td>
<td>Z</td>
<td>496</td>
<td>1410</td>
</tr>
<tr>
<td>2.068</td>
<td>300</td>
<td>0%</td>
<td>X-Y</td>
<td>292</td>
<td>813</td>
</tr>
<tr>
<td>2.068</td>
<td>300</td>
<td>5%</td>
<td>Z</td>
<td>486</td>
<td>1353</td>
</tr>
<tr>
<td>2.068</td>
<td>300</td>
<td>5%</td>
<td>X-Y</td>
<td>298</td>
<td>830</td>
</tr>
<tr>
<td>1.379</td>
<td>200</td>
<td>0%</td>
<td>Z</td>
<td>352</td>
<td>980</td>
</tr>
<tr>
<td>1.379</td>
<td>200</td>
<td>0%</td>
<td>X-Y</td>
<td>299</td>
<td>833</td>
</tr>
<tr>
<td>1.379</td>
<td>200</td>
<td>0%</td>
<td>X-Y (bottom)</td>
<td>216</td>
<td>707</td>
</tr>
<tr>
<td>1.379</td>
<td>200</td>
<td>5%</td>
<td>Z</td>
<td>287</td>
<td>799</td>
</tr>
<tr>
<td>1.379</td>
<td>200</td>
<td>5%</td>
<td>X-Y</td>
<td>191</td>
<td>630</td>
</tr>
<tr>
<td>0.689</td>
<td>100</td>
<td>0%</td>
<td>Z</td>
<td>112</td>
<td>312</td>
</tr>
<tr>
<td>0.689</td>
<td>100</td>
<td>0%</td>
<td>X-Y</td>
<td>109</td>
<td>339</td>
</tr>
<tr>
<td>0.689</td>
<td>100</td>
<td>5%</td>
<td>Z</td>
<td>92</td>
<td>256</td>
</tr>
<tr>
<td>0.689</td>
<td>100</td>
<td>5%</td>
<td>X-Y</td>
<td>167</td>
<td>465</td>
</tr>
</tbody>
</table>

### 4.1.2 Percent Porosity

The percent porosity measured using the ImagePro software matches very closely with the porosity calculated from the bulk density as seen in Figure 29. The foams with particles and in the z plane had a greater percent porosity compared to foams with no additives at the same processing pressure with the exception of the 0.689 MPa (100 psi) porosity calculated from the bulk density. A possible reason for this discrepancy is that the density and porosity of the 0.689 MPa (100 psi) samples is highly dependent on the location of the sample. There is a density gradient in the sample, with the top of the sample having significantly higher porosity compared to the bottom of the same sample.

A possible explanation for why the foams with particles had a higher percent porosity in the z plane compared to the foams with no additives is that the particle additives provided more
initial nucleation sites for bubble formation, which grew and created more porosity. This theory is explained in Chapter 2 Section 1.5: Influence of Particle Additives.

![Figure 29: Percent porosity measured from ImagePro and calculated from bulk density](image)

**4.2 Open Windows (SEM)**

The percent open windows measured with ImagePro software showed an increasing percentage for lower processing pressure as seen in Table 5. This can be explained by the lower processing pressure having fewer restrictions on the growth of the bubbles, allowing them to become larger and creating more openings as seen earlier in Figure 7. Also, the x-y plane had higher percentages of open windows compared to the z plane for the 1.379, 2.068, and 2.758 MPa (200, 300, and 400 psi) samples. This is most likely due to the ellipsoidal shape of the cells and their orientation with the elongation in the z-direction.
Table 5: Percent open windows measured from SEM images

<table>
<thead>
<tr>
<th>Processing Pressure (MPa)</th>
<th>Processing Pressure (psi)</th>
<th>X-Y Plane</th>
<th>X-Y Plane with particles</th>
<th>Z Plane</th>
<th>Z Plane with particles</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.758</td>
<td>400</td>
<td>14.91%</td>
<td>9.94%</td>
<td>5.92%</td>
<td>5.40%</td>
</tr>
<tr>
<td>2.068</td>
<td>300</td>
<td>16.29%</td>
<td>14.62%</td>
<td>8.26%</td>
<td>5.60%</td>
</tr>
<tr>
<td>1.379</td>
<td>200</td>
<td>17.15%</td>
<td>19.77%</td>
<td>13.50%</td>
<td>12.30%</td>
</tr>
<tr>
<td>0.689</td>
<td>100</td>
<td>27.78%</td>
<td>33.40%</td>
<td>31.86%</td>
<td>26.64%</td>
</tr>
</tbody>
</table>

The calculated number of cells per square inch decreases with an increasing percentage of open windows or decreasing processing pressure as shown in Figure 30. This is due to the size of the cells increasing for lower processing pressures and creating more open windows during the growth process of the foam.

