



Production and Characterization of Nickel-Phosphorous Microlattices by Electroless Deposition on an ABS Sacrificial Matrix

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Declaro que o presente documento é um trabalho original da minha autoria e que cumpre todos os requisitos do Código de Conduta e Boas Práticas da Universidade de Lisboa

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Abstract

The goal of reducing weight from structural components in vehicles and aircrafts has always been a key research point in the automotive industry. On this quest, the HRL Laboratories developed the first Nickel-Phosphorous Microlattice that had up to 99.99% of volume porosity, aiming to replace bulk structural materials of aircrafts [1]. This research is focused on the production of Ultralight Metallic Nickel-Phosphorous Microlattices through electroless deposition process onto an acrylonitrile-butadienestyrene (ABS) sacrificial matrix. The production of the matrix structures used the Fused Filament Fabrication (FFF) method, differing from the typical use of the Self-Propagating Polymer Waveguide (SPPW) technique and photopolymeric resins. The Nickel-Phosphorous Microlattices were produced by electroless deposition of the polymeric matrix in an acid bath at 75 °C, using sodium hypophosphite as the reducing agent, followed by the matrix dissolution in dichloromethane (DCM) at 45 °C. The produced structures had relative densities in the 0.34-0.48% range. The microlattices were mechanically tested to study their deformation behaviour, structural defects, and strain recovery ability. For standard compression tests the values of maximum compressive stress, compressive modulus and strain recoveries ranged from 11.3 - 31.3 kPa, 75-212 kPa, and 21.0-46.5 %, respectively, while for cyclic tests, strain recoveries of 81.0-89.2 % and 48.5-49.3 % were obtained for samples tested with 30 % and 60 % of their maximum load. The FFF technique proved to be a viable option to produce the sacrificial polymeric template and the compression tests showed very promising results, revealing the potential of the structures and the production method.

Keywords

Metamaterial; Microlattice; Fused Filament Fabrication; Electroless Deposition; Nickel-Phosphorous Alloy

Resumo

A redução de peso de aeronaves e veículos tem sido ao longo dos anos, um tópico de pesquisa fulcral da indústria automotiva. Nessa busca, os Laboratórios HRL desenvolveram a primeira microrrede de Níquel-Fósforo, que possuía até 99,99% de porosidade volúmica, visando a substituição de materiais estruturais volumosos de aeronaves [1]. Este trabalho focasse na produção de microrredes metálicas ultraleves de Níguel-Fósforo, através do processo de deposição autocatalítico sobre uma matriz sacrificial de acrilonitrila-butadieno-estireno (ABS). Utilizou-se a técnica de Fabricação de Filamentos Fundidos (FFF) para a produção das matrizes poliméricas, ao invés da técnica mais utilizada de Self-Propagating Polymer Waveguide (SPPW) com resinas fotopoliméricas. As microrredes de Níquel-Fósforo foram produzidas por deposição autocatalítica na matriz polimérica num banho ácido a 75 °C, utilizando hipofosfito de sódio como agente redutor, seguida da dissolução da matriz em diclorometano (DCM) a 45 °C. As estruturas produzidas apresentaram densidades relativas entre os 0,34-0,48%. De forma a estudar o comportamento mecânico e capacidade de recuperação de deformação, as microrredes produzidas foram testadas à compressão. Nos testes de compressão uniaxiais os valores de tensão máxima de compressão, do Módulo de Compressão e de recuperação à deformação variaram entre 11.3 - 31.3 kPa, 75-212 kPa e 21.0-46.5%. Nos testes cíclicos recuperação à deformação de 81.0-89.2% e 48.5-49.3% foram obtidos para amostras comprimidas com 30% e 60% da sua carga máxima. A técnica FFF demonstrou ser viável para produzir a estrutura polimérica sacrificial e os ensaios de compressão mostraram resultados bastante promissores, revelando o potencial do método de produção.

Palavras Chave

Metamaterial; Microrrede; Fabrico por Filamento Fundido; Deposição Autocatalítica; Ligas de Níquel-Fósforo

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Acronyms

ABS	Acrylonitrile-Butadiene-Styrene
ACE	Acetone
AM	Additive Manufacturing
ALD	Atomic Layer Deposition
AP	As-Printed
bct	Body-Centered Tetragonal
CAD	Computer-Aided Design
CVD	Chemical Vapor Deposition
cs	Cylindrical Sample
DCM	Dichloromethane
EBM	Electron Beam Melting
EDS	Energy Dispersive X-Ray Spectroscopy
EN	Electroless Ni-P
fcc	Face-Centered Cubic
FFF	Fused Filament Fabrication
PP	Polypropylene
PVD	Physical Vapor Deposition
PLA	Polylactic Acid
MS	Microlattice Structure
DMF	N,N-Dimethylformamide
SEM	Scanning Electron Microscopy
SPPW	Self-Propagating Polymer Waveguide

SM	Subtractive Manufacturing
SLM	Selective Laser Melting
SLS	Selective Laser Sintering
ST	Surface Treated
THF	Tetrahydrofuran
UV light	Ultraviolet Light
XRD	X-Ray Diffraction

Symbols

Α	Strut Cross-Sectional Area
b	Number of Struts
D	Strut Diameter
ε_{max}	Maximum Compressive Strain
Ε	Young Modulus
н	Microlattice Height
HK 100	Knoop Hardness (100 G)
Ι	Second Moment of Inertia
j	Number Of Nodes
К	Column Length Factor
L	Strut Length
LO	Initial Height
θ	Strut Angle
$oldsymbol{ ho}^*$	Relative Density
σ_{cr}	Critical Compressive Stress
М	Maxwell's Criterion
P _{cr}	Euler's Critical Load
r	Radius Of Gyration
t	Strut Thickness
VS	Strut Volume
V _T	Total Volume
W	Microlattice Width
wt. %	Weight Percentage
$\sigma_{Y,0}$	Base Material Yield Strength

1. Introduction

In the last years, one of the main goals of Materials Engineering has been to develop lighter materials, while maintaining or even improving their physical properties. The Metamaterial classification appeared from this research branch, being characterized as macrostructurally changed engineered materials whose properties differ from the bulk [2]. Metamaterials have not only been introducing new mechanical properties to well-known materials [3–5], but also have shown amazing results regarding magnetic [6], electric [7], optic [8], and acoustic properties [9,10].

The concept of Metamaterial is normally attached to the concept of Cellular Solids. These are networks composed by solid struts which interconnect to form edges and cell nodes [11]. From randomly ordered cells (stochastic topology), to well-ordered topologies there is a wide range of structures and geometries that allow materials to achieve very distinct, yet very useful properties in engineering [12]. For example, aerogels are stochastic cellular materials that hold the best insulation properties among all the existing materials [13]. On the other hand, having a stochastic structure is not the best when it comes to predictability and improvement of mechanical properties, since the randomness of these structures result in unpredictable results. This is where well-ordered and well-designed cellular materials gain the upper hand, allowing the tuning and attainment of unique properties, being already represented in the 2D plane by honeycombs, and emerging in the 3D space in the form of nano/microlattices [11,14].

A wide variety of microlattices have appeared over time, ranging from different sizes, geometries, and materials to different production methods. In 2011, HRL Laboratories reported, for the first time, a nickel-phosphorus microlattice with the purpose of reducing the weight of vehicles by replacing bulk materials used in flooring of aircrafts. Since these microlattices showed relative densities around 1x10⁻⁴, while maintaining the linear ratio between stiffness and density, it would result in a massive improvement in fuel consumption of the aircraft [1]. Since then, these structures started to appear in many scientific studies, indicating their great potential.

This Metamaterial drew the attention of a former IST student that proposed as his Master's Thesis the study of the production of hollow nickel-phosphorous microlattices using a sacrificial polymeric matrix template. Despite the progress made, there was still a lot of study and improvements to be made on this topic, since no hollow metallic structures were produced and mechanically tested. This work aims to improve the study of these microlattices even further, having as main goals to finally produce hollow nickel-phosphorous microlattices and to characterize them.

