SINTERED NICKEL PLAQUE DEPOSITED WITHIN NICKEL FOAM

THE DEPOSTION OF SINTERED NICKEL PLAQUE

WITHIN A

NICKEL FOAM SUBSTRATE

By

DAN BIELBY, B.A.Sc

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AUTHOR: Dan Bielby, B.A.Sc (University of Toronto),

SUPERVISOR: Dr. D. S. Wilkinson

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Abstract

With the world of technology constantly advancing, there will always be a need to improve the source of energy providing the power in a number of applications. Supercapacitors, specifically, have become important power components for cell phones, laptops, and, more recently, electric and hybrid vehicles. In order to increase the efficiency of supercapacitors, novel structures must be investigated to increase surface area, which is one key to the energy storage mechanism of supercapacitors. By infiltrating the open cells of high porosity nickel foam with sintered filamentary nickel plaque, a unique, high surface area structure with high porosity has been produced. The mechanical properties of the resulting structure are a compromise of the two constituents; nickel foam and nickel plaque. The nickel foam provides ductility, and the nickel plaque provides strength and stiffness, with a final composite structure that averages a yield strength of 1.87 MPa, a UTS of 2.25 MPa, an elastic Modulus of 515 MPa, and an average percent elongation of 7.6%. As the relative density of the composite increases, the strength and modulus both increase, while the percent elongation decreases. This high surface area, high porosity material could serve as a viable substrate for a thin coating, which would provide the electrical properties of a supercapacitor.

iii

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Table of Contents

Title	i
Descriptive Note	ii
Abstract	iii
Acknowledgements	iv
Table of Contents	v
List of Figures and Tables	vii
1.0 Literature Review	1
1.1 Electrochemical Capacitors	1
1.2 Supercapacitors vs. Batteries	1
1.3 Electrical Characteristics and Operation of Supercapacitors	3
1.4 Supercapacitor Electrodes	5
1.4.1 Design	5
1.4.2 Materials	6
1.5 Nickel	8
1.5.1 Nickel Substrates	9
1.5.2 Nickel Foam	9
1.5.3 Nickel Plague	11
1.6 Material Production	12
1.6.1 Slurry Preparation	12
1.6.2 Tape Casting/Pasting	14
1.6.3 Sintering	17
1.7 Mathematical Modeling	18
1.7.1 Cellular Structures	18
1.7.2 Fracture Analysis	19
2.0 Thesis Objectives	21
3.0 Experimental Method	22
3.1 Nickel Prepartation	23
3.1.1 Nickel Foam	23
3.1.2 Nickel Slurry	23
3.2 Tape Casting/Hand Pasting	26
3.2.1 Vertical Tape Casting	26
3.2.2 Horizontal Tape Casting	27
3.2.3 Hand Pasting	28
3.2.4 Drying	· 29
3.3 Sintering	30
3.3.1 Sintering Temperature	30

v

3.3.2 Sintering Environment	31
3.3.3 Sintering Time	32
3.3.4 The Final Product	32
3.4 Tensile Testing	34
3.5 SEM and EDS Analysis	35
3.5.1 Sample Preperation	35
3.5.2 EDS Analysis	36
3.6 Mathematical Treatment of Data	36
3.7 Summary of the Experimental Process	38
4.0 Results	40
4.1 Sample Observations During Processing	41
4.2 Experimental Results	44
4.2.1 SEM Analysis	45
4.2.1.1 SEM – Pasting Technique	45
4.2.1.2 SEM – Viscosity and Plaque Infiltration	52
4.2.1.3 SEM – Viscosity and Plaque Adhesion	55
4.2.1.4 SEM – Voids	59
4.2.1.5 SEM – Foam Ductility	62
4.2.1.6 EDS Analysis	64
4.2.2 Tensile Testing	65
4.2.2.1 Tensile Testing – Materials	66
4.2.2.2 Tensile Testing – Temperature	68
4.2.2.3 Tensile Testing – Sintering Time	73
4.2.2.4 Tensile Testing – H_2 Flow Rate	74
4.2.2.5 Tensile Testing – Viscosity	76
4.2.2.6 Tensile Testing – Pasting Technique	78
4.2.3 Experimental Results Summary	80
4.3 Mathematical Modeling	81
4.3.1 The Gibson and Ashby Model	81
4.3.2 The Rule of Mixtures Model	82
4.3.3 Summary of Mathematical Models	86
5.0 Discussion	87
5.1 Process Variables	87
5.1.1 Sintering Temperature	88
5.1.2 Gas Flow Rate	91
5.1.3 Pasting Technique	93
5.1.4 Slurry Viscosity	96
5.1.5 Process Summary	98
5.2 Mathematical Analysis	100
5.2.1 The Gibson and Ashby Models	100
5.2.2 The Rule of Mixtures	104

vi

5.2.3 Refining the Mathematical Models	106
6.0 Conclusions	111
7.0 References	114

List of Tables and Figures

Figures

Fig. 1.1 – A Ragone Plot	2
Fig. 1.2 – The Double-Layer Supercapacitor	4
Fig. 1.3 – Increasing Surface Area diagram	6
Fig. 1.4 – Nickel Foam SEM image	10
Fig. 1.5 – Nickel Plaque SEM image	11
Fig. 1.6 – Horizontal Tape Casting diagram	15
Fig. 1.7 – Vertical Tape Casting diagram	16
Fig. 1.8 – Hand Pasting diagram	17
Fig. 3.1 – Experimental Process flow chart	22
Fig. 3.2 – Slurry Preparation flow chart	24
Fig. 3.3 – Vertical Tape Casting diagram/photo	27
Fig. 3.4 – (a)Ni Plaque SEM, (b)Ni Foam SEM, (c)Combined diagram	33
Fig. 4.1 – SEM image of One-Side, Hand-Pasted Sample (one pass)	46
Fig. 4.2 – SEM image of One-Side, Hand-Pasted Sample (multiple passes)	47
Fig. 4.3 – SEM image of Vertically Tape Cast Sample	49
Fig. 4.4 – SEM image of Two-Side, Hand-Pasted Sample (one pass)	50
Fig. 4.5 – SEM image of Two-Side, Hand-Pasted Sample (multiple passes)	-51
Fig. 4.6 – SEM images of plaque infiltration at mid, low and high viscosity	54
Fig. 4.7 – SEM image of Plaque Adhesion (63% Water)	56
Fig. 4.8 – SEM image of Plaque Adhesion (56% Water)	57
Fig. 4.9 – SEM image of Plaque Adhesion (60% Water)	58
Fig. 4.10 – SEM image of Voids in Plaque	60
Fig. 4.11 – SEM image of Voids in Plaque	61
Fig. 4.12 – SEM image of Foam Fracture Surface	63
Fig. 4.13 – SEM image of Fractured Foam Strut	64
Fig. 4.14 – Yield Strain & Percent Elongation vs. Relative Density	66
Fig. 4.15 – Yield Strength & UTS vs. Relative Density	67
Fig. 4.16 – Elastic Modulus vs. Relative Density	67

Fig. 4.17 – Stress vs. Strain Curves for Nickel Foam (Temp.)	69
Fig. 4.18 – Stress vs. Strain Curves for Nickel Plaque (Temp.)	70
Fig. 4.19 – Stress vs. Strain Curves for Plaque-Infiltrated Foam (Temp.)	72
Fig. 4.20 – Stress vs. Strain Curves for Plaque (Sintering Time)	74
Fig. 4.21 – Stress vs. Strain Curves for Plaque-Infiltrated Foam (Gas Flow)	75
Fig. 4.22 – Stress vs. Strain Curves for Plaque-Infiltrated Foam (Viscosity)	77
Fig. 4.23 – Stress vs. Strain Curves for Plaque-Infiltrated Foam (Pasting Tech.)	79
Fig. 4.24 – Rule of Mixtures – Modulus vs. Mass Fraction	84
Fig. 4.25 – Rule of Mixtures – Yield Strength vs. Mass Fraction	85
Fig. 5.1 – A Comparison Against Zaitsev's Previous Research	89
Fig. 5.2 – SEM images of Plaque Penetration for Four Different Processes	94
Fig. 5.3 – The loading and fracture mechanisms of plaque-infiltrated foam	99
Fig. 5.4 – Differences between Experimental and Calculated Results	103

Tables

Table 3.1 – Slurry Composition	25
Table 3.2 – Summary of Processes	38
Table 3.3 – Observed Properties of Materials	38
Table 3.4 – Mathematical Treatments	39
Table 4.1 – Changes in Size and Mass Through Sintering	43
Table 4.2 – Tensile Results for Nickel Foam (Heat Treatment)	69
Table 4.3 – Tensile Results for Plaque-Infiltrated Foam (Sintering Temp.)	72
Table 4.4 – Tensile Results for Plaque-Infiltrated Foam (Viscosity)	77
Table 4.5 – Tensile Results for Plaque-Infiltrated Foam (Pasting Technique)	79
Table 4.6 – Theoretical Results (Gibson and Ashby Equations)	82
Table 4.7 – The Rule of Mixtures Model (Volume Fractions)	83
Table 4.8 – The Rule of Mixtures Model (Mass Fractions)	83
Table 5.1 – Tensile Properties vs. Sintering Temperature	90
Table 5.2 – Tensile Properties vs. Gas Flow Rate	92
Table 5.3 – Correlating Experimental Results to Gibson and Ashby Results	101
Table 5.4 – Correlating Experimental Results to Rule of Mixtures Results	102

1.0 Literature Review

1.1 Electrochemical Capacitors

Electrochemical capacitors otherwise known as supercapacitors, are energy storage devices that are commonly found in small to medium sized electronic products such as cell phones and laptop computers, and other electrical equipment ranging from power tools to pacemakers. Supercapacitors are also found in emergency components for aircraft, and solar energy systems.¹

High specific capacitance, in the order of thousands of Farads per gram, coupled with a very short charge time make the supercapacitor an attractive partner for batteries in applications such as battery-electric and hybrid automotive vehicles.

1.2 Supercapacitors vs. Batteries

The function of capacitors, supercapacitors, batteries and fuels cells is the same, to store electrical energy and to provide this energy when necessary for a mechanical or electronic purpose. How they differ is in their power density (W/kg) and their energy density (Wh/kg). Batteries store more energy relative to capacitors, while capacitors can provide more power relative to batteries. Supercapacitors have power and energy

densities intermediate between batteries and capacitors, as demonstrated in the Ragone plot in figure 1.1.





While the construction and capabilities of a supercapacitor differ from those of an electrolytic capacitor or a common capacitor, their electronic operation is fundamentally the same. They both output current with a varying voltage. The operation of a battery, however, provides a current output at a constant voltage. Besides the performance differences previously stated, batteries also have a shorter lifetime (thousands of cycles) relative to capacitors and supercapacitors (hundreds of thousands or millions of cycles).

Supercapacitors also have a faster rate of charge and discharge, which allows them to be recharged in a matter of seconds, while batteries can take hours to recharge.²

Finally, the active materials used in supercapacitors tend to be less toxic than those used in batteries. Supercapacitors are often made with carbon, metal oxides, and aqueous solutions, while batteries are often made with lead, cadmium, and mercury, elements that are dangerous to animals and the environment. Batteries also make use of an acid-based electrolyte, which can be corrosive.

1.3 Electrical Characteristics and Operation of Supercapacitors

Supercapacitors have a double-layer construction, shown in figure 1.2, composed of two current collectors (positive and negative) made of carbon fibres or metal foils encasing an electrolytic solution. This solution contains the electrodes in the form of highly porous activated carbon. The system is bisected by a separator, which prevents the electrodes from changing charge. This form of supercapacitor stores the electrical charge through a physical, microscopic charge separation, and is deemed the double layer effect. It's this physical charge storage that gives the supercapacitor its longer life, as the chemical energy storage of batteries degrades the active materials during usage.



Fig. 1.2 - The basic construction of a double layer supercapacitor¹

The materials that comprise the electrodes affect the storage mechanism. When activated carbon is used, the charge is stored only through the double layer effect. The surface area of the electrodes carry the charge, thus materials with a high surface area to volume ratio can increase the capacitance. Popular electrodes for the double layer effect include carbon aerogel and activated carbon powder, which have such a high specific surface area that the capacitance can reach thousands of Farads.¹

When the electrode is made of a transition metal oxide, such as NiO or MnO, more energy can be stored due to pseudocapacitance. Pseudocapacitance is charge storage through the changing of the valence state of the metal ions in the electrode. This form of charge storage is also limited to the specific surface area of the metal oxide, and

increasing the thickness of the electrode raises the resistance, limiting the capacity. However, the electrode must be thick enough to maintain structural integrity, as the charge and discharge process of electrical storage components can cause the electrode material to swell and shrink, subjecting the electrode to cyclical straining.^{25, 26}

1.4 Supercapacitor Electrodes

1.4.1 Design

As stated in section 1.3, the energy storage capabilities of the supercapacitor rely heavily on the specific surface area of the electrode material. Standard solid or sheet electrodes found in ordinary capacitors and batteries are inappropriate, due to a lack of efficiency. Suspended powders, aerogels, foams, and sintered powders have all been investigated, without one form clearly outperforming the others. Room for improvement still exists. More recently the process of increasing surface area by using a porous substrate coated with the electrode material has been suggested. Figure 1.3 demonstrates how a substrate with a rough surface profile increases capacitance. Based on this concept, infiltrating highly porous foam with a high surface area material, such as sintered powder, will both maximize the surface area and utilize the mechanical properties of the interconnected foam.



Fig. 1.3 – Schematic illustrating how an increase in the surface area of the substrate creates more reactive surface area for the supercapacitor coating.

1.4.2 Materials

The materials used for the fabrication of supercapacitor electrodes can be grouped into three categories; carbon, polymer, and metal oxide.