Figure 30: Number of cells per square inch versus percent open windows
4.3 Bulk Density

The bulk densities of the foam steadily decreased with decreasing processing pressures as seen in Figure 31, which is due to the increased cell sizes for lower processing pressures. The foams with particles had slightly lower bulk densities compared to the pure foams, which is most likely because the foams with particles having more nucleation sites that led to increased porosity. The bottom of the samples had similar densities to the top for the 1.379, 2.068, and 2.758 MPa (200, 300, and 400 psi) foams both with and without particles. For both of the 0.689 MPa (100 psi) samples, the bottom of the sample had a higher density compared to the top. It cannot fully be explained why the 0.689 MPa (100 psi) processing pressure had a density gradient, while the other samples did not, however it does make sense that the higher density would be on the bottom of the sample due to gravity during the foaming process.

Figure 31: Bulk density for different processing conditions
4.4 Compression tests

The ultimate stress achieved up to 20% reduction in height ($\varepsilon = \delta l/l_0$) increased with increasing bulk density as seen in Figure 32. This would be expected since higher density foams have more graphitic structure compared to lower density foams. Also, samples with particles had lower ultimate stresses than foams with no additives at the same processing pressure due to their lower densities explained in the previous section.

![Figure 32: Ultimate stress versus bulk density](image)

4.5 Archimedes density

The Archimedes density is another method to measure the bulk density of the foams and increases in a linear fashion as shown in Figure 33. Again, the bulk density is lower for the foam
samples with particles compared to the pure foam at the same processing pressure, so the bulk density measured based on the Archimedes principle is also lower for the foams with particles.

![Image: Archimedes density versus bulk density](image)

**Figure 33: Archimedes density versus bulk density**

### 4.6 Thermal conductivity

As shown in Figure 34, the z plane thermal conductivity was significantly higher than the x-y plane for the 1.379, 2.068, and 2.758 MPa (200, 300, and 400 psi) samples, which is due to the cells and graphite ligaments parallel to the foaming direction. Both of the 0.689 MPA (100 psi) samples had higher conductivities in the x-y plane, which is very atypical for graphite foams. For both of the 0.689 MPa (100 psi) samples in the x-y plane, the bottom had higher thermal conductivities compared to the top, which can be explained by the bottom of the foam having a higher density compared to the top. Also the foams with particles had lower
conductivities compared to the pure foam at the same pressure. This is most likely due to the particles disrupting the graphite ligaments and making the flow of heat more tortuous.

Figure 34: Thermal conductivity for different processing conditions

**4.7 Permeability and Heat Transfer**

For the permeability testing, the 2.758 MPa (400 psi) samples were not able to be tested because there was such a high resistance for air to flow through the pores that there were either noticeable air leaks or the samples de-bonded. Figure 35 shows that the permeability increases with a decreasing processing pressure due to the increased porosity (both overall percentage and open window porosity). The bottom of the 0.689 MPa (100 psi) sample had significantly lower
permeability compared to the top of the sample due to the density of the top being much lower than the bottom.

The thermal resistance of the 0.689 MPa (100 psi) samples varied widely as seen in Figure 36. The 0.689 MPa (100 psi) sample with particles had the highest thermal resistance but the heat transfer may have been hindered by the sample corroding since discoloration on the sample was apparent. The bottom of the 0.689 MPa (100 psi) sample without particles had the most favorable thermal resistance followed closely by the 1.379 MPa (200 psi) samples.
In order to take into account the thermal resistance and permeability together, a figure of merit was established. This figure of merit was equal to the thermal resistance times the pressure drop times the face velocity. This was plotted versus a measure of the pumping power (which is proportional to the face velocity times the pressure drop) as shown in Figure 37. Both a lower pumping power and lower figure of merit are better, so a “corner of goodness” can be established in the lower left-hand side of the graph as indicated by the light blue box.

Figure 36: Thermal resistance of foams at various processing conditions
The 0.689 MPa (100 psi) samples had the best heat transfer performance overall when taking both the permeability and heat transfer capabilities into account. The 1.379 MPa (200 psi) foams had the next lowest figure of merit and pumping power followed by the 2.068 MPa (300 psi) samples.