This thesis consists of 6 Chapters. The current Chapter 1 – Introduction, where the context, motivation, and objectives of the work are exhibited. Chapter 2 – State of Art, a review of the literature surrounding the production and properties of the nickel-phosphorous microlattices. Chapter 3 – Experimental Techniques and Procedure, as implied in the title, describes the experimental procedures carried out in this work. Chapter 4 – Results and Discussion, where a critical analysis and discussion of the obtained results is presented. Chapter 5 – Conclusions and Future Work, sums up the main results and achievements of the work, also pointing out unfinished tasks and improvements for future work.

2. State of art

This chapter outlines the most important information which will act as a theoretical basis for the better understanding of the processes involved in this work, providing a state of art on the main production techniques and properties of hollow metallic microlattices. It is subdivided into two main sections: the first subchapter provides information on the basic concepts of Cellular Solids and Microlattices and the second one offers a better insight into the production methods and properties of Metallic Microlattices.

2.1 Hollow Metallic Microlattice: A Man-Made Cellular Solid

Cellular Solids

A cellular solid is described as an interlinked network of solid plates or struts that create the faces and edges of unitary cells. These structures can be classified as closed-cell, if the cell faces are solid planes of material dividing different unitary cells, or open-cell, if they are only outlined by the edges [11]. Regarding the spatial arrangement and geometry of the cells, they can be separated into stochastic (being randomly ordered and having irregular dimensions) or periodic (well-defined and ordered unitary cells). [15]. *Figure 1* shows different classes of cellular materials according to these classifications.



Figure 1- Different classification of cellular solids and examples of materials classes [16].

From stochastic closed-cell foams to periodic open-cell lattice structures, cellular solids provide a wide variety of properties, since these are determined by the morphology of the cells (shape, topology, and connectivity), the material that constitutes the cellular solid, and, most importantly, its relative density, $\rho^* = \rho_l / \rho_0$, where ρ_l is the apparent density of the cellular solid, and ρ_0 is the density of the material the cells are made of [11]. The ρ^* has also been experimentally calculated as the quotient between volume of the struts (V_s), divided by the total volume of the unit cell (V_T), $\rho^* = V_s / V_T$ [17]. The properties attained from these structures are, normally, very different from the bulk material, and when this happens, they receive the classification of metamaterials.

Man-made metamaterials have excelled in magnetic [6], electric [7], optic [8], acoustic [9,10], and in mechanical structural applications [12], even exhibiting negative Poisson ratios to bulk materials that would never achieve these properties [18].

Microlattices

The word *lattice* has different meanings in the engineering world, since in crystallography a *lattice* is a grid where the intersections represent a crystal's atoms, but in architecture and civil engineering, a *lattice structure* is a strut arrangement bonded at their connection [19]. When the dimensions of *lattice structures* are in the magnitude of the millimetre to micrometre, they get classified as *Microlattices,* periodic open-celled cellular metamaterial, achieving tuneable properties based on their strut and cell's morphology and the material that they are made of [20]. *Figure 2* shows the principal parameters of an octahedral unit cell, where *L* is the length of the strut, θ is the truss angle, and *D* is the diameter of the struts, but also represents several secondary ones like *H*, *W*, and *t*, that are the height and the width of the repeating unit (result of *L* and θ), and the thickness of the strut (important for hollow microlattices only), respectively.



Figure 2- Unit cell topology and geometric parameters [21].

The unit cell's architecture is what defines the compressive behaviour of the microlattices, having the same performances as all the other cellular solids, being either bending-dominated or stretch-dominated [22]. In bending-dominated microlattices, the main deformation occurs at the nodes along with rotation of the struts and it is most common in stochastic and open-celled cellular materials. Their stress-strain curve is defined by three main regimes: firstly, a linear elastic strain occurs until yielding; then, an extended and flat stress plateau follows; and finally, a densification regime takes place, where under the applied load the struts collapse and merge into each other, leading to a rapid increase of the stress. It is the second regime that provides the great energy-absorbing property that bending-dominated microlattices are known for. On the other hand, the most common stretch-dominated microlattices are closed-cell and more open-celled periodic structures, and when loaded the struts are subjected to tensile stresses, leading to the difference in deformation mechanisms. The stress-strain curve of these structures also has three regimes as the bending-dominated ones, where after a much prominent elastic strain regime, a post yielding softening event takes place, until the final densification

phenomenon occurs. This behaviour results in properties of high stiffness and initial strength, that makes stretch-dominated microlattices more desirable for high stress applications [19,23,24]. *Figure 3* is a graphical comparison between the two compressive behaviours for two typical unit cell architectures.



Figure 3- Bending vs Stretch-dominated compressive behaviour generic charts [23].

To characterize and define the mechanical behaviour of a cell's architecture the *Maxwell's Criterion (M)* is used, having one relation for two-dimensional (2D) (Eq.(1)) and one for three-dimensional (3D) cells (Eq.(2)) [19]:

$$M = b - 2j + 3 \tag{1}$$

$$M = b - 3j + 6 \tag{2}$$

where *b* is the number of struts of the unit cell, and *j* is the number of nodes connecting the struts. When M<0, the unit cell, when loaded, exhibits a bending-dominated behaviour, whilst when $M\geq0$ the unit cell's compressive behaviour is stetch-dominated, with special attention for cells with M>0, that most likely have struts under self-stress due to geometrical constrains (*Figure 4.a*) shows the application of the criterion on three unit cells.



Figure 4- a) Maxwell's Criterion applied to three octahedral unit cells; b) W/H ratio obtained for different struts angles (Adapted from [23]).

Besides the cell's architecture there are other geometrical parameters that impact the properties of the cellular materials under compressive loading. In 2013, a study on Body-Centred Cubic unit cell (also known as simple octahedral) compressive properties was conducted, and one of the results showed the influence of the angle between struts, 2θ or α , and the increase in stiffness of the structure [25]. It concluded that, for a constant value of *L*, as α increases (and the aspect ratio *W/H* decreases), the initial stiffness of the lattice increases in the axial direction, while the same is not to be expected for the other directions [23]. This correlation adds another layer to the tuning of microlattices, that in conjunction with the unit cell's architectures may provide some extra initial stiffness to bending-dominated structures that otherwise could not be achieve.

Hollow Metallic Microlattices

In the search for lighter and strong materials by the Engineering Science Community, hollow metallic microlattices were developed, even being able to achieve the Ultralight regime in terms of relative density (<0,001) [5], while providing very interesting mechanical properties. As cellular solids, these Microlattices' mechanical properties also are very dependent on their relative densities, since normally bending-dominated structures have a relative compressive Young Modulus, E_l/E_0 , scaling with $C(\rho l/\rho 0)^2$ (where E_l and E_0 are, respectively, the experimental Young Modulus of the microlattice and the material it is made of, and C is a load transfer efficiency constant, usually 3 for microlattices and 1 for open-celled foams), while stretch-dominated lattices have enhanced stiffness performances for lower densities, and have a linear stiffness-density ratio [26,27]. *Figure 5* shows different materials and their Young Modulus and Relatives Compressive Modulus for their ranges of Density and Relative Density.



Figure 5- a) Typical Young Modulus vs Density values for different classes of materials [5]; b) Typical Relative Compressive Modulus vs Relative Density plots, with the linear slops for the different structures [16].