Activated carbon powder and carbon aerogel have been used to store energy through the double layer effect. With the surface area of aerogel ranging between $400 - 1000 \text{ m}^2/\text{g}$, and powder reaching 2000 m²/g,⁽¹⁾ carbon based electrodes have a capacitance on the order of thousands of farads. However, in practice, the specific capacitance (F/g) of these electrodes has only reached a fraction of their potential due to poor electrolytic flow and electrical connectivity.³

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Some conducting polymers have similar properties to electrodes found in electrochemical capacitors. They can store charge through a reduction-oxidation reaction that will create a negative charge within the polymer chains. This form of energy storage is reflective of pseudocapacitance. However, there is a significant amount of double layer storage within the electrolyte surrounding the polymer, and the supercapacitor functions more as a carbon-based double layer capacitor.⁴

Metal oxide electrodes have an advantage over carbon-based electrodes in that they can store energy through the double layer effect as well as via pseudocapacitance. Transition metals have the most promising oxides in terms of capacitance, with specific capacitance in the range of 160 - 720 F/g⁴. These values can be achieved using the oxides of metals such as nickel, cobalt, manganese, ruthenium, and iridium. Ruthenium and iridium are both expensive and toxic, and thus nickel, cobalt, and manganese are more popular. Of these three, manganese oxide provides the highest specific capacitance, reaching values over 700 F/g.

1.5 Nickel

Nickel is a transition metal mainly used in the production of metal alloys, the most popular being stainless steel. Over the last century, nickel has been used in electrical storage devices. In 1899, Waldmar Jungner invented the nickel-cadmium battery.⁵ Because of the toxicity of cadmium, as well as other disadvantages, the battery has slowly fallen out of favour. In the 1970's, nickel-metal-hydride (NiMH) batteries were developed and gradually introduced to the general public. Originally bulky and expensive⁵, these batteries have been improved upon to the point that they are commonly found in cell phones, laptops and digital cameras. NiMH batteries are also the electrical power source for hybrid vehicles such as the Toyota Prius and Honda Civic.⁶

Physically, nickel is hard and ductile. Solid nickel has a density of 8900 kg/m^3 , and an elastic modulus of 200 GPa.⁷ While the yield strength and tensile strength will vary with material processing (e.g. heat treatment), annealed Nickel 200 (commercially pure Nickel) has a yield strength of 148 MPa, and a tensile strength of 462 MPa, with an elongation of $47\%^7$.

1.5.1 Nickel Substrates

As mentioned in section 1.4.1, an increase in specific surface area, which is fundamental towards increasing specific capacitance, may be possible through the development of a highly porous material, infiltrated with a high specific surface area plaque.

Nickel, because of its material properties and its possible structures, is an ideal candidate for use as a supercapacitor substrate. In particular, nickel foam and nickel plaque can be combined to form a substrate, which has sufficient specific surface area, as well as appropriate mechanical properties. Furthermore, nickel oxide is a capable supercapacitor, with a specific capacitance of up to 260 F/g.⁴

1.5.2 Nickel Foam

Nickel foam is a high purity, highly porous foam celled structure. The foam can be made through electrodeposition, or through chemical vapour deposition (CVD). Inco, which has been producing nickel foam since 2000, uses CVD to deposit nickel onto polymeric foam by boiling nickel carbonyl⁹. The foam substrate is then removed through a burnout process, leaving an open-celled, thin-walled strut foam. These foams come in a range of porosities (70% - 98% by volume) and a variety of cell sizes (400µm – 3200µm

in diameter)⁹. The density of these foams are anywhere between one to thirty percent of the density of solid nickel. An SEM image of 98% porosity foam is shown in figure 1.4.



Fig. 1.4 – SEM Image of 98% porosity Nickel foam (Incofoam®) with 110 ppi (pores per inch).⁹

Mechanically, nickel foam is highly ductile. Although it is not nearly as strong as solid nickel, it benefits from the roughly uniform cellular structure. Currently, nickel foam is being used as an electrode material in NiMH batteries⁹.

As a supercapacitor electrode substrate, foam, on its own, is too porous. There is too much open space, which is of no use. Compressed foam, or lower porosity foam, also fails to make use of the open cell, by filling that empty space with smooth surfaced nickel struts, where a rougher, more particulate surface would increase the specific surface area.

1.5.3 Nickel Plaque

Nickel plaque is a moderately porous material created by the sintering of filamentary nickel powder or particles, as shown in figure 1.5. The nature of the powder, consisting of a finely branched structure, creates a high specific surface area plaque. The plaque may be created from an aqueous slurry, dried into a green tape (termed *slurry sintering*), or from dry, compacted filamentary powder (*loose sintering*). While both processes can result in a similar range of porosities (80% to 85% by volume), slurry sintering is favoured due to its more consistent, continuous structure.¹⁰



Fig. 1.5 – An SEM image of sintered nickel plaque.

Nickel plaque is relatively stronger and stiffer compared to nickel foam. However, the plaque is very brittle. Due to the trade off of strength for porosity during sintering¹⁰, increasing sintering temperature cannot be an option to strengthen the plaque, as porosity will drop below the required value.

1.6 Material Production

1.6.1 Slurry Preparation

In order to uniformly and completely infiltrate the foam, the aqueous solution (slurry) must have a proper balance of water, dispersant, binder, and the powder or particle material to be pasted or cast into a solid plaque. The viscosity must be low enough for the slurry to penetrate the cells of the material through the entire thickness of the material, but not so low that the slurry merely flows through the cells without filling and staying within the material.

Research by Zaitsev, et.al. (2003)¹¹ has led to improved techniques of preparing and processing the slurry. In particular, by mixing the filamentary powder with water and a dispersant before introducing the binder gives better dispersion of the powder and fewer, if any, conglomerates. This differs from the conventional method of simply mixing the powder with the binder before casting. The final result of Zaitsev's research

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was a plaque with more uniform structure than conventional plaque, which improves the efficiency of electrical discharging and recharging, as well as improved tensile strength.

The role of the dispersant is to allow for maximum saturation of the material within the slurry. It manages to separate the powder, filament by filament, and disperse it throughout the slurry solution. Without a dispersant, the filamentary powder may agglomerate, creating lumps of material, and result in inconsistent plaque formation. The type of dispersant depends on the material it is dispersing, and the desired properties of the finished plaque. For instance, a sulphur-free dispersant is necessary when producing a nickel plaque, as the sulphur will embrittle the plaque during sintering.¹¹

The binder is a polymeric or cellulose addition to the slurry, which holds the filamentary powder together relatively weakly during the drying stage (before sintering). It is the binder that solidifies the tape casting, allowing it to be sintered into a solid, one-piece material. The correct amount of binder is essential in producing a useful plaque. Not enough binder results in a very weak, green tape, which will fall apart before it can be treated further. Too much binder will not mix sufficiently within the slurry, resulting in agglomerated binder within the slurry, and large voids in the sintered tape. During the sintering, the binder is burned out of the material, leaving just the solid, sintered plaque.

Finally, the slurry must be well mixed, and the constituents must be added in the proper order. As per Zaitsev's procedure¹¹, the dispersant and filamentary powder are typically mixed together first with water, and the binder, which can be added as a powder, aqueous solution, or foam, is added later, when the slurry is ready to be pasted or tape cast.

1.6.2 Tape Casting/Pasting

Tape casting and pasting are two techniques for the physical infiltration of the foam with the slurry. While operations of the techniques differ slightly, the objective is the same, to cast the slurry into a thin tape, a thin coating on a substrate, or within a porous substrate.

Tape casting is an automated process in which a liquid solution is cast into a thin tape, or applied to a substrate. There are two general types of tape casting, horizontal and vertical. The key variables for both types of casting are the same; the viscosity of the liquid solution, the speed of the casting, and the thickness of the tape, which is determined by the doctor blades, which scrape the slurry along, leaving only a small volume behind.

In horizontal tape casting, a reservoir moves across a smooth surface or substrate, feeding slurry through one or multiple doctor blades set at staggered levels, the last blade being the lowest (see figure 1.6). This allows for a flat, more consistent tape because larger agglomerated particles in the slurry will be caught by one of the earlier blades. Horizontal tape casting is useful for creating a thin tape by pasting onto a smooth, slippery surface, or for applying the slurry to one side of a substrate material. Also, multiple passes can be made to achieve better consistency, or to stack different coatings.



Fig. 1.6 – The basic design of a horizontal tape casting system.

Vertical tape casting requires a substrate to rise vertically through a pair of doctor blades. Below the blades, the substrate is immersed in a slurry bath, sufficiently coating the surfaces of the substrate. The blades push the coating into the pores of the substrate, and also scrape excess slurry down to the oncoming substrate, or away altogether. This technique of tape casting is useful because it coats the slurry from both sides of the substrate at once. If both sides of the substrate require coating, and the consistency of the coating is not in question, the process needs only one pass to complete the pasting. However, consistency can be difficult due to gravitational effects. And, if the substrate is porous, there is a possibility of trapping air between the coated sides. A basic schematic of vertical tape casting is shown in figure 1.7.



Fig 1.7 – Vertical tape casting.

Hand pasting is another technique used in slurry infiltration. In this process, the individual pours the slurry onto the substrate and pushes the solution into the pores of the substrate by applying pressure with a flexible blade or roller, as depicted in figure 1.8. The ability to paste in multiple passes on each side of the substrate ensures this process is able to infiltrate the cells throughout the entire thickness. However, the process can be time-consuming when it comes to pasting over a large area.

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Figure 1.8 – The technique of hand pasting slurry into a highly porous foam substrate with a flexible wiper blade.

1.6.3 Sintering

Sintering is a process used to form one-piece objects from compacted powder, through heating the material at a temperature below its melting point until the particles adhere to themselves.¹² The dried tape, coated substrate, or infiltrated porous substrate, is subjected to this high temperature environment, and material transport through diffusion allows the particles to adhere to one another, or to the substrate. Thus, sintering increases the density of the composite material as well as increasing its strength, since the powder tape, coating, or plaque in the substrate is now a bonded, single material. This is a desirable process when there is a need to produce a high purity material with a high order

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of uniformity. The drawback, however, is that the process often results in significant shrinkage, putting stress on the material, and making complex shapes hard to produce.

The properties of the material after sintering are directly linked to the variables of the sintering process. Higher sintering temperatures and longer sintering times allow for more material transport, smoothing rough surfaces, and reducing surface area. It also leads to stronger, stiffer materials, which can lead to a decrease in ductility. Sintering environments are also important, as the material may be subject to a reducing atmosphere, or inert gas. In a reducing atmosphere, the flow rate of the reducing gas is important, as the material must be subject to enough of the reducing element for a sufficient length of time to achieve the desired concentrations.

1.7 Mathematical Modelling

1.7.1 Cellular Structures

Cellular materials, such as nickel foam or the bones in our body, utilize specific properties, such as the mechanical strength or electrical conductivity, of the solid material, while benefiting from decreased density or increased surface area relative to the solid material at equal volume. This is achieved through the complex structural design of the open or closed cell materials.

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Gibson and Ashby¹³, have developed mathematical models which define the mechanical behaviour of cellular solid materials. By incorporating the relative density of the cellular material (ρ */ ρ _{Solid}, where ρ * is the density of the porous material and ρ _{Solid} is the density of the solid material) with the mechanical properties of the solid material, equations have been defined to determine cellular material properties such as yield strength, ultimate tensile strength and elastic modulus.

1.7.2 Composite Materials

Composite structures are designed and fabricated with the intention of combining specific characteristics of the base materials to meet the requirements of a particular function. Reinforced concrete is the classic example, in which the compression strength of concrete is complimented by the tensile strength of steel to provide an extremely useful structural material.

Composites are described quantitatively by the volume fractions (Vf) of the constituents, which make up the whole. These fractions can be used to predict the contribution of a particular material to a specific property. This concept is defined by the rule of mixtures⁷. The rule of mixtures uses two models, Voigt and Reuss, to provide upper and lower boundaries, respectively, for the composite material's behaviour, dependent on the composition of the material.

The Voigt model assumes an isostrain condition, and defines the yield strength, σ_{y_2} and elastic modulus E, of the composite as follows:

$$E_{c} = E_{m}Vf_{m} + E_{f}Vf_{f}$$
$$\sigma_{c} = \sigma_{m}Vf_{m} + \sigma_{f}Vf_{f}$$

Where terms with subscripts 'm' and 'f' denote the 'matrix' and 'fibre' base materials, and the 'c' subscript denotes the composite material.

Conversely, the Reuss model assumes an isostress condition, and is described as:

 $E_{c} = [(Vf_{m}/E_{m}) + (Vf_{f}/E_{f})]^{-1}$ $\sigma_{c} = [(Vf_{m}/\sigma_{m}) + (Vf_{f}/\sigma_{f})]^{-1}$

Ultimately, the rule of mixtures provides only a first-order estimation of the behaviour of a composite material, and only during elastic deformation. Furthermore it is ideally for an aligned, long-fibre composite, which does not describe plaque-infiltrated foam.

2.0 Thesis Objectives

The purpose of this research project is the production of a Ni substrate for a supercapacitor electrode. The substrate would be coated with a thin film of a metal oxide, such as MnO, to provide the electrochemical characteristics. More specifically, the goals of this research are as follows:

- To produce a mechanically robust Ni substrate that will withstand the physical stress of continual movement, as well as the stresses endured during the charging and discharging cycles.
- To compare the effect of different experimental production processes on the quality of a high specific surface area Ni substrate.
- To identify the most likely production process for further development and application in a manufacturing environment. The Ni substrate should be a strong and porous material with a high specific surface area plaque filling in the open foam cells, an ideal substrate for supercapacitor coatings.