4.8 Analysis of Variance (ANOVA)

A two-way ANOVA analysis was conducted on the results to indicate whether or not the influence of pressure or particles were significant to the responses. The samples fit a Taguchi L8 array, with 2 factors: pressure (4 levels) and particles (2 levels). In all cases, the pressures were significant on the resulting macroscopic structure and properties and had much more of an effect compared to the particles. There were four instances where the analysis of variance indicated
with a 95% confidence interval that the particles were not significant, but this only occurred with samples in the x-y plane. The responses in the x-y plane that indicated the particles did not have a significant impact were: percent porosity using ImagePro, anisotropy ratio, percent open windows, and number of cells/square inch. Based upon this analysis, it appears the particle additions have more of an impact on the macroscopic structure in the z plane than the x-y plane. This could be beneficial because the pore structure could be slightly altered in the z plane with relatively no change in the x-y plane through the particle additions.
Chapter 5: Conclusions 

This study focused on the characterization of graphite foams under various processing conditions, specifically the influence of porosity and the material’s structure on the thermal properties. It was found that with an increasing processing pressure, the graphite foams generally had decreased cells sizes, increased number of cells per square inch, decreased percent open porosity, increased density, and an increased ultimate compressive strength. Most importantly, the higher processing pressures had higher thermal conductivities, but the foams also had higher thermal resistances and higher permeabilities. The addition of particles particle additives increased the porosity of the foams, which decreased the strengths and thermal conductivities slightly, but did not have an incredibly strong influence on the thermal resistances.

Although the 0.689 MPa (100 psi) samples had the most favorable thermal resistances and permeabilities, the compressive strength was so low that the foams would not be feasible for applications such as a heat exchanger. Unless the low strength could be overcome through some type of reinforcement or strength enhancement through an outer coating, the 1.379 MPa (200 psi) graphite foams should be used as a basis for heat exchanger applications.
Chapter 6: Future Work

Building upon the research of this study, different concentrations of particles could be studied or other types of particles. It would be most beneficial to use the 0.689 MPa (100 psi) and 1.379 MPa (200 psi) processing pressure, since this study concluded that those pressures resulted in the most favorable thermal resistance and permeabilities. Additionally, other processing pressures can be tried (i.e. 150 psi, 175 psi, etc.).

Also beneficial would be metallization studies to increase the strength of the foams. The 0.689 MPa (100 psi) samples performed the best with respect to heat transfer, but they were the weakest samples. If the strength could be significantly improved without hindering the permeability or ligaments of the foam, this processing pressure may be feasible for the application of foams in heat exchangers and provide better heat transfer compared to higher processing pressure foams.

Finally, stereological analysis would be beneficial in order to obtain more information about the three dimensional structure of the foams, which would be very helpful for modeling purposes. The models could then be used to estimate the properties of the material before spending the time and costs on processing and testing the materials.
References


Appendix A: Optical Images

A1: 300 psi; z plane

A2: 300 psi with 5% particles; x-y plane
A3: 300 psi with 5% particles; z plane

A4: 300 psi; x-y plane
A5: 200 psi; z plane

A6: 200 psi x-y plane
A7: 200 psi with particles; z-plane

A8: 200 psi with particles; x-y plane; bottom half of sample
A9: 200 psi with particles; x-y plane; top half of sample

38A10: 100 psi; z plane
A11: 100 psi; x-y plane

A12: 100 psi with particles; z plane
A13: 100 psi with particles; x-y plane
Appendix B: SEM Images

SEM images before (left) and after (right) rendering for open porosity measurements

B1: 400 psi; z plane

B2: 400 psi; x-y plane

B3: 400 psi with particles; z plane
B4: 400 psi with particles; x-y plane

B5: 300 psi; z plane

B6: 300 psi; x-y plane
B7: 300 psi with 5% particles; z plane

B8: 300 psi with particles; x-y plane

B9: 200 psi; z plane
B10: 200 psi; x-y plane (bottom of sample)

B11: 200 psi; x-y plane (top of sample)

B12: 200 psi with particles; z plane
B13: 200 psi with particles; x-y plane

B14: 100 psi; z plane

B15: 100 psi; x-y plane
B16: 100 psi with particles; z plane

B17: 100 psi with particles; x-y plane