Another important factor to the mechanical behaviour of Microlattices is the buckling of the struts during compression. This phenomenon is described as being a sudden change in shape of columns, that under a critical compression stress abruptly curve sideways [28]. It is possible to estimate the

Critical Compressive Stress (σ_{cr}) of the struts from a microlattice by using Euler's Critical Load formula [29](Eq.(3)):

$$\sigma_{cr} = \frac{P_{cr}}{A} = \frac{\pi^2 E_0 I}{A(KL)^2} = \frac{\pi^2 E_0 I}{(KL/r)^2}$$
(3)

where P_{cr} is the Euler's critical load, *A* the cross-sectional area of the struts, E_0 the Young Modulus of the base material, *I* the minimum second moment of inertia of the cross-section, *L* the length of the strut, *r* the radius of gyration, and *K* is a column length factor (being equal to 1 for fixed translation but free rotation of the nodes). From this formula it is possible to conclude that the bigger the E_0 and the *I*, the greater the σ_{cr} , and, on the other hand, as *L* and *A* increase, σ_{cr} decreases. Since *I* and *A* share dependence on the strut cross-sectional geometry and dimension, it is not possible to generalise what should prevail for all of them, but a very interesting study made in 2007 compared the compressive behaviour of hollow circular cross-section microlattices and solid rectangular one's, and observed that for the same relative density, same base material and same unit cell's architecture, the hollow circular struts showed greater compressive stress values than the rectangular struts (*Figure 6*). This is the result of a bigger second moment of inertia of the hollow circular struts when compared to the solid rectangular struts, and despite the cross-sectional area also being greater, it is not enough to influence their σ_{cr} , showing that, for constant and low relative densities, hollow circular struts are better than the solid rectangular, since they require higher compressive stresses to be applied for buckling to occur.



Figure 6- Compressive Stress vs Strain curves for microlattices with hollow circular struts and solid rectangular struts with approximatly same relative densities [17].

2.2 Production of Hollow Metallic Microlattices

Metallic Lattices have been produced for a long time providing good mechanical properties, saving heavy and expensive material with well-engineered structures. One of the biggest metallic lattices is the Eiffel Tower, that has a very low relative density due to its architecture, which removes unnecessary material and distributes the forces through a simple, yet effective, system of struts [12].

With the evolution of manufacturing methods, the ability to produce different metallic lattices has also improved. Techniques such as Investment Casting and Deformation Forming have been responsible for metallic lattices production for years, but with the advances of Additive and Subtractive Manufacturing (AM and SM, respectively) different techniques such as Selective Laser Melting (SLM), Selective Laser Sintering (SLS) and Electron Beam Melting (EBM) have appeared and promoted new possibilities, either by providing more detailed products, or by allowing the use of more diverse materials [12,16]. Complex processes like Physical and Chemical Vapor Deposition (PVD and CVD) and Atomic Layer Deposition (ALD) have widen the variety even more [26].

The production of hollow metallic microlattices by electroless deposition on a sacrificial polymeric template is a recent, but a very interesting alternative to make super light metallic microlattices. In fact it is the only technique that has reached the Ultralight classification (<10 Kg/m³) [5], matching materials like silica aerogels [30], carbon nanotube aerogels [31], and few metallic foams [32]. The production process is divided into three main steps: the production of the polymeric template; the metallization of the polymeric surface; and finally, the removal of the polymeric matrix living only the hollow metallic lattice. These steps are further explored in the following subchapters.

2.2.1 Production of Polymeric Templates

The production of polymeric templates has seen a lot of improvements over the years, since AM processes have been evolving too. Without the need for machining or the use of dies, 3D printing allows the manufacture of physical objects by converting 3D virtual models of computer-aided design (CAD) files. Software like *Cura*, allow the digital slicing of CAD, promoting the layer-by-layer building mechanism that AM is known for [33]. 3D printing, in general, has very strong pros like quick prototyping, building flexibility and relatively low-cost setups when compared to more robust and industrial manufacturing processes. There are a wide variety of 3D printing techniques varying in physical/chemical manufacturing principles, materials used and machinery setups, but not all of them are suitable for hollow metallic microlattices production, being only a few of them used until this day.

The most used AM process to produce polymeric sacrificial matrix for the manufacture of Ni-P microlattices is the Self-Propagating Photopolymer Waveguides (SPPW) [1,21,34,35].

In this process a tank filled with liquid thiol-ene photomonomer is exposed to a collimated Ultraviolet (UV) light, that passes through a two-dimensional mask with circular apertures, forming a self-propagating waveguide inside the tank from a single point exposure with the UV radiation, being the result of the self-focusing effect created from the difference in refractions indexes of solid polymer and

liquid photomonomeric mixtures. The polymerization occurs in the direction of the previous formed waveguide, due to the internal reflexion of the radiation that focuses on the edge of the solid polymer, promoting a continuous polymerization. At the crossings of the waveguides the struts intersect, forming the nodes of the microlattice [35]. Microlattices with different architectures and dimensions can be produced by changing masks and angle of the incident UV radiation. This technique has very high resolution, with features as small as 100 nm up to 5 μ m [33]. SPPW is a very uncommon process, being only used for very specific applications, and it was not available for this experimental work, creating the need to seek a different alternative.

Another technique that is used to manufacture detailed and smooth polymeric lattices is the Polyjet technology. This process deposits liquid material as droplets that polymerize by exposure to UV radiation in a layer-by-layer system, onto a building platform that moves in the z-axis [36]. Multiple jetting heads can be used to deposit the main and the support material needed for more complex geometries. The typical feature resolution is around the 25 µm, still making it a very precise and geometrically flexible option [33]. However, both this and the SPPW process use photopolymers that have high decomposition temperatures, as well as being very chemically stable, which may imply problems when it comes to the removal part of the polymeric matrix, since very high temperatures or very aggressive chemical environments can compromise the final metallic Ni-P microlattice's properties.

The most common 3D printing technique is the Fused Filament Fabrication (FFF). It relies on the extrusion of thermoplastics, such as Acrylonitrile Butadiene Styrene (ABS) and Polylactic Acid (PLA), that are fed from a filament spool into a pre-warmed nozzle that heats up to the melting or glass temperature of the used polymer (depending on the type of polymer). The extruder moves in a X-Y plane and deposits the first layer of material onto a glass or metallic platform, building from the bottom-up the desired object (*Figure 7*). FFF has a layer height resolution around the 200 μ m (minimum of 50 μ m for more precise devices) and a width resolution of the deposited polymer extruded around 400 μ m (same size of the nuzzles diameter) [37].



Figure 7-Schematics of the FFF 3D process [38].

Even though FFF does not have as good resolutions, surface finishing, etc., as SPPW and Polyjet techniques, it still remains a very inexpensive and accessible manufacturing process with very acceptable print rates. It also has the advantage of working with polymers that are not as chemically stable as the resins used in the other two techniques, proving to be a possible alternative that could allow a non-aggressive chemical removal of the polymeric matrix from the metallic lattice through the use of the appropriate organic solvent.

2.2.1.1 Surface Finishing of FFF Templates

As previously described, FFF printed parts have high roughness surfaces when compared to the more sophisticated printing techniques. However, there are post-manufacturing processes that aim to mitigate this problem, providing mechanical or chemical approaches to smooth out the printed surfaces. Mechanical methods are normally used for geometrically simpler parts, since it requires for the treated surface to be accessible for the treating tools (like sandpaper or an abrasive bead blast), making them very keen to produce irregular smoothing of the surfaces. In contrast, chemical methods are known to produce smooth and uniform surfaces across all the treated part, being way less susceptible to small or hard-to-reach features. The two main chemical approaches are: the dipping in solvent method, being very aggressive and difficult to control due to high reaction rates; and the vapour smoothing method, that can provide incredible results, whilst allowing for more controlled and repeatable results [39,40].

The vapor smoothing method consists of exposing the 3D printed object to a close chamber with a reservoir filled with a liquid solvent. The object is placed onto a raised platform inside the chamber, and it is left there for a determined amount of time. During this time the liquid solvent partially evaporates filling the chamber's atmosphere with vapours. These condense when interacting with the object's surfaces, resulting in the partial solubilization of the surface polymer that slightly flows and covers pores and space between layers, leading to surface smoothness [41]. This process can also be done by heating the liquid solvent or by using it at room temperature (hot and cold method, respectively), where the first promotes faster treatment speeds, by sacrificing some control over the uniform evaporation of the solvent (that can lead to a non-uniform finishing), being the total opposite when working with the cold vapour method.