3.0 Experimental Method

Production and testing of the proposed material was required to achieve the goals set out in this research thesis. The production stages included nickel foam and slurry preparation, sample casting/pasting, and sintering. Once the material was processed, it was subjected to analysis, including tensile tests, and scanning electron microscopy (SEM) and energy dispersive x-ray spectroscopy (EDS) analysis. The procedure is outlined in the chart below (figure 3.1).



Fig. 3.1 – The experimental method.

3.1 Sample Preparation

3.1.1 Nickel Foam

The nickel foam used in this thesis was Incofoam®. This type of foam has an area density of 420 g/m², with a pore size of 110 pores per inch (PPI)⁹, which gives an average pore diameter of 230 μ m. The foam was received in sheets that were 1.7mm thick. These sheets were cut, using a mechanical press, into sample sizes 2cm x 10cm x 0.17cm. The average mass of the sample was 0.85g, within a sample volume of 3.4cm³. Therefore the sample density was 250 kg/m³, which gives a relative density of 0.0281.

When doing tensile tests on the Ni foam samples, without plaque infiltration, the majority of the tests were performed on as-received samples. However, four foam samples were subject to the sintering process to investigate the process' effect on the properties of the Ni foam.

3.1.2 Nickel Slurry

The key ingredient of the slurry was Inco's filamentary nickel powder. Type 255 powder was received screened to a maximum particle size of $44 \mu m$.¹⁴

The slurry composition and mixing procedure was based on the methodology described by Zaitsev, et al.¹¹, outlined in figure 3.2. The nickel powder was added to

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deionized water with a few drops of sulphur-free dispersant (Polacryl B55-50AN or Polacryl A70-40N), then mixed vigorously. Meanwhile, cellulose powder was mixed with deionized water, which had been heated to 90^{0} C, in order to encourage particle dispersion.¹⁵ The cellulose powder was hydroxypropyl methyl cellulose (HPMC, $C_{6}H_{7}O_{2}(OH)_{x}(OCH)_{y}(OC_{3}H_{7})_{z}$, where x + y + z = 3). The nickel solution and cellulose binder solution were then combined, and mixed until a uniform consistency without any agglomerates was achieved.



Fig. 3.2 – The slurry preparation procedure.

In the cases where the slurry was used on multiple samples, or for multiple passes on a single sample, the slurry was mixed between sample runs/passes, in order to prevent any settling or agglomeration of particles, which would disrupt the flow of the slurry during casting or pasting. In order to test various viscosities for plaque infiltration, adhesion, and consistency, the amount of water included in the final slurry solution was 56% (as per Zaitsev¹¹), 60% and 63% by weight. The increased water concentrations are used to improve the flow of the slurry throughout the nickel foam. The compositions of the slurries are shown in table 3.1.

Viscosity ↓	Constituent →	Nickel Solution		Cellulose Solution	
		Nickel Powder (g)	Water (g) with ~ 1g dispersant	Cellulose Powder (g)	Water (g)
High visco (56 wt.%	osity H ₂ O)	42.5	40	2	16
Medium v (60 wt.%	riscosity H ₂ O)	42.5	50	2	16
Low visco (63 wt.%	sity H2O)	42.5	60	2	16

Table 3.1 – The compositions of the nickel slurries used in sample casting.

The viscosity of the slurry also determined the uniformity of the horizontal tape casting. At sufficient viscosity, a long, single sheet of tape could be produced without any significant voids. At lower viscosities, the wet tape could separate in some places and pool in others, and could also spill outside of the casting system. If the viscosity was too high, or if the slurry was not sufficiently mixed, clumping could clog the blades, resulting in streaking voids which could run from a few centimetres to the entire remaining length of the tape.

3.2 Tape Casting/Hand Pasting

3.2.1 Vertical Tape Casting

Vertical tape casting was one of two methods used to infiltrate the nickel foam with the slurry. The vertical tape casting mechanism involved a metal frame with three key components. At the bottom of the frame, a reservoir containing the foam samples was filled with the nickel slurry. The foam samples were attached to a pair of hooks using thin nylon wire. These hooks were moved in a vertical manner with an electrical motor placed at the top of the frame. Placed between the hooks and the reservoir, a pair of thin, plastic sheets acted as doctor blades forcing the slurry into the foam. The flexibility of the blades provided the necessary pressure to infiltrate the foam, as well as the scraping of excess slurry from the surface of the foam. A schematic of the vertical tape caster is shown in figure 3.3.



Figure 3.3 – The vertical tape casting system.

3.2.2 Horizontal Tape Casting

The horizontal tape caster consisted of a pair of conveyer belts that pulled a raised, flat bar over a smooth surface placed between the two moving belts. This flat bar pushed the blade/reservoir component along the surface, leaving a thin trail of nickel slurry behind (see fig. 1.6, pg. 15). The slurry was cast on a thin sheet of smooth Mylar, which was secured to a smooth glass sheet with adhesive tape. The blade system included two blades, set at staggered heights, approximately 3 cm apart. The height of the blades was adjusted using two knobs on the top of the blade system.
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knobs would raise and lower the height of the blade by tenths of millimetres (0.1 mm). The first blade acted as a catch for any impurities or clumps of slurry or cellulose. This blade was often set 0.3 - 0.5 mm higher than the final blade, which determined the thickness of the wet tape. The height of the final blade was set between 1 - 3 mm, in 0.5 mm intervals.

The speed of the conveyer belts was approximately 5 cm/s. In general, this casting speed achieved a reliable tape. Because the weight of the system varied with the amount of slurry in the reservoir, the speed was difficult to control and gauge accurately. While slower speeds were acceptable, the process took more time. At higher speeds, the system risked becoming unstable, as well as not giving the blades sufficient time to catch clumps or control the flow of the slurry, resulting in a streaky casting.

3.2.3 Hand Pasting

The hand pasting of slurry into nickel foam samples ensured that the entire surface and thickness of the foam was covered with nickel slurry.

The Ni foam sample was laid on a small sheet of Mylar secured to a smooth glass surface. Slurry was poured from a beaker along the length of the foam, and then spread across the foam sample using a plastic blade. This process can be done in single or multiple passes, from one side or both sides of the foam. When done from both sides, the foam was flipped by hand, and an equal number of passes were made on each side.

3.2.4 Drying

After casting, the samples were dried before sintering. For the vertically cast samples or the hand pasted samples, this involved hanging the samples inside an oven for up to an hour, at a temperature of about 90° C. For a horizontally cast tape, the slurry was left to dry at room temperature for 24 hours or longer on the Mylar sheet, which was still on the glass surface. This removed moisture, leaving a dry, weak, nickel plaque.

3.3 Sintering

Sintering the pasted foam and the nickel tape solidified the Ni plaque. The filamentary powder particles fused to each other, as well as to the walls of the hollow struts that make up the Ni foam. Furthermore, the cellulose was burned out of the sample, and excess oxygen, hydrogen, and carbon was removed. The properties of the final product were determined by the temperature and gas flow of the sintering furnace, as well as the process time.

3.3.1 Sintering Temperature

The temperature at which the material is sintered is the key variable in determining the final physical properties. Higher temperatures promote material transport, particles join closer together, and a stronger, denser material is formed. Higher temperatures also allow for the plaque to adhere more strongly to the struts of the foam. However, a lower sintering temperature will preserve the porosity and maintain higher surface area. Thus, a balance of strength and porosity must be achieved with an optimum sintering temperature. To find this temperature, sintering was carried out over a range of 850 - 1000 ⁰C (monitored by the furnace readout – the actual temperature of the sample may vary). Lower temperatures will result in a weak material through lack of fusion and

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adhesion, while higher temperatures significantly decrease the surface area of the final plaque with increased fusion of the filamentary nickel particles.

3.3.2 Sintering Environment

The type of gas during sintering influences the physical and chemical properties. In order to create the final product, a reducing atmosphere must be present to prevent the oxidation of the nickel. Therefore 100% hydrogen gas was passed over the sample through a glass tube with an inner diameter of 27 mm. The gas flow rate throughout the system also affects the material properties. The flow must be high enough that it reacts with the material, and carries away the unwanted impurities. However, high flow rates may result in hydrogen embrittlement of nickel, and also risk the stability of the system. To satisfy these issues, the gas flow rate was 0.38 L/min for the majority of the samples. Sintering at 0.47 L/min and 0.57 L/min flow rates was also tested for improved strength. In order to ensure the gas was able to reach the sample as completely as possible, a meshed wire tray was used to hold and transport the sample in the furnace.

3.3.3 Sintering Time

Sintering time, similar to sintering temperature, affects how dense the material becomes. Longer sintering times promote higher strength, but less porosity, and vice versa for shorter sintering times. The majority of the samples were sintered for 10 minutes, while three samples were sintered for 15 minutes.

3.3.4 The Final Product

After the sintering process, the resulting product would be a strong yet porous material, with a high specific surface area plaque filling in the open cells of the foam, ideal for use as a substrate for supercapacitor coatings. To illustrate this concept, the combination of the materials in figure 3.4a and 3.4b produce a composite shown in 3.4c.

Following sintering, the plaque-infiltrated foam samples were ready for mechanical testing and visual analysis.



Fig. 3.4 - High surface area nickel plaque (a) combined with high porosity open celled nickel foam (b)⁹ to create an ideal substrate (c) for a supercapacitor coating

3.4 Tensile Testing

The mechanical capabilities are important qualities of the material covered in this thesis. In particular, the yield strength and yield strain, the elastic modulus, the ultimate tensile strength (UTS), and the percent elongation to failure were of concern. In order to better understand these properties, the sample material, as well as the two material components, nickel plaque and nickel foam, were subject to tensile tests.

In order to prepare a material for tensile testing, a gauge length is needed within the total length of the sample. This allows for a concentration of stress and deformation to occur in a measurable section during testing. For solid materials, the gauge length is created by using a "bone" shaped sample, with the thinner section in the middle being the focus of the test. However, the risk of deformation or breakage of the plaque or foam material during any cutting or shaping process prevented the bone-shape from being reasonable from a tensile data point of view. A viable alternative was to coat the ends of the sample with epoxy, which, after hardening, left a weaker foam and plaque gauge length to act as the focal point of stress and elongation. The epoxy also served a second purpose by being a stronger sample section for the testing machine clamps to hold the sample securely.

The tests were performed using an Instron tensile machine, with the sample held by a clamp at each end. To measure the extension of the sample, an extonsometer was attached to the material's gauge length with elastic bands.

3.5 SEM and EDS Analysis

Observation and analysis of the material's structure was done through scanning electron microscopy (SEM). The infiltration of nickel plaque into the cells of the nickel foam, the adhesion of the plaque onto the struts of the foam, and the fracture surface were all investigated with a Phillips 515 SEM.

3.5.1 Sample Preparation

In preparation of a sample for imaging, it was very important to ensure that the fracture surface of the sample was not damaged, deformed or contaminated. For this reason, no grinding, polishing or etching was done before observation. By using a sharp blade, the sample was cut about one centimetre from each of the fractured ends. These two ends were placed on a microscope mount and secured by conductive adhesive tape and silver paint, such that the fracture surface and the coated surface were both exposed and oriented towards the electron beam of the SEM.

3.5.2 EDS Analysis

Energy dispersive X-ray spectroscopy (EDS) analysis helped determine the elemental composition of the material. EDS was used to identify the elements present in the sample through the detection of irradiated x-rays. By counting these x-rays, a concentration of the elements present was also reported.

The EDS system was combined with the SEM, so EDS tests were done during the same session as the SEM analysis, and the samples needed no further preparation.

3.6 Mathematical Treatment of Data

The mathematical models developed by Gibson and Ashby¹³, as well as the rule of mixtures for composites, were used to predict the mechanical properties and compared with the data determined from experimental results. Furthermore, they provided a basis for a potential model to predict the behaviour of the plaque-infiltrated foam.

Volume and mass measurements were taken to determine the relative density (ρ^*/ρ_{Ni} , where ρ^* is the density of the porous nickel material and ρ_{Ni} is the density of solid nickel) of nickel foam, nickel plaque, and plaque-infiltrated foam, which was then used to calculate the three Gibson and Ashby equations:

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Yield Strength:

 $\sigma^* / \sigma_{\text{Ni}} = 0.3 (\rho^* / \rho_{\text{Ni}})^{3/2}$ (5.27a, pg. 145)¹³

Ultimate Tensile Strength (UTS):

 $\sigma^*/\sigma_{Ni} = \rho^*/\rho_{Ni}$ (5.41, pg. 155)¹³

Elastic Modulus:

 $E^*/E_{Ni} = (\rho^*/\rho_{Ni})^2$ (5.6a, pg. 130)¹³

In these equations, terms expressed with a superscript (i.e. E^*) indicate properties of the cellular nickel structure, while terms expressed with a subscript (i.e. E_{Ni}), are for the properties of solid nickel.

Because the plaque-infiltrated foam is a composite material, the rule of mixtures was also used as mathematical support for the experimental data. The two models, Voigt and Reuss, provided upper and lower boundaries, respectively, for the elastic properties (yield strength and elastic modulus). The key variable to these models is the volume fraction (Vf) of the two constituents of the composite material.

> Voigt: $E_c = E_{foam}Vf_{foam} + E_{plaque}Vf_{plaque}$ $\sigma_c = \sigma_{foam}Vf_{foam} + \sigma_{plaque}Vf_{plaque}$ Reuss: $E_c = [(Vf_{foam}/E_{foam}) + (Vf_{plaque}/E_{plaque})]^{-1}$ $\sigma_c = [(Vf_{foam}/\sigma_{foam}) + (Vf_{plaque}/\sigma_{plaque})]^{-1}$

3.7 Summary of the Experimental Process

The following tables summarize the processing treatments of the three distinct sample types (table 3.2), the mechanical properties that are of concern to this research (table 3.3), and the mathematical calculations (table 3.4).

	Nickel Foam	Nickel Plaque	Plaque-Infiltrated Foam
Processes	 Sintering temp. (Untreated, 900 - 1000⁰C) 	 Sintering temp. (900 - 1000°C) Sintering time (10 - 15 mins) 	 Slurry viscosity (56 – 63% H₂O) Pasting technique (by hand or vertically cast) Sintering temp. (850 - 1000⁰C) Gas flow rate during sintering (0.38 – 0.57 L/min)

Table 3.2 – Summary	y of the processes	to which the three	Ni formats were sub	ojected

	Nickel Foam	Nickel Plaque	Plaque-Infiltrated Foam
Physical Properties	 Length, width and thickness Mass Appearance 	 Length, width and thickness Mass Appearance Voids 	 Length, width and thickness Mass Appearance Plaque infiltration depth Plaque adhesion to foam Voids
Mechanical Properties		 Yield strength Yield strain Elastic Modulus % Elongation UTS 	

Table 3.3 – The observed physical and mechanical properties of the treated Ni materials.

McMaster – Materials Engineering

	Nickel Foam	Nickel Plaque	Plaque-Infiltrated Foam
Mathematical	 Gibson & Ashby: Yield Strength Elastic Modulus UTS 	 Gibson & Ashby: Yield Strength Elastic Modulus UTS 	 Gibson & Ashby: Yield Strength Elastic Modulus UTS
Treatments			 Rule of Mixtures Voigt & Reuss Yield Strength Elastic Modulus

Table 3.4 – The mathematical treatments to predict the mechanical properties and compare with the experimental results.

4.0 Results

Quantitative and qualitative analyses of the nickel products were carried out throughout the material processing and testing stages of research.

- Section 4.1 reports the general observations made from the pre and post sintering stages of the Ni materials.
- Section 4.2 summarizes the scanning electron microscopy (SEM) analysis as well as the tensile properties of the Ni foam and Ni plaque components and the combined Ni substrate and compares them with the processing variables.
- Section 4.3 investigates the mechanical properties of the porous Ni samples, as expected from mathematical models based on their structure and relative densities.

4.1 Sample Observations During Processing

Sample measurements and observations were taken during processing and prior to material testing. Length, width, thickness and mass were all recorded both before and after sintering, and general observations were also made. The figures for the three types of nickel samples (foam, plaque, and plaque-infiltrated foam) are given in Table 4.1.

The **nickel foam** had no noticeable changes in appearance or dimension after being subjected to the sintering process. The foam had a reflective, metallic finish before sintering, and retained that finish after sintering at temperatures of 900 ^oC and 1000 ^oC. Furthermore, the samples showed no change in either size or mass.

The **nickel plaque** had a dark gray, nearly black colour prior to sintering. With well-mixed slurry and a successful tape casting, the plaque had a consistent, flat, onepiece appearance with the presence of small holes or voids that were visible to the eye. The voids were distributed randomly and sparsely. The tape was smooth on the underside, where it lay on the Mylar sheet. The topside was slightly irregular, but still relatively smooth to the touch. After sintering, the plaque was a light gray colour, sometimes with darker edges when sintered at lower temperatures or for shorter times. The sample shrank noticeably in size, decreasing by almost 30% from its pre-sintered form (see table 4.1). The mass of the plaque also decreased by approximately 8%, due to the burning off of the cellulose binder. Any hairline fractures present in the material became more apparent, and widened significantly during sintering. In most cases, the

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plaque sample deformed and curved slightly both along its length and width during sintering. This deformation is due to changes in density throughout the sample as well as gravitational affects.²⁷

Plaque-infiltrated foam had the same dark gray colour as the tape cast plaque, and turned a lighter gray as well after sintering. Also, similar to the plaque tape, there was sometimes a darker 'swirl' or marbling where the plaque does not completely sinter. However, the sample had a rougher texture than the tape cast plaque. The initial mass of infiltrated foam samples depended heavily on the pasting technique. For instance, 1sided/1-pass pasting averaged to 2.0g, while 2-sided/1-pass and vertical casting averaged to 2.4g. 1-sided/5-pass pasting had an average mass greater than 3.0g. There was a five to ten percent decrease in mass during sintering, again, mostly due to binder burn off (See table 4.1). Because the foam itself did not shrink during sintering, there was no noticeable warping or decrease in the size of the sample, although the plaque did pull in to the foam, as it shrunk and adhered to the foam's struts.

Often with a high porosity material, the defining physical attribute is its relative density, (ρ^*/ρ_S) . The highly porous foam had a relative density of 0.0281, while less porous plaque had a relative density ranging from 0.15 to 0.21. Plaque infiltrated foam had an overall relative density ranging from 0.063 to 0.109. While the relative density of the nickel foam remained unchanged after infiltration, the plaque within the foam had a relative density ranging from 0.081, which indicated that the plaque was less dense within the foam than it was on its own.

Furthermore, the percent porosity of the material is defined as:

$$P = 100(1 - \rho^*/\rho_{Ni})$$

Which gave a percent porosity of 97% for the foam, and a range from 79.3% to 84.6% for the plaque. The plaque-infiltrated foam ranged from 89.1% to 93.7%.

Material	Sample Size before Sintering (mm)	Sample Mass before Sintering (Avg.)	Sample Size after Sintering (mm)	Sample Mass after Sintering (Avg.)
Nickel Foam	100 x 20 x 1.7	0.860g +/- 0.005g	No Change	No Change
Nickel Plaque	100 x 20 x 2	2.60g +/- 0.05g	90 x 17 x 0.7 (~30% decrease)	2.40g +/- 0.05g (~10% decrease)
Foam With Infiltrated Plaque	100 x 20 x 1.7	2.0g – 3.6g	No Change	1.95g – 3.3g (5 to 10% decrease)

Table 4.1 - A summary of the effects of sintering on the size and mass of the material.

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4.2 Experimental Results

Experimental data were collected from image analysis through SEM (section 4.2.1), EDS analysis (section 4.2.1.6), and tensile tests (section 4.2.2). The results for plaqueinfiltrated foam are compared in the following sections against the following process variables:

- Slurry viscosity through water content
- Pasting technique
- Sintering temperature
- Gas flow rate during sintering

Strictly plaque samples were subject to the following process variables:

- Sintering temperature
- Sintering time

Strictly foam samples were also subjected to various sintering temperatures, despite the absence of plaque to be sintered.

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infiltration (see figure 4.1). When the nickel slurry was pasted once into the foam, the average depth was 0.70mm. It typically penetrated only the first and second layer of cells, and little to no plaque reached the second half of the foam, much less the opposite surface.



Fig. 4.1 – SEM image of the cross section of nickel foam pasted from one side in a single pass.

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A sample pasted from one side with multiple passes using the hand pasting process resulted in more slurry penetrating the nickel foam. Plaque reached the third and fourth layer of cells within the foam (approximately 1.2mm to 1.5mm), with some plaque passing through to the opposite side of the foam from that being pasted. However, the cells of the foam were only completely filled with plaque in the first layer, with only about 25 - 50% fill in the middle layers, and some whole cells entirely devoid of plaque. An example is shown in figure 4.2.



Fig. 4.2 – SEM image of the cross section of a sample pasted 5 times from one side.

When samples were pasted from both sides, either by hand or with a vertical tape caster, plaque infiltrated the cells of the foam from both sides, achieving greater coverage. However, this method did not ensure more penetration depth. The average depth of penetration for a sample pasted with the vertical tape casting technique was 0.45 mm, or about one layer of cells into either side of the foam structure. This coverage also resulted in a middle section that lacked plaque, representing approximately 0.80 mm of the 1.7 mm sample thickness (see figure 4.3). Similar coverage was achieved in samples pasted by hand, where a single pass with the slurry was made on each side of the nickel foam. Single passes on each side resulted in an average penetration depth of 0.47 mm, again leaving an empty middle layer of foam nearly 0.80 mm thick (see figure 4.4).

The most effective experimental technique was hand pasting from both sides, making multiple passes. Consistent coverage was achieved throughout the thickness of the foam after repeating the pasting process once after the initial pass on each side, as shown in figure 4.5. However, voids or air pockets could not be eliminated with any of the techniques.

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Fig. 4.4 - SEM image of a sample pasted from both sides, with one pass on each side.

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Fig. 4.5 – SEM image of a hand pasted sample, pasted twice on each side, for a total of four passes. The water content of the nickel slurry pasted was 56 wt.% H₂O.

4.2.1.2 SEM – Viscosity and Plaque Infiltration

The water content (wt.% H₂O) of the nickel slurry determined its viscosity, and thus its ability to flow throughout the nickel foam, and still remain within the cells of the foam while the solution dried. In section 4.2.1.1, plaque-infiltrated foam samples pasted using various techniques were produced with 56 wt.% H₂O nickel slurry (high viscosity/low water content), and resulted in incomplete plaque depth and coverage. These samples failed to fully penetrate the cellular structure of the foam, and therefore the water content was increased to 60 and 63 weight percent to increase coverage. Figure 4.6 shows an array of the cross-section and pasted surfaces of plaque-infiltrated samples hand-pasted on both sides with the three slurry viscosities.

At 60 wt.% H₂O, the slurry infiltrated through all layers of cells. The crosssectional image, figure 4.6(a), shows plaque reaching from top to bottom, and filling right to the fracture surface, unlike figure 4.5. Although pockets without plaque exist in the midsection of the foam, they were isolated voids no greater than 1 mm wide. The pasted surface, figure 4.6(b), depicts filled cells with only 6 voids in a 5 mm² area, the largest being 0.3 mm in diameter, indicating that the slurry stayed in the cells and did not have significant dropout during pasting and drying.

While the high viscosity slurry resulted in the highest relative density, it was unable to flow freely into the cells of the foam. The cross section of the high viscosity pasting, figure 4.6(c), shows plaque throughout the thickness of the foam. However,

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there is a large void in the right half of the image, from nearly top to bottom of the sample's thickness, and more than 2 mm along its width. Also, a layer of plaque covers the pasted surface, outside of the nickel foam structure (figure 4.6(d)).

The low viscosity slurry flowed too freely to remain within all cells of the nickel foam. This is shown by the large section of foam devoid of plaque in figure 4.6(e). This bare section represents at least 2 mm of the sample's width and at least one cell layer thick (about 0.5 mm). As seen in the image, not even the foam struts are coated with plaque, which occurs in the higher viscosities. Furthermore, the surface image, figure 4.6(f), has 14 voids within a 5 mm² area, with the diameters ranging from 0.2 mm to 0.5 mm, indicating significant dropout.

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Fig. 4.6 – The cross section and surface images of samples pasted with mid viscosity (a and b), high viscosity (c and d), and low viscosity slurry (e and f).

4.2.1.3 SEM – Viscosity and Plaque Adhesion

Plaque adhesion to the foam structure would benefit the mechanical properties of the composite nickel structure, and is dependent on the water content and, subsequently, the viscosity of the slurry during the pasting process.

High water content not only results in slurry fall-out during pasting, discouraging nickel plaque from reaching and coating the foam struts (section 4.2.1.2, figures 4.6 e and f), but it decreases the concentration of the cellulose binder in the nickel slurry, hampering the ability of the slurry to adhere to the walls of the foam struts through the pasting and drying process. An example of how low viscosity/high water content slurry adhered to the foam struts is shown in figure 4.7, in which the foam was pasted with slurry containing 63 wt.% H_2O . Bare strut surfaces can be seen, and where the plaque did reach to the foam struts, little of the plaque adhered.

As mentioned in the section 4.2.1.1, lower water content results in a slurry that is more viscous and will not flow completely and evenly throughout the cellular structure of the foam. However, the cellulose binder has a greater concentration, and more plaque will adhere where the slurry has reached the cells and the walls of their struts. The image in figure 4.8 of a foam sample pasted with slurry containing 56 wt.% H₂O shows a lesser amount of plaque when compared to the sample in figure 4.7, but there was more plaque actually attached to the walls of the struts.



Fig. 4.7 – An SEM image of the nickel foam pasted with slurry containing $63wt.\% H_2O$.

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Fig. 4.8 – An SEM image of nickel foam sample pasted with high viscosity slurry $(56 \text{wt.\% H}_2\text{O})$.

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In order to reach a balance between infiltration and adhesion, slurry containing 60wt.% water was pasted into the nickel foam. The sample in figure 4.9 shows foam struts surrounded by nickel plaque. Furthermore, the plaque was firmly bound to the walls of the struts.



Fig. 4.9 –An SEM image of a nickel foam sample pasted with slurry containing 60 wt.% $\rm H_2O.$

4.2.1.4 SEM - Voids

Voids or gaps in the nickel plaque and plaque-infiltrated foam samples have two negative effects, they weaken the structure, and deter conductivity.

The presence of nickel plaque within the nickel foam is controlled by the pasting technique used to infiltrate the cells of the foam with the slurry, as well as the flow characteristics of the slurry itself. Images such as figure 4.3 (pg. 49) show how inadequate pasting, in this case vertical tape casting, can result in limited plaque penetration and whole layers of foam cells devoid of nickel plaque. In regard to slurry viscosity, when the nickel solution is too thin, it flows too freely and drops out of the cells, leaving empty cells such as those seen in figure 4.6f (pg. 54), and fails to adhere completely to the surface of the nickel foam struts, as seen in figure 4.6e (pg. 54). Thick, high viscosity slurry can produce large voids such as the empty section in the bottom right of the SEM image in figure 4.5 (pg.51).