For ABS objects, cold vapour treatment has shown amazing results when using dimethyl ketone or acetone as the solvent. *Figure 8* exhibits the setup and the results of a research led by *Allessandro Colpani* in 2019 [41], who studied the influence of cold acetone vapour treatment times on the surface roughness of 3D printed ABS samples. The process not only made the surfaces more visually appealing, giving them a glossy look, but most importantly it decreased a lot the surface roughness (R_a) of the samples for all the build angles, proving to be a very efficient method.



Figure 8- Plot of the evolution of Surface Roughness (Ra) with the time of treatment with cold acetone vapour treatment for different building angles [41].

With this treatment the adhesion between the layers increases, tending to result in better resistance to shear forces, this being one of the most common failure mechanisms of 3D printed objects. However, this process can also cause several problems, since excess exposure times lead to the degradation of the polymer, making it very soft and slimy, ruining not only the mechanical properties, but also the handling of the object, even if only used for aesthetic purposes [42].

2.2.2 Metallization of Polymers using Electroless Process

Electroless plating is a metal deposition process, which is based on the reduction of metallic salts to the metallic form by using a chemical agent in an aqueous solution. This process has the ability to plate non-conductive materials, does not require external current and it is appropriate for coating geometrically complex parts, differentiating itself from the well-known and most commonly used electroplating process. The variety of coatings produced by this method has been increasing its popularity in the last years, ranging from nickel-phosphorous to more complex multi-alloyed coatings [43,44].

Although electroless processes can plate non-conductive materials (as most polymers are), they add one extra step when compared to platting conductive parts, requiring what is called a *surface activation step*. This activation promotes the formation of catalytic nuclei on the non-conductive materials, conferring them the ability to exchange charges with the metallic ions in aqueous solution, and allowing the coatings deposition [45]. The next subchapter explains the process of *Polymer Surface Activation*, followed by the principles, chemical reactions, and dynamics of the *Electroless Nickel-Phosphorous Deposition*.

2.2.2.1 Polymer Surface Activation

The definition of *surface activation* dates back to 1950, being described as the deposition process of catalytic particles on a surface, causing it to become conductive and suitable for electroless coating [46,47]. The activation process can be done by an electrochemical or a photochemical process, the first

being the most used for Ni-P coatings. The activation process is described by the following general oxidation-reduction (*redox*) reaction,

$$M^{z+} + Red \to M^0 + Ox \tag{4}$$

where M^{z^+} is the nucleating agent and M is the metal catalyst, *Red* is the reducing agent and *Ox* is its oxidised product. The preferred catalyst is Palladium (Pd), having as the nucleating agent Pd²⁺, and the preferred reducing agent is the Tin ion (Sn²⁺), oxidising to the Sn⁴⁺ state (Eq.(5)).

$$Sn_{ads}^{2+}(aq) + Pd^{2+}(aq) \to Sn^{4+}(aq) + Pd^{0}(s)$$
 (5)

The *redox* potentials of Sn^{4+}/Sn^{2+} and Pd^{2+}/Pd are 0,15 V and 0,987 V, respectively, resulting in a flow of electrons from Sn^{4+}/Sn^{2+} to Pd^{2+}/Pd .



Figure 9-Schematics of both the one step and two step surface activation methods [48]

There are two types of Pd activation process: the one or two-step method. The one-step method is the most used industrially, due to it is faster procedure compared to its contender, while the two-step method is used for more delicate processes, showing better results when it comes to the homogeneity of the samples produced. Both techniques start with a *surface oxidation* step, where an acidic solution is used to clean and degrease the surface while also increasing the surface area by chemical etching, since some surfaces might need to promote the adsorption of the catalytic nuclei (for surfaces with already high roughness this step may not be needed, saving time and resources). Then the one-step method proceeds to have the *activation* step, where the sample is submerged in an aqueous solution

of stannous chloride (SnCl₂), Palladium (II) chloride (SnCl₂) and Hydrochloric acid (HCl), followed by the *acceleration* step, that aims to increase the speed of the activation reaction by moving the sample to a HCl solution, finishing the process [49]. On the other hand, the two-step method starts with a *sensitization* step, where the samples are exposed to an aqueous solution of SnCl₂ and HCl, resulting on the adsorption of Sn ions to the substrate surface, moving on to the *activation* step, taking the sample from the previous solution into another aqueous solution [45]. This time a PdCl₂ and HCl solution is used, that allows the reduction of Pd²⁺ into Pd at the surface (Figure 9 presents a schematic of both methods). It is also important to note that every step above mentioned is time limited by the user, needing to follow each stoppage with water rinsing of the polymer [48].

2.2.2.2 Electroless Nickel-Phosphorous Deposition

Electroless Ni-P (*EN*) coatings are produced by immerging a substrate with conductive or activated surfaces, in a bath of nickel salt (nickel sulphate, nickel chloride, nickel acetate), reducing agent (sodium hypophosphite), and other chemical agents, such as complexing agents, pH regulators, stabilizers, and buffers [50]. Every component has its function, where: the nickel salt is the source of metal; the reducing agent promotes the chemical reduction of the Ni ions; the complexing agents (sodium acetate or monocarboxylic acids) prevent the excess of free Ni ions in solution, stabilizing and preventing the precipitation of Ni phosphate; pH regulator (sulphuric acid or caustic soda) to adjust the pH of the bath; and some secondary agents like the stabilizers and buffers, that prevent the solution breakdown and control the pH of the bath for long depositions [51,52]. The *EN* coating's thickness is controlled by the time of immersion in the deposition bath, while its chemical composition is determined by the bath's agents and pH [53].

The following sections will focus on the chemical reactions and other important data needed to better understand the effects that different elements of the *EN* process have in its deposition rate, in the chemical composition and mechanical properties of the final coating.

Chemical Reactions involved in EN process [52–55]

Starting by looking at the chemical reactions of nickel deposition by hypophosphite, there is one main anodic reaction (Eq. (6)) and one main cathodic reaction (Eq. (7)), where the adsorbed hydrogen reduces the nickel ions on the catalytic surface, promoting the growth of the coating.

$$H_2PO_2^- + H_2O \to HPO_3^{2-} + H^+ + 2H_{ads}$$
 (6)

$$Ni^{2+} + 2H_{ads} \rightarrow Ni^0 + 2H^+ \tag{7}$$

If looked carefully, it is possible to detect that neither of the main redox reactions account for the deposition of phosphorous (P) that is characteristic of this process. Equations (8), (9) and (10) describe secondary reactions that explain the co-deposition of P while the main deposition of nickel occurs, and hydrogen gas is released from the surface of the sample.

$$H_2 P O_2^- + H_{ads} \to H_2 O + O H^- + P_{ads} \tag{8}$$

$$3H_2PO_2^- \to H_2PO_3^- + H_2O + 2OH^- + 2P_{ads}$$
 (9)

$$2H_{ads} = H_2 \tag{10}$$

Besides the main hydrogen reduction reaction, another source of H_2 is the secondary reaction (11). Hydrogen can be dissolved in the Ni-P coatings, leading to massive damage of the coating's mechanical properties, making a post-deposition annealing very necessary and advisable.

$$H_2 P O_2^- + H_2 O \to H_2 P O_3^- + H_2$$
 (11)

The last secondary reaction that can be observed in *EN* deposition processes is the precipitation of nickel hydrogen phosphite ($NiHPO_3$), a black precipitate that not only can attach to the coatings surface increasing its roughness, but also affects the synergy of the main reactions by reducing the concentration of Ni²⁺ in the bath. This reaction describes the bath decomposition that can be promoted by excessive bath temperature (Eq. 12).

$$HPO_3^{2-} + Ni^{2+} \to NiHPO_3 \tag{12}$$

Effect of Reducing Agent Concentration in the EN Deposition Rate

The deposition rate of the *EN* process is directly dependent on the Ni^{2+} bath concentration and $Ni^{2+}/H_2PO_2^-$ concentration ratio. Even though an increase in the reducing agent concentration normally reflects in an increase of the deposition rate, an excessive concentration may cause the reduction of nickel in the bulk of the solution, leading to bath decomposition. If the following equation (13) is considered, to reduce one mole of Ni ion three moles of hypophosphite are needed:

$$3NaH_2PO_2 + 3H_2O + NiSO_4 \rightarrow 3NaH_2PO_3 + H_2SO_4 + 2H_2 + Ni$$
 (13)

From the equation, the theoretical optimal ratio 0.33 of $Ni^{2+}/H_2PO_2^-$ is attained.