Voids, however, are bound to occur at any slurry viscosity, and cannot be prevented by pasting. Empty sections within the plaque are caused by gas unable to escape the slurry before being pasted. Commercial nickel plaques include voids such as these that are typically kept to a maximum diameter of 100 μ m¹¹. In this project, these voids ranged in size from 100 μ m to 1500 μ m in diameter, as can be seen in figure 4.10. Voids in this range can occur with a frequency of 7 voids per 5 mm². This was measured through image analysis and is shown both in the figure 4.10, and in figure 4.11.

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Fig. 4.10 – An SEM image of a large void in the fracture surface of a sintered nickel plaque sample.

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Fig. 4.11 - The frequency of voids in the fracture surface of a nickel plaque sample.

4.2.1.5 SEM – Foam Ductility

The fracture surfaces of the nickel materials were an indication of how the samples failed. The brittle fracture of the plaque was easily identified by the jagged and uneven fracture surface, the result of a quick, often instantaneous failure without significant plastic deformation during tensile testing. The lack of a discernible yield point, and low percent elongation of the nickel plaque samples, which averaged 0.86%, further supports the brittleness of the plaque(see section 4.2.2.1, figures 4.14 and 4.15). Two such examples can be seen in section 4.2.1.4, in figures 4.10 and 4.11.

Nickel foam, on the other hand, failed in a ductile manner, and had a percent elongation of 16.3%. This ductility carried over to the plaque-infiltrated foam samples, which had an average percent elongation of 7.6%. The fracture surface of the foam struts showed both necking before failure and striations perpendicular to the loading direction. An example of a fractured foam strut displaying necking is shown in figure 4.12.



Fig 4.12 – An image of a ductile-fracture surface of a foam strut from a vertically tape cast sample

While all of the foam samples and 8 of the 17 plaque-infiltrated samples failed with an elongation above 10%, 7 of the plaque-infiltrated foam samples exhibited a more brittle failure in which elongation was less than 4%. This transition from ductile to brittle occurs when the relative density of the sample increases from 0.08 to 0.1 (see figure 4.14, page 66). While necking in the nickel foam was less apparent, striations are still visible along the surface of the fractured foam struts, as seen in figure 4.13.

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Fig. 4.13 – Striations parallel to the brittle-fracture surface of a foam strut.

4.2.1.6 EDS Analysis

EDS analysis was done on only two samples, as the composition analysis found the material to be dominated by nickel with no noted impurities. No further tests or findings were of importance from the EDS data.
4.2.2 Tensile Testing

Tensile tests were performed on all three Ni materials with an Instron tensile testing machine. The tests were used to determine the following mechanical properties:

- 0.2% offset yield strength ($\sigma_{0.2\%}$)
- Elastic Modulus (E)
- Ultimate Tensile strength (UTS)
- Yield Strain 0.2% offset ($\varepsilon_{0.2\%}$)
- Percent elongation

In determining these mechanical properties, the materials' characteristics such as strength and ductility can be understood. Tests were performed on mostly plaqueinfiltrated foam, but also strictly plaque and strictly foam samples. Due to the fragility of the sintered nickel plaque, few tensile tests were possible. In the case of strictly foam samples, testing showed a lack of variation, even after being subjected to heat treatment, meaning little could be gained from a high number of tests. All tensile tests were performed at room temperature.

4.2.2.1 Tensile Testing – Materials

The tensile properties of nickel foam and nickel plaque were compared to each other, as well as to the plaque-infiltrated foam composite structure.

In general, foam samples have higher ductility than plaque, with lower relative density (Figure 4.14). Plaque, on the other hand, demonstrates more yield and tensile strength (Figure 4.15), at a higher relative density. Plaque-infiltrated foam, with relative density between the two combines the strength of plaque with the ductility of foam. Furthermore, samples of foam with plaque infiltration average a higher stiffness than either foam or plaque (Figure 4.16).



Fig. 4.14 - 0.2% offset yield strain and percent elongation as it relates to the relative density of the material constituents.



Fig 4.15 - 0.2% offset yield strength and UTS versus the relative density of the materials.



Fig 4.16 – The modulus of elasticity versus the relative density of the three materials.

4.2.2.2 Tensile Testing – Temperature

Sintering is a thermal manufacturing process, and therefore temperature is the primary control variable to produce a material with specific characteristics. In brief, higher sintering temperatures produce stronger materials, at the cost of a lower percent porosity (Tracey¹⁶). However, at excessively high sintering temperatures, brittle failure may occur.

For nickel foam, two samples were tested as received, without any heat treatment process, and two samples were subject to sintering at 900°C and 1000°C each at an H₂ flow rate of 0.38 L/min. The treatment had little effect on the foam samples, as shown by the stress versus strain curves in figure 4.17. There was no change in the volume or mass of the foam, thus no decrease from 97.1% porosity (or increase in the relative density of 0.0284). The most discernable difference in these samples is the earlier failure of the asreceived foam sample, resulting in a lower percent elongation and UTS. This early failure came as a slow propagation of fracture from one side of the sample to the other, as opposed to widespread failure that occurs relatively instantaneously. Also, there was a slight decrease in yield strength after heat treatment. The average mechanical properties are listed in table 4.2.



Fig 4.17 – Typical stress versus strain curves for nickel foam samples. Two of the samples were subjected to sintering (900 and 1000 degrees Celsius, respectively).

Material Treatment	0.2% Offset Yield Stress (MPa)	UTS (MPa)	% Elongation (%)	Modulus of Elasticity (MPa)
As Received	0.70-0.73	1.46-1.50	13.8-14.0	108-152
900 °C	0.40-0.54	1.54-1.67	17.1-17.6	99-116
1000 °C	0.47-0.49	1.64-1.67	17.5-18.0	132-243

Table 4.2 – The average results for mechanical properties of foam samples, as compared with heat treatment, if any.

The plaque samples, as mentioned previously, were very fragile, making handling during processing and testing difficult, and reproducible results were hard to produce. However, tensile data was collected from a sample sintered at a temperature of 1000° C, and two samples sintered at 900° C (both at 0.38 L/min). At 1000° C, the plaque had a

yield strength of 5.50 MPa, a UTS of 7.13 MPa and a modulus of 1370 MPa, much higher than the two plaque samples sintered at 900 $^{\circ}$ C, which had tensile strengths of 1.65 MPa and 1.73 MPa, and a modulus range of 182 – 333 MPa. Both temperatures resulted in the plaque failing in a brittle manner, with a percent elongation of 1.13% for the sample sintered at 1000 $^{\circ}$ C, and the 900 $^{\circ}$ C plaque samples from 0.61 – 1.00%. These differences are shown by two stress versus strain curves in figure 4.18. Of note is the increase in relative density from 0.154 – 0.160 when sintered at 900 $^{\circ}$ C to 0.207 for the 1000 $^{\circ}$ C sample.



Fig. 4.18 - A comparison of the stress versus strain curves of nickel plaque sintered at 900 $^{\circ}$ C and 1000 $^{\circ}$ C.

Plaque-infiltrated foam was tested at temperatures ranging from 850 to 1000 degrees Celsius (all at a flow rate of 0.38 L/min). Previous research by Tracey¹⁰ has shown that at temperatures below this range plaque does not sufficiently sinter, while temperatures above this range result in increased brittleness and decreased porosity. The majority of the plaque-infiltrated foam samples were sintered at 900^oC and 1000^oC (12 and 3 samples tested, respectively), while single tests were performed on samples that had been sintered at 850° C and 950° C.

When samples were sintered at 850 0 C, their appearance was a mottled light grey with dark grey swirls, compared to the solid, light grey colouring of samples sintered at higher temperatures. From a mechanical perspective, there was little difference between samples sintered at 850, 900, and 950 degrees Celsius (See table 4.3). For the 5 vertically tape cast samples sintered at 900^oC, the yield strength ranged from 1.356 – 2.093 MPa, with an elastic modulus from 188 – 786 MPa. The UTS of these samples ranged from 2.05 to 2.34 MPa, with a percent elongation ranging from 1.33 – 15.1%. In comparison, the 850^oC sample had lower yield strength, but similar elastic modulus, UTS, and percent elongation. At 950^oC, the sample had similar yield and tensile strength, as well as percent elongation, but a lower elastic modulus than the 900^oC samples. At 1000 ^oC, however, the samples had consistently brittle fracture, as well as a slightly lower range of elastic modulus, although slightly increased yield strength. These results are shown in figure 4.19.

Unlike nickel plaque, the relative density of plaque-infiltrated foam was not related to sintering temperature, but instead depended on viscosity and pasting technique

(see sections 4.2.2.5 and 4.2.2.6). This is because the Ni foam did not shrink during sintering, the volume of the sample did not change, regardless of sintering temperature.

Modulus of Sintering 0.2% Offset % Elongation UTS (MPa) Temperature Yield Stress Elasticity (%) (degrees C) (MPa) (MPa) 1.99 15.5 1.03 224 850 900 1.36-2.09 2.05-2.34 1.33-15.1 188-786 950 1.26 1.96 14.1 154 1.77-2.49 1000 1.74-2.33 1.43-2.23 131-542

Table 4.3 – The mechanical properties of plaque-infiltrated foam, as a function of sintering temperature.







4.2.2.3 Tensile Testing – Sintering Time

Longer sintering times, similar to increased sintering temperature, increased the densification of the material and thus improved the mechanical strength. The tensile strength and modulus did improve from the longer duration, though not in every case, as seen in Figure 4.20, and not to the same extent as increased sintering temperature (see figure 4.18, pg. 70). The tensile strength of two plaque samples sintered for 10 minutes were 1.69 MPa and 1.73 MPa, while three, 15-minute sintered samples resulted in tensile strengths of 1.42 MPa, 1.62 MPa and 3.24 MPa. For the 10-minute sintered plaque, the elastic modulus of the two samples was 182 MPa and 333 MPa, and the 15-minute sintered plaques had a modulus 165 MPa, 276 MPa and 352 MPa. The percent elongation for the times was also similar, at 0.61% and 1.00% for the 10-minute sintered plaques, and from 0.83 - 1.06% for the 15-minute sintered plaques. Also, longer sintering times increased the relative density of the nickel plaque samples. The two samples sintered for 10 minutes at 900°C had a relative density of 0.154 and 0.160, while the three samples sintered for 15 minutes resulted in a relative density between 0.17 and 0.18. From a mechanical perspective, the longer sintering time did not necessarily produce a better plaque.



Fig 4.20 – The tensile curves for nickel plaque sintered at 900°C for 10 and 15 minutes.

4.2.2.4 Tensile Testing – H₂ Flow Rate

The majority of samples (15 of 17 plaque-infiltrated foam samples, all foam and plaque samples) were sintered at H₂ flow rate of approximately 0.38 L/min (0.8 ft³/hr). This flow rate was chosen because it achieved complete sintering at 900 $^{\circ}$ C, and was well within safe operating conditions. Flow rates of 0.47 L/min and 0.57 L/min (1 ft³/hr and 1.2 ft³/hr, respectively) were also attempted on single plaque-infiltrated foam samples that had been vertically cast. As flow rate increased, material ductility decreased significantly (as shown in figure 4.21), from an average of 11.2% elongation for the lowest flow rate,

McMaster - Materials Engineering

to 6.4% at the mid flow rate, to 1.3% at the highest flow rate. Conversely, minor increases in yield strength were also notable with increasing flow rate, from an average of 1.58 MPa at low flow rate, to 1.61 MPa, to 1.77 MPa for the highest flow rate.



Fig 4.21 – Tensile curves for plaque-infiltrated foam, as a function of hydrogen gas flow rate during sintering. (High = 0.57 L/min, Mid = 0.47 L/min, Low = 0.38 L/min. All samples sintered at 900^{0} C)

4.2.2.5 Tensile Testing – Viscosity

One of the most important factors in the processing of the composite material is the viscosity of the nickel slurry. The viscosity affects the amount of plaque that can infiltrate the foam, and the level of penetration and adhesion achieved by the plaque within the cells of the foam. Although the actual viscosity of the slurry was not measured in standard units, it can be characterized by the water content. Nickel slurries of 56, 60, and 63 wt.% H₂O were tested. Of the 12 tested plaque-infiltrated foam samples sintered at 900^oC, 6 were pasted with 56 wt.% H₂O, 5 with 60 wt.% H₂O, and a single sample was pasted with 63 wt.% H₂O, which had significant slurry dropout, resulting in unsatisfactory coverage of plaque within the foam (see section 4.2.1.2).

The slurry viscosity also affected the mechanical properties of the plaqueinfiltrated foam (see table 4.4). Lower percentage water in the slurry (higher viscosity) resulted in higher relative density for the composite samples, with a wide range for yield and tensile strength, as well as percent elongation and elastic modulus. Lower viscosity slurry with higher water content produced lower relative density, which translated to lower yield and tensile strength, and a low elastic modulus. Mid-range water content and viscosity had a slightly lower range for relative density than the high viscosity slurry, and produced a composite material with a narrower range of properties, inside of the range of the 56 wt.% H₂O samples, although with consistent, ductile failure. Typical stress/strain curves are shown in figure 4.22.

Wt.% H ₂ O of Ni Slurry	Relative Density	0.2% Offset Yield Stress (MPa)	UTS (MPa)	% Elongation (%)	Modulus of Elasticity (MPa)
56	0.083-0.109	1.36 - 2.97	2.05 - 3.11	1.06 - 15.1	188 – 1129
60	0.077-0.096	1.55 - 2.15	2.25 - 2.40	8.45 – 12.2	393 - 488
63	0.083	1.43	2.12	10.87	357

Table 4.4 – The tensile properties of plaque-infiltrated nickel foam, as a function of water concentration in the nickel slurry during pasting.



Fig 4.22 – Tensile curves for 3 plaque-infiltrated foam samples of various water content/viscosity. The samples were all hand pasted and sintered in the same manner.

4.2.2.6 Tensile Testing – Pasting Technique

Several methods of pasting the nickel slurry into the foam were tested and compared for their mechanical properties. Vertical tape casting involved an automated process pasting the slurry in from both sides simultaneously in a single pass, while hand pasting is a manual technique that pasted the slurry in from one or both sides in single or multiple passes.

These different techniques resulted in varying amounts of plaque within the foam, as well as different coverage throughout the nickel foam, and, as such, produced different characteristics when tested with the tensile machine (see figure 4.23). As seen in section 4.2.1.1, hand pasting on both sides and vertically casting proved to have more coverage throughout the cells of the foam, compared to hand pasting from a single side. Thus, 6 vertically cast plaque-infiltrated foam samples were tested, and 5 two-sided, hand pasted samples were tested, while only single samples of one-pass, one-sided and 5-pass, one-sided hand pasted samples were tested.

While the two-sided hand-pasted and vertically cast techniques resulted in similar relative densities, as seen in table 4.5, the hand-pasted samples had higher ranges for yield and tensile strength, as well as elastic modulus, although slightly lower percent elongation. For the one-sided hand pasted samples, multiple passes on one side had more plaque infiltration, and the material had high strength, but low ductility. The single pass by hand sample had the least amount of plaque within the foam and resulted in the lowest strength and low stiffness, but improved ductility.

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Pasting Technique	Relative Density	0.2% Offset Yield Stress (MPa)	UTS (MPa)	% Elongation (%)	Modulus of Elasticity (MPa)
Vertical Tape Cast	0.077 - 0.093	1.35 - 2.09	2.05 - 2.34	1.33 – 15.1	188 - 786
2-Sides/ 1-Pass	0.079 - 0.109	1.43 - 2.97	2.11 – 3.11	1.06 - 11.0	357 - 1129
1-Side/ 1-Pass	0.063	1.16	1.83	11.4	321
1-Side/ 5-Passes	0.097	2.15	2.30	1.8	450

Table 4.5 – The tensile properties of the nickel plaque-infiltrated nickel foam, compared against the pasting technique and it's subsequent relative density of the material.

Stress v. Strain (pasting technique)



Fig 4.23 – Tensile curves of plaque-infiltrated foam as a function of slurry pasting technique.

4.2.3 Experimental Results Summary

In production of the plaque-infiltrated foam, the most important processing variables, in terms of plaque infiltration, are the pasting technique and the viscosity of the slurry. Consistent coverage and adhesion of the plaque within the cells of the foam is best achieved by hand pasting on both sides of the nickel foam, in multiple passes, with a nickel slurry containing 60 wt.% H₂O. Furthermore, the pasting technique and slurry viscosity determine the amount of plaque within the foam, and thus, the relative density of the composite material. The higher the relative density (and lower porosity) is, the higher the yield and ultimate tensile strength, and the higher the elastic modulus. However, as the relative density increases above 0.08 (92% porosity), the plaque-infiltrated foam transitions from ductile to brittle failure.

To a lesser extent, the sintering process will affect the mechanical behaviour of the nickel plaque. Increased sintering temperature and time can provide stronger plaque, but at the cost of porosity, and in the case of temperature, ductility. Similarly, increasing the flow rate of hydrogen gas during sintering may embrittle the material. However, this increase in mechanical properties through sintering is not as significant for the plaqueinfiltrated foam.

4.3 Mathematical Modeling

4.3.1 The Gibson and Ashby Model

Gibson and Ashby¹³ have created mathematical equations to predict the mechanical behaviour of a cellular solid based on the relative density (ρ^*/ρ_s) . Three equations are used to predict three properties (yield strength, ultimate tensile strength, and modulus of elasticity). These equations are defined for open-celled structures (such as Ni foam):

Yield Strength:

$$\sigma^*/\sigma_{\rm Ni} = 0.3(\rho^*/\rho_{\rm Ni})^{3/2}$$
 (5.27a, pg. 145)¹³

Ultimate Tensile Strength (UTS):

 $\sigma^* / \sigma_{Ni} = \rho^* / \rho_{Ni}$ (5.41, pg. 155)¹³

Elastic Modulus:

$$E^*/E_{Ni} = (\rho^*/\rho_{Ni})^2$$
 (5.6a, pg. 130)¹³

The average of the modulus, yield, and ultimate tensile strength for both plaque and foam, as well as the combined material were predicted by the Gibson and Ashby models and are summarized in Table 4.6.

				Gi	ıby	
	Exp. Yield (MPa)	Exp. Modulus (MPa)	Exp. UTS (MPa)	5.27a Yield (MPa)	5.6a Modulus (MPa)	5.41 UTS (MPa)
Foam	0.553	142	1.58	0.213	165	4.21
Plaque	2.52	446	2.79	3.12	5913	25.2
Foam with Plaque	1.87	515	2.25	1.13	1533	12.7

Table 4.6 – A comparison of the measured and calculated tensile properties for the various nickel materials.

4.3.2 The Rule of Mixtures Model

The plaque-infiltrated foam material was composed of two differently processed forms of nickel, and thus the rule of mixtures for composite materials was applied using the experimental results for nickel foam and nickel plaque, as well as the Gibson and Ashby results for each nickel constituent. The yield strength and the modulus of elasticity were calculated using the following equations:

> Voigt: $E_c = E_{foam}Vf_{foam} + E_{plaque}Vf_{plaque}$ $\sigma_c = \sigma_{foam}Vf_{foam} + \sigma_{plaque}Vf_{plaque}$ Reuss: $E_c = [(Vf_{foam}/E_{foam}) + (Vf_{plaque}/E_{plaque})]^{-1}$ $\sigma_c = [(Vf_{foam}/\sigma_{foam}) + (Vf_{plaque}/\sigma_{plaque})]^{-1}$

These values are compared to the experimental results for the plaque-infiltrated foam in Table 4.7.

McMaster – Materials Engineering

Master's Thesis – Dan Bielby

Mechanical Property	Experimental Results	Rule of M Calculated Res	fixtures – from Exp. sults	Rule of Mixtures – Calculated from Gibson & Ashby	
1 0		Voigt	Reuss	Voigt	Reuss
0.2% Offset Yield (MPa)	1.87	0.161	13.5	0.186	6.58
Modulus of Elasticity (MPa)	515	29.7	3044	345	5488

Table 4.7 – The experimental results from plaque-infiltrated foam samples are compared with the rule of mixtures (based on <u>volume</u> fractions). The Voigt and Reuss models are calculated using the results from both the tensile tests and the Gibson and Ashby equations for Ni-plaque and Ni-foam.

Because the composite material was very porous, the volume fractions of the foam and the plaque did not total 100%, as they represented only 3% and 6% - 8% of the samples' total volume, respectively, and the balance is non-contributing open space. Consequently, the rule of mixtures produced results that were atypical of composite materials, and incongruous with the experimental results. Thus, the mass fractions of foam and plaque were substituted in for the volume fractions, in order to account for all solid material comprising the plaque-infiltrated foam composite (see table 4.8).

Mechanical Property	Experimental Results	Rule of M Calculated Res	lixtures – from Exp. sults	Rule of Mixtures – Calculated from Gibson & Ashby	
		Voigt	Reuss	Voigt	Reuss
0.2% Offset Yield (MPa)	1.87	1.86	1.16	2.15	0.57
Modulus of Elasticity (MPa)	515	344	260	3991	472

Table 4.8 – The experimental results from plaque-infiltrated foam samples are compared with the rule of mixtures (based on <u>mass</u> fractions). The Voigt and Reuss models are calculated using the results from both the tensile tests and the Gibson and Ashby equations for Ni-plaque and Ni-foam.

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While the values in tables 4.7 and 4.8 represent the average result, the rule of mixtures' models provide upper (Voigt) and lower (Reuss) boundaries for a composite material with a range of volume fractions (in this case, mass fractions). These boundaries are depicted in figure 4.24 for the elastic modulus, and figure 4.25 for the yield strength. Again, the models are calculated using both the Gibson & Ashby predictions and the experimental results.



Modulus v Mass Fraction

Figure 4.24 – The experimental results for the elastic modulus are compared to the upper and lower limits provided by the Voigt and Reuss models. (G&A - Gibson and Ashby, Exp – Experimental).



Yield Strength v Mass Fraction

Figure 4.25 – The experimental results for the yield strength are compared to the upper and lower limits provided by the Voigt and Reuss models. (G&A - Gibson and Ashby, Exp – Experimental)

4.3.3 Summary of Mathematical Models

The models given by Gibson and Ashby and the rule of mixtures did not accurately predict values for the mechanical properties of nickel plaque or plaqueinfiltrated foam that agreed with the experimental results. Specifically, while the three Gibson and Ashby equations were at least in proximity of the nickel foam characteristics, their approximations of the elastic modulus significantly overestimated the two plaquebased materials.

Similarly, the rule of mixtures, when based on the experimental results for Ni foam and Ni plaque, failed to provide reasonable boundaries for the elastic modulus. However, it did provide an accurate range for the yield strength. On the other hand, the rule of mixtures, based on the Gibson and Ashby predictions for Ni foam and Ni plaque, did provide upper and lower limits that framed the experimental results. Although these limits, particularly for elastic modulus, are significantly far apart.

5.0 Discussion

The strengths and weaknesses of the various processing methods are discussed, and, where applicable, conclusions are drawn in section 5.1. In section 5.2, discrepancies and trends are compared between the experimental data and the mathematical analysis, and adjustments are made to improve mathematical predictions.

5.1 Process Variables

The most significant process variables, sintering temperature, gas flow rate, slurry viscosity, and pasting technique, had significant impacts on the properties of the Ni plaque. While the un-infiltrated Ni foam showed minor variation in behaviour, the penetration of the plaque within the cellular structure and its adhesion to walls of the foam's struts affected the tensile behaviour of the composite samples. In general, the plaque prolongs the foam's resistance to plastic deformation, effectively stiffening and strengthening the composite, and the foam provides improved ductility and percent elongation (See section 4.2.2.1).

5.1.1 Sintering Temperature

The effects of sintering temperature on the nickel materials are described in section 4.2.2.2. While there were no significant changes in the physical or tensile properties of nickel foam samples (as seen in table 4.2, pg. 69), increased sintering temperature resulted in the nickel plaque becoming denser and stronger, but less brittle.

The relative density of the plaque rose from 0.157 when sintered at 900^oC to $0.207 \text{ at } 1000^{\circ}$ C. An increase in the strength and elastic modulus of plaque was also associated with increased sintering temperature, as shown in figure 4.18 (pg. 70). The ultimate tensile strength (UTS) of plaque increased from 1.93 MPa when sintered at 900° C to 7.13 MPa when sintered at 1000° C. Similarly, the percent elongation rose from 0.81% to 1.13% when sintered at 900° C and 1000° C, respectively. The modulus of elasticity also increased from 261 MPa to 1370 MPa when the temperature increased from 900° C to 1000° C. These improved mechanical properties were due to the increased fusion between the filamentary particles of the nickel plaque, as indicated by the increased relative density.

The Ni plaque strength, as it relates to the porosity of the sample, shows agreement with the results reported by Zaitsev¹¹ (see figure 5.1). However, the sintering temperatures for the plaque are different. Zaitsev concluded that the yield strength of plaque sintered at 900^oC would be approximately 4.5 to 5 MPa, with a porosity of about 79.5%. However, the 900^oC samples in this work had an average porosity of 83.2%, with

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yield strength at 1.93 MPa. Zaitsev's samples with a porosity of 83.5% had similar yield strength, approximately 2 MPa, but had been sintered at 750° C. A similar comparison is seen when sintering at 1000° C. Despite the differences in sintering temperature, the tensile strength of the plaque versus the porosity is comparable.



Fig. 5.1 – A comparison between Zaitsev's findings¹¹ and the yield strength of sintered nickel plaque in this project.

Plaque-infiltrated foam behaved differently than sintered plaque alone. The relative density of the samples did not change significantly with temperature, as the 900^{0} C-sintered samples averaged a relative density of 0.0854, and the 1000^{0} C-sintered samples had an average relative density of 0.0859. Sintering at 900^{0} C produced a

material with yield strength of 1.68 MPa, and an ultimate strength of 2.22 MPa at a percent elongation of 8.33%. While sintering at 1000^oC resulted in higher yield strength of 2.06 MPa, the combined material suffered from brittle fracture, reaching 2.13 MPa at a percent elongation of only 1.87%. Contrary to the standalone plaque samples, the plaque-infiltrated foam samples averaged a higher elastic modulus when sintered at 900^oC, at 554.7 MPa, than it did when sintered at 1000^oC, which had a modulus of 307.7 MPa. The effects of sintering temperature on the tensile properties of the nickel materials are summarized in table 5.1.

Material	Yield Stress, 0.2% offset (MPa)	Yield Strain, 0.2% offset (%)	UTS (MPa)	% Elongation	Elastic Modulus (MPa)
Plaque (900 ⁰ C)	1.93	0.81	1.93	0.81	262
Plaque (1000 ⁰ C)	5.50	0.6	7.13	1.13	1370
Foam + Plaque (900 ⁰ C)	1.68	0.59	2.22	8.33	555
Foam + Plaque (1000 ⁰ C)	2.06	1.08	2.13	1.87	308

Table 5.1 – The tensile properties of nickel plaque and plaque-infiltrated foam as a function of sintering temperature.

While sintered Ni plaque was strong but brittle, the Ni foam was much more ductile, yet weaker. The composite material, when sintered at 900^oC, benefited from the characteristics of both base materials' properties. The percent elongation of the ductile foam complimented the higher yield, elastic modulus, and ultimate strength of the plaque.