In 2003, Taheri studied the influence of $Ni^{2+}/H_2PO_2^-$ ratio in the deposition rate of the *EN*, and was able to find that the optimal experimental value for the $Ni^{2+}/H_2PO_2^-$ ratio ranged between 0.3 and 0.45, and for ratios higher than 0,45 a drastic decrease in deposition was observed [56].



Figure 10- Dependence of deposition rate in an acetate-containing solution on the $Ni^{2+}/H_2PO_2^-$ ratio: $NaH_2PO_2 = 0.224 \text{ mol/L}$; acetate ion = 0.12 mol/L; initial pH = 5.5. [56]

Effect of Temperature in the EN Deposition Rate

Since the *EN* process relies on oxidation and reduction reactions that require external energy in the form of heat to occur, it becomes clear that the temperature of the deposition bath have a great impact on the deposition rate of the coating. These impact holds true to both alkaline and acidic baths. For deposition baths that use hypophosphite, the normal operating temperature is between 60 °C and 95 °C [57]. As shown in Figure 11, as the temperature of the bath increases the deposition rate also increases at an exponential rate. Although higher deposition increases, being recommended to use temperatures around the 80 °C and 85 °C for most baths, to achieve the full deposition potential when it comes to the temperature used [50].



Figure 11- Effect of solution temperature on the deposition rate of electroless nickel coating in acidic bath [56]

Effect of pH in the EN Deposition Rate and Phosphorous Content

The pH of the *EN* bath not only influences the deposition rate, but also has a prominent effect over the phosphorous reduction and final weight percentage on the *EN* coating. For higher pH the nickel reduction reaction increases speed while retarding the self-reduction of phosphorous from the hypophosphite. This leads to an increase in the deposition rate, but also to low phosphorous nickel-alloy characteristic of alkaline baths. On the other hand, acidic baths are known to produce high content Ni-P alloys despite the reduction of the deposition rate, making the pH a very important tunning element to produce the desired Ni alloy [57]. *Figure 12* shows the influence of the bath's pH on both deposition rate and phosphorous content and allows for a better understanding of the guidelines that can help the user to achieve the desired coating.

Not to forget that during the *EN* deposition the values of pH tend to decrease as H^+ concentration increases in the bath, resulting in the deposition stoppage if the pH value drops below 4 [56]. This is most important for big deposition systems that rely on longer deposition times for thicker coatings, being harder to recover the deposition flow of the *EN* bath once it reaches these values of pH [58,59].



Figure 12- Effect on solution pH on deposition rate and phosphorus content of the coating [56].

Equilibrium and Metastable Ni-P Phase Diagrams

The equilibrium Ni-P diagram suffered small modifications over the 19th century, being a major help not only to a better understanding of the deposition mechanisms, but also of the *EN* coating properties (Figure 13) [60]. Below the melting point the equilibrium diagram presents two phases: fcc Ni- α phase, which is a solid solution of 0.17 wt.% phosphorous in nickel, and bct nickel phosphide Ni₃P, an intermetallic containing 15 wt.% phosphorous. In between 0.17 and 15 wt.% of phosphorous a mixture of these two phases coexists.



Figure 13- Ni-P equilibrium phase diagram [61].



Figure 14- Ni-P Non-equilibrium phase diagram (Adapted from [62]).

Although this diagram describes the Ni-P alloys microstructures in equilibrium condition (such as *EN* coatings after certain heat treatments), it does not cover the microstructure present in as-platted Ni-P coatings [62]. *EN* deposition does not follow the equilibrium conditions, since the coatings grow with the deposition of isolated particles, that by subsequent joining with each other increase the thickness of the metallic film. This leads to a lamellar structure that can have compositional variations along the coating's thickness, due to pH variations of the *EN* bath as explained before [63]. The non-equilibrium phase diagram (Figure 13) shows a better picture of the microstructure found in as-platted Ni-P coatings. On

it, a β and a γ phase can be found at temperatures below 300 °C, where the first one is a crystalline solution of phosphorous in nickel very similar to the equilibrium α phase but with 4.5 wt.% P, and the second is a totally amorphous phase with 11-15 wt.% phosphorous, both coexisting in range of 4.5 and 11 wt.% P. Two decompositions reactions define the upper temperature boundaries of these phases. On the solvus lines of β (<4.5 wt.%P) and γ (>11 wt.%P), there is only one transformation of one these metastable phases into α phase and Ni₃P at temperatures around the 350 and 450 °C. However, between 4.5 and 11 wt.% P a second reaction takes place, where the β phase becomes α phase, leading to the precipitation of fine particles in the coating, and the γ phase originates Ni₃P and α phase at around 320°C (Figure 14).

Influence wt.%P in EN Coatings Mechanical Properties

The properties of *EN* coatings are dependent on their microstructures and, as seen before, they are heavily influenced by the phosphorous content deposition during the *EN* process. The *EN* microstructure is not fully comprehended, although as-plated *EN* coatings have been classified as amorphous, crystalline, or a mixture of both. As-platted *EN* coatings are supersaturated solid solutions, with phosphorous dissolved interstitially in the fcc nickel crystalline structure [64,65]. The as-plated coatings are expected to be brittle and hard, with grain size around the 7 nm. The distortion caused by the interstitial phosphorous leads to an amorphous microstructure (γ phase). Because of this, the coatings are separated into: high phosphorous (10 to 13 wt.%) *EN* coatings, normally known to produce amorphous microstructures, that can crystallize after certain heat treatments into nickel and nickel phosphides; medium phosphorous (6 to 9 wt.%) coatings, which consist of mixed amorphous and crystalline microstructure; and finally, low phosphorous (1 to 5 wt.%) coatings, that tend to be crystalline [66].

Composition (wt.%P)	Youngs Modulus (GPa)	Tensile Strength (MPa)	Elongation (%)	HK ₁₀₀
1 to 3	50-60	150-200	<1	650
5 to 7	62-66	420-700	<1	580
7 to 9	50-60	800-1100	1	550
10 to 12	50-70	650-900	1	500

Table 1- Mechanical Properties of electroless Ni-P deposits (adapted from [53])

In *Table 1* it is possible to see that from the low to the high phosphorous coatings there are big differences in tensile strength and elongation, ranging from 150 to 900 MPa and from less than 1% to 1%, respectively. It is also good to point out that, for compositions of 7 to 9 wt.%P of phosphorous, the coatings revealed to have the higher tensile strength of all of them, while maintaining good elongation percentage. Although these results were not obtained from testing microlattices with these composition ranges, but from normal surface coating specimens, it is possible to say that the 7 to 9 wt.%P range should be one to aim when it comes to manufacturing of Ni-P microlattices.

There is also a great influence of heat treatments on *EN* coatings microstructures that directly translate into their mechanical properties, where annealing for 1 hour at 200 °C lead to the crystallization of the as-plated coating and an increasing of the grain size to about 10 nm, reducing internal tensions

and improving the mechanical properties of the *EN* coating, without promoting the appearance of the hard and brittle Ni₃P, that brutally reduces the ductility of the coating. However, if the annealing temperature is increased to 400 °C for one hour, the precipitation of Ni₃P occurs alongside the coarsening of the microstructure, which can lead to a drastic decreased in the ductility of the coating [67]. Once again, these experimental results were not obtained from microlattices specifically, but a similar phenomenon is expected for this type of structures, since the material and the manufacturing process are the same.

2.2.3 Polymer Template Removal Methods

When, finally, the metallization of the polymeric template is over, it is time to remove the sacrificial template to achieve the final and wanted metallic hollow structure. Since the whole structure is going to be subjected to the conditions of the polymer's removal, it is important to analyse the effects that this process can have in the final microlattice properties.

Depending on the polymer used, the removal methods differ slightly, having always a thermal or a chemical route. The first focuses on the thermal decomposition and pyrolysis of the template, while the second one focuses on its chemical degradation or attack with chemical agents.

For the removal of photopolymeric resin templates, one of the only reported type of polymer used for producing hollow metallic microlattices, researchers tend to take the Chemical route by using sodium hydroxide solutions (NaOH) at 60 °C for 24 hours [1,69–71]. Although the use of strong alkaline solutions may interfere with the nickel passive layer (*Figure 15*) and form damaging products on the microlattice metallic surface there are no records of such incidents for NaOH solutions used, meaning that even if damage was inflicted with these solutions, it did not cause substantial problems in the final product. Furthermore, nickel-phosphorous alloys are known to have greater corrosion resistance than the simple nickel, solidifying the idea that the use of NaOH solutions would not cause significant damage to the metal.



Figure 15- Pourbaix Diagram for Nickel-Water system at 25 °C [68].

Despite ABS being known for having good chemical stability when compared to other FFF polymeric filaments, it is not even close to be as chemically stable as the photoresins used in SPPW, not requiring strong alkaline solutions to be removed and instead allowing its removal by using the right organic solvents. As organic solvents do not react in anyway with the nickel structure, there is no risk of chemically changing or affecting the surface and structure of the microlattice surface. However, when in contact with good solvents polymer tend to expand and, if care is not taken, the pressure from the expanding template may cause physical damage on the metallic structure. ABS has different organic solvents that are used for dissolution/reprecipitation techniques, such as acetone and dichloromethane [72]. Figure 16 presents the results of a dissolution test at room temperature that shows the time needed for acetone and dichloromethane to fully dissolve a piece of ABS polymer. In the same research, the ability to reprecipitate the dissolved ABS by using methanol (non-solvent) was also studied, and the results show that it was possible to recover up to 96 wt.% of the ABS used in the beginning of the process, implying that the polymer used for the production of the sacrificial template could be reutilised, if the properties of the recovered ABS have similar chemical and mechanical properties as the virgin one [72].



Figure 16- Dissolution time as a function of ABS concentration in acetone and dichloromethane ate room temperature (25°C) [72].

For the thermal route, both polymers mentioned previously do not differ that much from each other, with the photoresins suffering thermal decomposition or pyrolysis at 500 °C [5], and the ABS polymer around 466 °C [73]. Even though this type of removal promotes a total elimination of the polymer from the microlattice, the high temperatures reached act as metallic heat treatments that can promote grain growth, hardening precipitation, and hydrogen loss. As discussed in the *Electroless Nickel-Phosphorous Deposition* section, for heat treatments above 200 °C the precipitation of Ni₃P occurs, increasing the hardness of the structure and affecting the nickel microlattice's ductility. Since both polymers need to reach temperatures way above this point, the presence of these precipitates is expected and should be avoided, and the thermal route should only be performed in case all other techniques fail [74].

2.2.4 Properties of Ni-P Hollow Microlattices

With the hollow microlattice production process totally covered, it is time to proceed to the properties, defects and characteristics that define these metamaterials.

The microlattices produced from the presented method have specific defects associated, since it involves a lot of different steps, techniques and thin structures that are very sensitive to external influences. The main four defects detected in just-produced microlattices are: geometric variations across the struts of the structure, such as different thickness or diameter of the struts (*Figure 17.(a)*); variation of the circular cross-section of the struts, tending more to an oval-shape (*Figure 17.(b)*); presence of cracking near the nodes (*Figure 17.(c)*); and, finally, cracking along the struts of microlattices, with the cracks providing starting points to catastrophic failure of the structures when compressed and the geometric variations promoting uneven distribution of tension across the whole structure, due to heterogenous dimensions. The more the production process gets improved, and these defects get rarer, the greater the improvement on the microlattices' mechanical properties will be.



Figure 17 - SEM images of common geometric defects observed in hollow metallic microlattice materials [21]

When it comes to mechanical properties, Nickel-phosphorous microlattices have shown an almost linear scaling of the young modulus and compressive strength with the structure relative density [75] and, also have shown, amazing properties on the energy-abortion department, where their ability to deform until catastrophic failure is incredible for such light structures. Alongside this, Ni-P microlattices also have shown very good mechanical recovering abilities, with studies showing up to 50% of strain recovery after uniaxial compression. This was achieved by 120 nm thick 93%Ni-7%P hollow microlattices with relative densities of 0.01% and a wall thickness to diameter ratio of the struts (t_S/D_S) of 2x10⁻⁴ [69]. This is possible due to the deformation mechanism near the nodes, that promotes their rotation with the applied strain, typical in bending-dominated structures, promoting great elastic recovery after compression unloading [21]. Figure 18 shows different stress behaviours of these microlattices structures depending on their relative densities (wall thicknesses), and it is possible to see that for wall thicknesses of 150nm (ρ^* = 1x10⁻⁴), these structures had a total recovery from a 25% strain, with the second cycle revealing a decrease in the stress and young modulus values, showing that the structure had suffered damage during the first compression, nevertheless, followed a similar hysteresis path. For a higher wall thickness of 500 nm (ρ^{2} = 2x10⁻³), the structures achieved strains up to 50% and showed a near total strain recovery. However, when compared to the thinner ones, the reduction in stress and
young modulus is more prominent, and the following cycles do not trail the same path as the first compression cycle. This trend tended to become more relevant the thicker and denser the structs got, with *Figure 18.(c)* perfectly showing it. Although the lower the relative density of the structures show an improvement on their deformation recovery, it should not be forgotten that it also reflects in a decrease of their young modulus and compressive stress, since both properties scale linearly with density, allowing for the tune up of the structures depending on their desired application [1].



Figure 18- Multicycle compression tests of hollow metallic microlattices with increasing wall thickness:(a) δ s=150 nm; (b) ts=500 nm; (c) ts=3 μ m; (d) ts=26 μ m [1].

A mechanical analysis that was associated with these mechanical results was developed, allowing the prediction of the transition between the elastic recovery regime and the plastic regime from a critical thickness-to-diameter ratio of the strut:

$$\left(\frac{t_S}{D}\right)_{cr} = \frac{\sigma_{Y,0}}{E_0} \frac{0.25}{\theta_i - \sin^{-1}[(1 - \varepsilon_{max})\sin\theta_i]} \tag{14}$$

where $\sigma_{Y,0}$ is the base material yield strength, ε_{max} is the maximum compressive strain applied and θ_i the angle of the struts. From the model and using the values correspondent to the Ni-P microlattices, the researchers predicted that the critical ratio was 5×10^{-3} , and by running experimental trials values in same order of magnitude were obtained, ranging from 1×10^{-3} to 8×10^{-3} , corresponding to relative densities of 0.06 and 0.3, respectively [1,26,76].

After the axial loads applied on the microlattices during the compression tests, new defects are formed on the structures. The increase in size and number of the nodal and strut cracks formed during

production is normally noticeable, with the addition of partial (and sometimes total) fracture of the nodes, buckling of the struts and hinging of the metal near the nodes. In *Figure 19* it is shown SEM imaging of these three types of defects associated with the compression of the metallic lattices [1,69].



Figure 19- SEM images of uniaxial compressed microlattices with different defects: (a) partial fracture at a node, (b) localized buckling and (c) plastic hinging at a node (Adapted from [1]).