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While the plaque became stronger when sintered at higher temperatures, the same effect was not seen with the plaque-infiltrated foam. When sintered at 1000° C the composite had improved yield strength, but a lower elastic modulus and percent elongation. Considering the mechanical properties, the optimum temperature for sintering the plaque-infiltrated foam material is 900° C.

5.1.2 Gas Flow Rate

The flow rate of the hydrogen gas during sintering affected the mechanical behaviour of the plaque-infiltrated foam, in particular, the plastic deformation characteristics (See section 4.2.2.4). The most noticeable difference was the decrease in percent elongation at failure. Vertically tape-cast samples, sintered at 900^oC at a low gas flow rate of 0.38 L/min, behaved in a ductile manner, with an elongation of 11.24%. When the flow rate was increased to 0.47 L/min, the sample remained ductile, but elongation decreased to 6.37%. At the highest flow rate, 0.57 L/min, the sample became brittle, fracturing at a low elongation of 1.33%. Similar decreases in the ultimate tensile strength and yield strain occur as hydrogen flow rate increased. Conversely, small increases in both yield strength and elastic modulus corresponded to increased gas flow rate during sintering. Comparisons of material properties are given in table 5.2.

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Master's Thesis - Dan Bielby

Gas Flow Rate (L/min)	Relative Density	Yield Stress, 0.2% offset (MPa)	Yield Strain, 0.2% offset (%)	UTS (MPa)	% Elongati on	Elastic Modulus (MPa)
0.38	0.086	1.58	0.48	2.34	11.2	675
0.47	0.089	1.61	0.46	2.25	6.37	712
0.57	0.093	1.77	0.44	2.05	1.33	786

Table 5.2 – The mechanical behaviour of plaque-infiltrated foam compared with hydrogen gas flow rate during sintering.

A possible explanation for this decrease in ductility is that the increased exposure to hydrogen embrittled the material. Studies by Bockris, et.al.¹⁷, as well as Volkl and Alefield¹⁸ and Kolachev¹⁹, have shown that nickel is susceptible to intergranular weakening from hydrogen diffusion. In particular, the nickel is vulnerable to this diffusion when it is heated to approximately 900^oC (Kolachev, pg. 182)¹⁹, which is the most beneficial sintering temperature, as explained in section 5.1.2. However, in this research, when the Ni foam samples were subject to sintering at 900^oC and 1000^oC, no embrittlement was apparent. In fact, the heat-treated foam samples had both higher UTS and percent elongation than untreated foam (see section 4.2.1.2). Thus, the loss of ductility for the plaque-infiltrated foam samples may only be due to the previously discussed increase in relative density.

A solution to reduce or prevent hydrogen embrittlement may be to change the sintering atmosphere to limit the exposure to H₂. Previous research by Zaitsev involved sintering nickel plaque in a mixed gas environment $(15\% H_2, 85\% N_2)^{11}$, producing higher tensile strengths at the same sintering temperatures used in this research, although at lower porosity.

5.1.3 Pasting Technique

The techniques used for the pasting process affected the nickel plaque coverage within the cellular structure of the nickel foam. The technique determined the depth of penetration from the pasted surface through the thickness of the foam, as well as the amount of nickel slurry that was pushed into the foam cells. Ultimately, the pasting technique determines the relative density of the final combined structure, and thus the mechanical properties. Examples of how pasting technique affects plaque infiltration are shown in figure 5.2 below.

The most significant difference between the vertical tape casting and hand pasting was the control over the volume of slurry that was pasted into a given foam sample. Vertical tape casting subjected the foam sample to a slurry bath before passing through dual blades, meaning the volume of slurry pasted through the foam by the blades was dependent on how much slurry was carried away from the bath by the foam sample in a single pass. Although this resulted in a consistent amount of plaque within the foam (1.45 - 1.94 grams of plaque), it led to incomplete infiltration, most notably in the middle section of the foam sample (see figure 4.3, pg. 49).

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Figure 5.2 – SEM images of the plaque penetration from (a) vertical tape casting, (b) hand pasting two sides/one pass, (c) hand pasting one side/one pass and (d) hand pasting one side/five passes. The pasted surface of single sided pasting is denoted by the *.

For the hand pasting technique, the amount of slurry pasted into the foam sample was dependent upon the number of repetitions of the pour and paste process, allowing for more complete infiltration from one or both sides, and giving a wider range of plaque within the foam (1.03 - 2.44 grams). However, vertical casting was able to paste the

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nickel slurry into both sides of the nickel foam quickly and simultaneously in one pass, while hand pasting, which only pasted the foam sample from one side at a time, took more time.

As mentioned above, the pasting technique determined the amount of slurry within the foam, directly affecting the relative density, which in turn was an indication of the tensile characteristics of the combined material. A trend of increased strength with increased relative density appeared, as well as the loss of ductility at higher relative densities (see table 4.5, pg.78). While similar relative densities were found in vertically tape cast samples and samples hand pasted on both sides (0.077 - 0.093 and 0.079 - 0.109, respectively), the hand pasted samples had higher ranges for yield and ultimate tensile strength, as well as elastic modulus, but with lower percent elongation. The single-sided, single-pasted material, which had the lowest relative density at 0.063, also had the lowest yield strength and UTS, and a low elastic modulus. The material pasted five times from one side, which had a high relative density (0.097), had yield strength and modulus of elasticity comparable to the 2-sided samples (hand-pasted and vertically cast). However, the sample had a low percent elongation, fracturing in a relatively brittle manner, without extensive yielding past the 0.2% offset yield, which was typical of the other pasting techniques.

To summarize, more plaque infiltration is achieved when the foam is pasted, by hand, from both sides, when compared to the other methods. This process also provides the best strength and stiffness of the four pasting techniques, but with reduced elongation. It is also the most time-consuming pasting process of the four.

5.1.4 Slurry Viscosity

The viscosity of the nickel slurry affects the plaque infiltration during processing, and, subsequently, the mechanical properties of the combined material. The slurry must be viscous enough to flow throughout the nickel foam, as well as fill and stay within the cells (see section 4.2.1.2). However, by adding more water to the nickel slurry, the cellulose binder is diluted, affecting the adhesiveness of the plaque to the strut walls of the nickel foam (section 4.2.1.3). For these reasons, three water concentrations were investigated: 56 wt.% (high viscosity, thickest slurry), 60 wt.% (mid viscosity), and 63 wt.% (low viscosity). Figure 4.6 (pg.54) displays the cross-sections and pasted surfaces of the plaque-infiltrated foam.

High viscosity Ni slurry resulted in a dense plaque that was concentrated on the surface of the foam and mostly within the first layers of the Ni foam's cells, failing to fully penetrate to the core of the foam. On the other hand, diluted, lower viscosity slurry infiltrated the deeper cells of the foam, but resulted in a less dense plaque throughout the composite, and less adhesion to the struts of the foam. The best infiltration and adhesion was achieved by hand pasting with the nickel slurry containing 60 wt.% H_2O . The mid-viscosity solution had the most plaque in the cells of the foam, as shown in the two images in figure 4.6 (a) and (b) (pg.54).

The effect that slurry viscosity has on the tensile properties of the plaqueinfiltrated foam reinforces the composite nature of the material in table 4.4 (pg.76).

McMaster - Materials Engineering

When the foam was pasted with the high viscosity slurry, which had the lowest concentration of water and the highest concentration of nickel (56% and 42.3% by weight, respectively), the final, sintered material had a total mass of 3.3 g, which was composed of 26.1 wt.% nickel foam, and 73.9 wt.% nickel plaque. The high viscosity curve in figure 4.22 (pg.77) shows that the high yield strength and low ductility of the plaque dominates. On the other hand, the low viscosity slurry (63% water, 35.3% nickel, by weight) resulted in a sintered sample of only 2.5 g, composed of 34.4 wt.% nickel foam and 65.6 wt.% nickel plaque. The stress/strain curve of a sample pasted with the low viscosity slurry shows much greater ductility, but at roughly half the yield strength, similar to the characteristics of nickel foam. The mid viscosity slurry, 60 wt.% water, 38.5 wt.% nickel, when pasted into foam and sintered, weighed 2.75 g with 31.3 wt.% foam and 68.7 wt.% plaque. It had improved strength over the low viscosity material, without the brittleness of the high viscosity material.

The viscosity and slurry composition further reinforced the relative density factor in determining mechanical characteristics, since higher percentages of nickel in the slurry resulted in higher sample weight, and thus, higher relative density. As relative density increased, the yield strength, UTS and elastic modulus all increased, while the percent elongation decreased (see figure 4.22, pg. 77).

5.1.5 Process Summary

The characteristics of the plaque-infiltrated foam material are determined by the method by which the nickel slurry is pasted into the nickel foam, and the water content of that slurry. These two factors control the amount of nickel plaque that fills the cells of the foam, and thus, the porosity and mechanical properties of the composite material. In general, more plaque in the foam increases the relative density (decreasing porosity), thereby increasing the strength and stiffness of the material. However, as relative density increases above 0.09 (or decreases below a porosity of 91%), the material becomes more brittle. This transition is as result of the different fracture mechanisms illustrated in figure 5.3. As the plaque-infiltrated foam is loaded in tension (figure 5.3 b), it begins to strain elastically by stretching in the axial direction - parallel to the load - and compressing in the transverse direction - perpendicular to the load. For samples with a lower relative density (or less plaque within the foam), the plaque fails first within the cells of the foam, leaving the struts of the nickel foam to carry the load, and ultimately fail after elongation between four and 16 percent (figure 5.3 c). With more plaque in the sample, the relative density climbs above 0.09, and the nickel plaque is able to sustain higher loads. In this case, the plaque and foam fracture simultaneously, and the material fractures in a more brittle manner, with elongation below four percent (figure 5.3 d).

McMaster - Materials Engineering



Fig 5.3 – The loading and fracture mechanisms of plaque-infiltrated foam. a) Unloaded foam, b) Under tension, compression occurs perpendicular to the load, c) Plaque may fracture first, allowing more elongation before complete failure, or, d) Plaque and foam may fail simultaneously, resulting in less elongation, and brittle failure.

To summarize the processing, hand-pasting Ni slurry with 60 wt.% H_2O into the Ni foam achieves infiltration throughout the material, and porosity between 91 and 92 percent. Finally, sintering the composite at 900^oC and with a flow rate of 0.38 L/min provides adequate strength and stiffness, without sacrificing ductility.

5.2 Mathematical Analysis

The results in section 4.3 reported the predicted values for the properties of the nickel materials. However, significant differences, comparisons and trends are discussed for the experimental tensile test data and the Gibson and Ashby models in section 5.2.1, as well as the rule of mixtures' models in section 5.2.2. Section 5.2.3 looks at refinements to improve the accuracy of the models.

5.2.1 The Gibson and Ashby Models

In section 4.3.1, equations 5.27a, 5.6a, and 5.41 from Gibson and Ashby are used to determine the yield strength, elastic modulus, and UTS, for nickel foam, nickel plaque, and plaque-infiltrated foam.

The experimental modulus of elasticity and the calculated modulus for nickel foam were in the closest agreement, with the model being 16% higher than the test result, an overestimation of 23 MPa on average. However, nickel foam had an experimental yield strength 2.6 times greater than the yield strength predicted by Gibson and Ashby, with differences between 0.19 MPa and 0.51 MPa. This underestimation by the theoretical model may be attributed to the assumption of a solid strut in the cellular structure, which differs from the hollow structure of the nickel foam (see section 5.2.3). Furthermore, the model's ultimate tensile strength was 2.7 times higher than the UTS
McMaster - Materials Engineering

found experimentally, with differences from 2.53 MPa to 2.74 MPa. Despite these differences, the Gibson and Ashby models predicted the mechanical behaviour of nickel foam with more accuracy than for the plaque-based materials.

Where nickel plaque is concerned, the Gibson and Ashby model overestimated the mechanical behaviour, particularly the elastic modulus. The experimental modulus of the plaque represented only 7.5% of the modulus expected from calculation, nearly 6000 MPa less on average than the mathematical model. Also, the model overestimated the yield strength by 0.6 MPa on average. Finally, the UTS of the plaque was only 11% of the Gibson and Ashby model's prediction, with an average difference of 22.4 MPa.

Plaque's deficiency of strength and stiffness is similar to that found in the previous research by Zaitsev¹¹, and is attributed to the lack of a "continuous, regular cellular structure" that describes nickel foam, but not sintered nickel plaque. The Gibson and Ashby models, however, are based on the relative density of uniform materials with a high level of interconnectivity. The tensile stress applied to the foam material is efficiently shared amongst the struts. On the other hand, the relative density of nickel plaque includes both a non-uniform structure (varying densities within the sample volume) and ligaments of plaque that do not connect to adjacent sections. In a plaque sample, the tensile stress is spread only amongst sections connected throughout the sample, and intensifies in the narrowest regions. As Zaitsev¹¹ points out, it is important to note that although these ligaments do not contribute to the mechanical properties of the material, they do provide more surface area, and contribute to the material's electrical properties.

For yield strength, plaque-infiltrated foam had a greater average underestimation between experimental results and the Gibson and Ashby model than Ni foam, at 0.74 MPa, and overestimations were much larger for the composite's modulus and UTS than those for nickel foam. The experimental elastic modulus for plaque-infiltrated foam was less than 30% of its model-based prediction, with an average difference of 1018 MPa, and only 17% of the value forecasted for the UTS, or 10.5 MPa lower on average.