Now that all the relevant information has been presented, it is possible to see why these structures have been in the scope of different engineering areas, as their properties, such as lightweight, good compressive behaviour, energy-absorption and tunability make them a metamaterial with great potential. This microlattices can be used in lightweight sandwich panels and protective padding (similar applications as the well-known honeycombs), medical paddings, thermal management, high-temperature ceramic filters, battery electrodes, blast protection solutions, and others [16,77]. Their ability to massively reduce weight of structural parts has already caught the attention of the aeronautical industry, since companies like Boeing have been studying the possibility to use this metamaterial in panels for aircrafts' walls and floors, which would result in an energy consumption reduction of the vehicles, while also reducing the manufacturing time, tooling costs and number of parts required to assemble the aircraft [16].

3. Experimental Techniques and Procedures

The current chapter aims to provide insight into the experimental methodologies used in this work and it is chronologically arranged in five Sections: 3.1- presents information about the methodologies used in the production, solubility and surface treatment of the polymeric template produced and used as matrix for the microlattices; 3.2, 3.3 and 3.4- report the surface activation and EN deposition conditions for the cylindrical and cellular structures templates; 3.5- details the polymer removal conditions for both templates; 3.6- describes the characterization techniques used to evaluate the properties of the final metallic microlattices, these being SEM/EDS analysis, X-ray diffraction and axial compression tests.

3.1 Polymer Templates Development

The initial step in the production of the hollow metallic microlattices is the development of the sacrificial polymeric matrix. These were designed using the *SolidWorks2018* software. Two templates were used throughout the work: the simpler template consisted in a 4 x 24 mm cylinder (diameter x length, respectively); and the final microlattice template consisted in a 34 x 34 x 29.23 mm lattice with 32 octahedral unitary cells, having struts with diameter, length, and internal angle (θ) of 2 mm, 8 mm and 60°, respectively.

The cylindrical samples were designed on top of a 40 x 40 x 5 mm base, which made possible the production of sixteen cylinders in only one print, allowing for a better carriage and storage (*Figure 20*). The base also provided stability during the printing process, since vertical printing of lean structures may lead to the fall of a template segment, and to unfinished and deformed samples, while still risking damage to the 3D printer. This way the cylinders were able to be built without the use of support material.



Figure 20- SolidWorks template with 16 Cylindrical Samples with the corresponding dimensions in millimetres.

The microlattice templates were printed individually, but also had the addition of two support structures (*Figure 21*). At the top of the lattice were added eight cylindrical pins to help in the metal deposition stage, providing a place to hold the structure when submerged in the EN bath, being then removed when at the end. At the bottom, sixteen conical structures were designed to help, once again, in the template building stability, since building it from the 2 diameter extremities revealed to be unstable and resulted in several failures. These bases were removed after the activation of the polymer surface.



Figure 21- SolidWorks lattice template with close-ups of the two support structures and relevant dimension in millimetres.

Since the SPPW technique was not available for this work and the Polyjet technique did not prove to be a good alternative in the previous work on microlattices [78], it led to the choice of the FFF process to produce the sacrificial polymeric templates, using ABS filament as polymer source. A *Ultimaker S5* 3D printer was used with a 0.4 mm nozzle, with XYZ resolutions of 0.0069 mm, 0.0069 mm, and 0.0025 mm, respectively, and layer resolution of 0.02 mm. The filaments used were the Green, Red, Blue, Gray and Black ABS Ultimaker filaments with 2.85 ± 0.10 mm diameter [79]. This technique is very accessible and has enough precision to handle the production of the designed polymeric templates, with reasonable time of production and cost. On one hand, this choice closed the possibility of using the most researched photopolymeric resins, but, on the other hand, opened the option to work with other polymers, like ABS, PLA, and PET-G.

The polymer's choice was limited by the temperatures of the EN baths and their ability to be removed chemically. Considering that EN baths normally operate between 55 ° and 90 °C, the chosen polymer needed to have a softening temperature higher than 90 °C. Since the softening of PLA and PET-G are 63 ° and 85 °C, respectively, ABS gained the upper hand with a softening temperature of 97 °C. This encouraged the choice of ABS as the material for the polymeric template, allowing a greater deposition temperature range. ABS, also, presented viable chemical solvents that could be used for the removal of the matrix latter on. After these considerations, ABS was chosen.

The CAD files created in the SolidWorks software were then loaded into the slicing software *Cura*, that allows the template to be sectioned into layers and to define the parameters of the printing process. Both templates shared the same parameters, these being: layer thickness of 0.2 mm; line width of 0.4 mm; printing temperature of 240 °C; build plate temperature of 85 °C; and printing speed of 55 mm/s. It was also set a retraction of the nozzle when moving from one feature to the other, in order to reduce the risk of collision of nuzzle with structure and subsequent fracture of the templates. All the cylinder templates and the initial lattice templates were produced with 100% infill, meaning that no open spaces were left inside the samples. Later, the final microlattice templates were improved, by reducing the ABS used inside the struts, making it partially hollow (<100% infill). This led to an improvement, not only in the printing time and ABS consumed in the 3D printing process, but also, to a huge improvement in the sacrificial polymer template removal later in the process.

For both templates there was no need for support material, making them ready to be used in the following stages, needing only to detach the cylinders from their base.

3.1.1 ABS Solubility Test

To study the viability and effectiveness of the ABS sacrificial template removal by chemical dissolution, later needed in the metallic microlattice production, solubility tests in as-printed ABS were conducted. This simple test consisted of submerging the 3D printed cylinders in different organic solvents at room temperature, observing their efficiency (total or partial dissolution of the polymer) and the time needed for the dissolution of said cylinders.



Figure 22- Solubility tests setup.

As *Figure 22* shows, the setup consisted of a 20 mL round-bottom flask connected to a condenser that limited the loss of solvent by evaporation. The cylinder and the solvent were placed inside the flask with a 5g polymer/100 mL of solvent ratio. Magnetic stirring was promoted by using an *Heidolph Mr. Hei-Tec magnetic stirrer* and a small magnet, spinning inside the solution at 1000 rpm. The times were recorded until total dissolution or no progression in the dissolution process was observed. The used organic solvents where acetone, dichloromethane (DCM), tetrahydrofuran (THF) and N,N-dimethylformamide (DMF).

3.1.2 Surface Treatment of 3D Templates

As said in chapter 2.2.1, the templates produced by FFF are rougher than the ones produced by the SPPW process. To bring the produced ABS templates closer to the roughness of those produced by the SPPW technique a cold vapor acetone surface treatment station was developed.

There are several commercial stations out in the market, but their high cost, dependence in specific commercial solvents and low versatility in terms of provided treatments make them an uncommon equipment and were not available for this experimental work. Nevertheless, the goal of reducing the polymeric template roughness still existed and the station presented in *Figure 23*Figure 23- was designed. A 34.5 x 25 x 20 cm polypropylene (PP) box worked as the chamber for the surface treatment station. To the walls of the box a stainless still plate was attached using 4 *L* shape normal steel holds and 8 bolt-screw-washer sets, acting as the working table for the polymer templates. To the lid a *Noctua NF-R8 redux-1800* computer fan was attached, to provide air flow inside the chamber, which promoted a more homogeneous atmosphere. An USB connector was added to the fan, allowing it to be connected to a plug, being powered by the common power grid. Also, several small openings were made in the lid to prevent excessive pressure from the acetone vapours inside the chamber.



Figure 23- Three perspectives of the acetone surface treatment station: a) chamber's dimensions and closed lid; b) open chamber showing the metallic working platform; c) fan set up on the chamber's lid.

The surface treatment consisted of the following steps: deposition of 0.5 L of acetone at the bottom of the PP box; close the lid, turn the fan on and let the system stabilize for 15 min; quickly open the lid and place the part to be treated on top of the metallic plate; leave it inside the chamber for the desired time; finally, remove it carefully from the chamber and let it dry for at least 12 h.

The acetone was reused from treatment to treatment, only being added new acetone to replace the volume that was lost to the atmosphere through evaporation. It is recommended to use this surface treatment station in a well-ventilated area, since when the lid is opened, acetone spreads across the room's atmosphere, which can affect the user's welfare.