	0.2% Yield Strength			Elastic Modulus			UTS		
Material	Model (MPa)	Exp/ Model	Diff. (MPa)	Model (MPa)	Exp/ Model	Diff. (MPa)	Model (MPa)	Exp /Model	Diff. (MPa)
Foam	0.213	2.60	0.341	165	0.859	-23.2	4.21	0.376	-2.63
Plaque	3.12	0.81	-0.593	5913	0.075	-5467	25.2	0.111	-22.4
Foam with Plaque	1.13	1.65	0.735	1533	0.336	-1018	12.7	0.177	-10.5

 Table 5.3 – The average differences and factors between the Gibson and Ashby model and experimental result.

The ratios and average differences between the experimental results and the Gibson and Ashby models are listed for the three properties of each of the tested materials in table 5.3. The relative densities for the materials were 0.0284 for the foam, 0.154 - 0.207 for the plaque, and 0.063 - 0.109 for the plaque-infiltrated foam.

If the model accurately represented the material, the ratio between the experimental value and the Gibson and Ashby value would be as close to unity as possible, and differences would be negligible. However, as figure 5.4 depicts, as relative density of the samples increased, the differences tended to increase negatively for all

McMaster - Materials Engineering

Gibson and Ashby equations. Furthermore, the ratios between the experimental results and the predictions are all below unity for the plaque material, and for two of the three properties for plaque-infiltrated foam. This shows that the Gibson and Ashby models may have greater deviation from material behaviour as relative density increases, and provides further evidence that the models cannot accurately describe the mechanical behaviour of sintered nickel plaque, either on its own or within nickel foam.



Fig. 5.4 – The differences between the actual experimental value and the calculated value are shown for the three Gibson and Ashby equations.

5.2.2 The Rule of Mixtures

The plaque-infiltrated foam is a composite structure comprised of nickel plaque and nickel foam. Thus, the mechanical behaviour of the composite material is a combination of the properties of the plaque and foam. The rule of mixtures, which includes the Voigt and Reuss models, is a popular tool for predicting the strength and elastic modulus of composite materials based on their composition.

The Voigt model, which represents the upper boundary in the rule of mixtures, provides an accurate estimate of the yield strength of the composite material, with an average difference of 0.389 MPa (see table 5.4). However, it overestimates the elastic modulus of the plaque-infiltrated foam by an average difference of 3472 MPa, due to the similarly large overestimation of plaque's modulus by Gibson and Ashby's equation 5.6a.

		Rule of Mix	xtures - Voigt	Rule of Mixtures – Reuss		
Mechanical Property	Experimental Result (MPa)	Result (MPa)	Average Difference (MPa)	Result (MPa)	Average Difference (MPa)	
Modulus	515	3987	3472	472	163	
Yield Strength	1.87	2.14	0.389	0.565	1.30	

Table 5.4 – A comparison between experimental results and results found using the Rule of Mixtures with Gibson and Ashby.

The lower boundary provided by the Reuss model produces a more accurate result than the Voigt model for the elastic modulus, with an average difference of 163 MPa. It

also gives a good lower limit for the yield strength, which had an average difference of 1.30 MPa.

The Voigt and Reuss models, when based on the mass fractions of foam and plaque and their respective Gibson and Ashby properties, showed agreement with the experimental results for the plaque-infiltrated foam in Section 4.3.2. While the experimental elastic modulus results consistently fell near the lower boundary (figure 4.24, pg. 83), the experimental yield strength results were closer to the higher boundary (figure 4.25, pg. 84).

However, the rule of mixtures, while setting boundaries for the composite, may not provide the most accurate prediction of the material's properties, due to the nature of the nickel foam and nickel plaque. Experimentally, the plaque-infiltrated foam averaged a higher elastic modulus than either the nickel plaque and nickel foam on it's own. This contradicts the rule of mixtures in the sense that the properties of the composite will fall between those of the constituents. As shown in figure 5.3 b), subjecting the material to a tensile load will result in compression in the plane perpendicular to the load. This causes the cells of the nickel foam to compress or flatten out in a direction parallel to the load. However, due to the presence of plaque within the foam, the cells will resist this compression more than if the space were empty, effectively stiffening the foam, and increasing the elastic modulus of the composite material.

5.2.3 Refining the Mathematical Models

The results predicted by Gibson and Ashby's equations do not correspond to the experimental results for the plaque and foam materials, but incorporating a coefficient for the hollow struts of the foam and the inherent brittleness of the plaque can improve the accuracy of the predictions.

Previous research by Fan and Fang²⁰ investigated the increase in the strength modulus of open-celled structures that have hollow struts. They introduced a coefficient, f, which is the ratio of the inner (b₁) to outer (b₀) dimensions of the strut. The hollow struts of the nickel foam in this research, which are best described as equilaterally triangular, have an inside length of 51.2µm and an outside length of 67.7µm on average. This results in a value for f of 0.76. Fan and Fang use f to develop a ratio for the yield strength of hollow strut structures to that of solid strut structures. This ratio is defined as:

 $\sigma_{\text{hollow}} / \sigma_{\text{solid}} = (1 - f^3) / (1 - f^2)^{3/2}$ [20]

For this research, the average ratio of hollow-strut to solid-strut yield strength is 2.04, resulting in an increased Gibson and Ashby yield strength of 0.435 MPa (79% of the experimental strength). In fact, the highest of the f values measured (0.83) brings the theoretical strength up to 0.525 MPa, only 0.03 MPa lower than the experimental yield strength. However, this increase in mechanical strength due to strut shape does not apply

to the elastic modulus, possibly because the samples were tested under axial loading conditions.

The nickel plaque lacks a uniform cellular structure, and does not benefit from the connected network of hollow struts, as nickel foam does. It is not unexpected, therefore, that the mechanical behaviour of the plaque did not meet the expectations of the cellular material models. Furthermore, the plaque is a fragile material, which made handling the material without damaging the integrity of the sample difficult. Gibson and Ashby adjusted equation 5.27a in order to predict the brittle failure of an open cellular structure under compression (σ_{cr}^{*}).

$$\sigma_{\rm cr}^{*}/\sigma_{\rm Ni} = 0.2(\rho^{*}/\rho_{\rm Ni})^{3/2}$$
 [13]

This equation yields a brittle fracture strength of 2.08 MPa, which is 0.44 MPa below the experimental yield, but closer to the experimental value than the tensile version of equation 5.27a. That the tested yield strength of nickel plaque fell between the brittle and ductile models proposed by Gibson and Ashby indicates that the plaque was sintered to a point at which the powder particles were beginning to cohere, but not to their full potential. This may also explain the decreased elastic modulus. Besides the lack of interconnectivity within the plaque globally, the individual particles of nickel were not allowed to sinter at a high enough temperature or long enough time to fuse completely with one another locally, decreasing the cross-sectional area of the bond between nickel

McMaster – Materials Engineering

plaque ligaments. These two factors would contribute to lowering the elastic modulus of the plaque by an order of magnitude.

Two major aspects of the composite material's constituents must not be overlooked when applying the rule of mixtures with Gibson and Ashby. First, the nickel foam, whether on it's own or infiltrated with nickel plaque, is essentially the same structure. The relative density of the foam is the same in both types of samples, and any changes to the yield strength or modulus of the foam component are unlikely. Hence the application of the rule of mixtures, which assumes a percentage of the strength or stiffness of a component based on its volume (or mass) fraction of the composite, would unnecessarily reduce the contribution by nickel foam, and does not apply in the case of the foam portion of the composite.

Second, the plaque-infiltrated foam material's predictions were based in part on the mechanical properties of standalone plaque. While the preparation of the nickel slurry was the same for standalone plaque and pasted foam samples, there were several differences in the processing of the samples. Plaque samples were horizontally tape-cast and dried at room temperature before sintering, while plaque-infiltrated foam was pasted either by hand or through a vertical tape-casting process, and subsequently dried in an oven. And, although the nickel plaque on it's own was free to contract during sintering, this shrinkage would be hindered by the struts of the foam which did not show any signs of contraction after sintering. More importantly, the relative density of nickel plaque that had been sintered within nickel foam was much lower than when it had been tape cast on it's own. The relative density dropped to an average of 0.06 when pasted and sintered

McMaster – Materials Engineering

within nickel foam samples, as opposed to 0.17 in the standalone plaque samples. This drop is an indication not only of incomplete infiltration of the plaque in all cells of the foam (see sections 4.2.2, 5.1.3 and 5.1.4), but also of decreased interconnectivity in a material that already suffers mechanically from a non-uniform, porous structure.

Plaque, on its own, would have a higher interconnectivity than it would inside the foam. As seen in section 5.2.1, the lack of interconnectivity greatly influences the stiffness, and the modulus falls well short of results expected from Gibson and Ashby (table 5.3). With regards to the rule of mixtures, the average mass fraction of plaque in the composite was 0.67. However, the lower relative density of the plaque within the foam described a material that has a density that was 65% less than standalone plaque, and thus the rule of mixtures would significantly overestimate the contribution of nickel plaque, and again fails to accurately predict the behaviour of plaque-infiltrated foam.

In regard to the concepts discussed previously, instead of the rule of mixtures providing a prediction of the mechanical properties of the composite material, more accurate results might be expected from simple combination of the two constituents, including the adjustment for the relative density of the plaque within the foam. The combined elastic modulus of the composite is 864 MPa, still higher than the experimental result (515 MPa), but significantly closer than either the Voigt (3987 MPa) model or Gibson and Ashby's equation 5.6a (1533 MPa – based on the relative density of the entire composite). However, this theory does not appear to improve the prediction of the yield strength of the composite. The combined yield strength would be 0.835 MPa, lower than Master's Thesis – Dan Bielby McMaster – Materials Engineering the experimental result (1.867 MPa), as well as the Voigt model (2.14 MPa) and Gibson and Ashby's equation 5.27a (1.12 MPa).

In spite of these refinements, none of the mathematical treatments accurately predicted the mechanical properties for Ni plaque or plaque-infiltrated foam. This is due to the wide range of results from the plaque and plaque-infiltrated foam samples, which is a symptom of the non-uniform structure of nickel plaque. Developing a mathematical relationship between the mechanical and physical properties of sintered nickel plaque will require a better understanding of the structure of the plaque and the effects of the sintering process variables.

6.0 Conclusions

Next generation energy storage devices will need to provide more energy for applications ranging from portable electronics to automotives. At the same time, the marketplace will seek products with decreased system size and weight. This will require new combinations of materials and modification of current fabrications methods in order to achieve the desired characteristics and properties.

The objective of this project was to produce a porous, high surface area substrate for application as the electrode of a supercapacitor. For commercial application the new substrate must be mechanically robust and efficiently manufactured. To achieve this goal, nickel slurry was pasted and sintered within the open cells of nickel foam to create a plaque-infiltrated foam composite. The resultant material, a sintered filamentary nickel powder integrated within highly porous nickel foam, provides a connected network of hollow struts surrounded by high surface area plaque.

Consistent coverage of the plaque throughout the cells of the nickel foam was best achieved by hand-pasting the slurry into both sides of the nickel foam, making no less than two passes on each side with the slurry and blade. The slurry containing 60 wt.% H_2O had the viscosity necessary to flow from cell to cell, remain within the layers of the foam structure and result in a relative density of the composite that maintained ductility. Furthermore, this water content maintained the concentration of the cellulose binder in the nickel slurry, which encouraged adhesion amongst the powder particles, and between the plaque and the struts of the nickel foam.

McMaster - Materials Engineering

The sintering process greatly affected the mechanical properties of the Ni plaque. Higher sintering temperatures and longer sintering times increased the strength and modulus of the plaque but reduced the porosity, and the surface area. These increases, however, were not as apparent in the plaque-infiltrated foam. On the other hand, increasing the flow rate of hydrogen gas during the sintering of either the plaque or plaque-infiltrated foam reduced the percent elongation of the material and resulted in brittle failure. Sintering at a temperature of 900^oC, for at least 10 minutes, with a hydrogen gas flow rate of 0.38 L/min, provided a solid plaque structure with adequate yield strength and elastic modulus, while maintaining ductility.

While both plaque and foam substrates are nickel based, their mechanical properties are very different. Ni plaque is brittle, and has a higher elastic modulus and yield strength than Ni foam. The Ni foam, on the other hand, is ductile, with significant percent elongation at failure. Plaque-infiltrated foam is, in general, a compromise of the foam and plaque's mechanical properties. While plaque-infiltrated foam is stronger than the foam on its own, it is less physically robust than plaque, and while the composite has a higher percent elongation than the plaque, it is not as ductile as the foam. The elastic modulus of the plaque-infiltrated foam, on the other hand, is higher than the nickel foam *and* the nickel plaque. As relative density increases (more plaque), the yield and ultimate tensile strength and the elastic modulus increase, and porosity decreases. However, when relative density increased above 0.08 - 0.09 (or below 91-92% porosity), the percent elongation of the composite decreased significantly, and the material became brittle.

To conclude, in regard to the objectives of this research project:

- Plaque-infiltrated foam is stronger than Ni foam on its own, more ductile than Ni plaque on its own, and has a higher elastic modulus than both plaque and foam. The relative density primarily determines the mechanical properties of the composite. As more plaque is pasted within the foam, the strength and elastic modulus increase, while percent elongation decreases.
- The pasting technique and the concentration of water in the slurry significantly influenced the infiltration of nickel plaque within the cells of the foam samples. The sintering process affected the mechanical properties of the Ni plaque, as longer sintering times, higher temperatures, and increased gas flow rate raised the values of yield strength and elastic modulus, but at a loss of ductility.
- Substrate production by vertical tape casting did not provide sufficient nor consistent plaque infiltration throughout foam. However the hand-pasting process, which requires multiple steps to infiltrate the foam from both sides, addressed the plaque infiltration issue and produced a superior substrate. Consistent substrate production will require multiple infiltration stages on each side, increasing the process complexity.

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