3.1.2.1 Roughness Analysis of Surface Treated 3D Templates

In order to study the effectiveness of the acetone surface treatment, a quantitative evaluation of the surface roughness of treated samples was done. For this, the *Filmetrics Profilm3D Optical Profilometer* was used to obtain the samples surface profile (*Figure 24.a*)), allowing the measurement of the surface *Ra* (in μ m) with the help of the *Profilm Online* software (*Figure 24.b*)).

In this experiment 24 samples were analysed for surface treatment times of 0, 15, 30, 45, 60, 75, 90, 120 min (3 samples for each time), following the experimental procedure described in the previous *subchapter 3.1.2*. The profilometer collected information of 15 partially overlapping areas for each sample, which were latter stitched together in the Profilm software (generating a 0.425 x 5 mm image), promoting a better representation of the overall sample roughness. For each stich file, 3 *Ra* values were obtained following ISO 4287, the final results being an average of these values for each treatment time.



Figure 24- a) Roughness analysis with optical profilometer; b) Quantitative roughness analysis of the treated surfaces in the Profilm Software.

3.2 Activation of the Polymeric Surfaces

The next step of the microlattices production is the surface activation of the polymeric templates. This step aims to develop conductive catalytic nuclei on the non-conductive ABS surface, making it possible to use the EN deposition process. The activation process of all samples, in this work, followed the same procedure and used the same palladium and tin solutions throughout its extension [5,78].

The two-step activation method was used to activate the polymeric templates. A sensitization and an activation 100 mL solutions were used, containing respectively: 3.5 g/L of SnCl₂. H₂O plus 5 mL/L of 37% HCl; and 0.5 g/L of PdCl₂ plus 4 mL/L of 37% HCl.

The procedure was very straight forward: the ABS templates where firstly rinsed with Millipore water for 30 s before the sensitization step; then, the samples were submerged in the 100 mL sensitization solution for 2 min, followed by another 30 s of water rinsing; finally, the samples were immersed in the Pd activation solution for 2 min and water rinsed one last time for 30 s, finishing the surface activation process.



Figure 25- The two surface activation solutions used: on the left, the sensitization Sn aqueous solution and on the right, the activation Pd aqueous solution.

The tin sensitization solution had a white coloration, and the palladium activation solution had a very intensive brownish coloration (*Figure 25*). During this work two of each solution were used, to assure the effectiveness of this step for all the produced samples. It is also important to mention that before the use of these solutions it is advisable to shake them, since they tend to form small aggregates when not used for a few hours.

3.3 EN deposition on Cylindrical Templates

After the polymer surface's activation, the samples were ready for the electroless deposition. To analyse the influence of deposition temperatures on the polymer templates and the Ni-P coatings, the cylinder templates were used because of their simpler geometry, faster production times and reduced surface area, acting as an optimization step for the final microlattice structures.

There was a large variety of bath solutions in the literature, so its choice was made based on the desired aspects for: the bath itself and the Ni-P deposit. Based in *Electroless Nickel-Phosphorous Deposition* section, the desired wt.%P, in the deposit Ni-P alloy was somewhere between 7 % to 10 %, meaning that an acid bath was required. Then, it was important that the bath was able to operate at lower temperatures than the ABS softening temperature (lower than 97 °C). Finally, to maximize the deposition rate, the bath should have the right ratio between nickel salts and hypophosphite. The EN solution had nickel sulphate as the metal sourced, sodium hypophosphite as the reducing agent and sodium acetate as the complexing agent. The bath solution used for the EN deposition in this work consisted of 25 g/L NiSO4. H₂O (nickel(II)sulphate), 23 g/L NaH₂PO₃. H₂O (sodium hypophosphite), 9 g/L NaC₂H₃O₂ (sodium acetate), with Millipore water as solvent. This bath composition allowed for bath pH ranges of 4 to 8, having advisable deposition temperatures from 70 ° to 85 °C [50,80].

In this work 250 mL EN solutions were used, with a pH between 5 and 5.5. This pH adjustment was made by adding drops of 97% H₂SO₄ until the desired pH was attained.

The deposition set up used consisted of: a thermostatic bath, which allowed a precise and continuous control of the EN deposition temperature while providing the heat needed for the same to occur; a magnetic stirrer, that promoted the homogeneity of the deposition and helped with the reduction of

hydrogen on the deposition surface; a 300 mL flask was heated by the thermostatic bath water, acting as a stably-warmed container for the EN depositions; and a gripping element, that held the samples submerged in the EN bath without letting them interact with the rotating magnet (Figure 26).

The EN deposition of surface-treated and as-printed cylinder templates was performed by using only one solution of 250 mL, with a deposition time of 1 h. The deposition temperatures of 55, 60, 65, 70, 75 and 80 ° C for the surface treated samples were studied, while the as-printed templates were only coated at 70, 75 and 80 °C. The evaluation of the best bath conditions was made by observing the quality of the obtained EN coatings and, afterwards, the ability to remove the polymer matrix without compromising the Ni-P alloy integrity.



Figure 26- EN deposition setup with the thermostatic bath on the left, and the magnetic stirrer, the glass container, and the gripping element on the right.

3.4 EN deposition on Microlattice Templates

The EN deposition of the microlattice templates used the exact same setup as the cylinder template. Although the EN bath solution used was also the same, the deposition temperature was fixed at 75 °C, the deposition time was reduced to 30 minutes for each EN solution used, and for these templates 1, 2 or 3 EN solutions of 250 mL were used. It is important to mention that all microlattice polymer templates used were not surface treated with acetone (being as-printed samples). These choices were made based on the cylinder template's results.

Fourteen microlattice samples were coated in this work, where 2 of them were coated with only one immersion in the EN solution, another five were subjected to two immersion steps in the EN baths, and

the last seven were coated with three immersion steps in the EN solutions. This led to microlattices with different thicknesses and masses. The integrity of the Ni-P coating was only really evaluated in the next production step (*Polymer Matrix Removal*), since all the coatings produced in this stage appeared homogeneous and good to produce metallic microlattices.



Figure 27- EN deposition on microlattice polymer template.

3.5 Polymer Matrix Removal

The last step of the ultralight metallic microlattices production was the removal of the sacrificial polymer matrix, to reveal a hollow Ni-P cellular solid.

A chemical route was chosen to remove the ABS polymer matrix. Based on the results achieved in the *ABS Solubility Tests*, the selected solvent was dichloromethane (DCM). The removal process consisted of the immersion of the Ni-P plated polymer template in 200 mL of DCM at 45 °C (when working in the lab) or 35 °C (during night hours). For the cylindric template, 200 mL of DCM proved to be enough to achieve a full removal of the polymer from the metallic structure, whilst for the final microlattice structures more DCM was needed. The organic solvent was changed when its colouration became very saturated with the same colour as the ABS (*Figure 28*). When the removal was complete, the hollow microlattices were carefully removed from inside the organic solvent and washed in Millipore water.

The removal setup was composed by the same thermostatic bath used in the EN deposition step and a 300 mL glass flask, with a small hole on the lid to prevent a dangerous increase in pressure since DCM is highly volatile.



Figure 28- DCM highly concentrated in grey ABS.

3.6 Characterization of the Metallic Microlattice

After the production of Ni-P microlattices, the characterization of their metallic structure was carried out. Axial compression tests, SEM/EDS and XRD analysis were used to obtain qualitative and quantitative results. The details on their experimental set ups and parameters are presented in following subchapters.

3.6.1 Axial Compression Tests

With all the previous Ni-P microlattices production steps reliably leading to solid and light structures, the main goal of this work was reached. The second main goal was to characterize these structures, with the aim of obtaining information on the microlattices properties.

One of the major ambitions since the beginning of this research work was to study the mechanical behaviour of the Ni-P microlattices under compressive loads. Most of the data was obtained testing eight Ni-P microlattice samples: four of them being produced with 3 EN depositions and the other four with only 2 EN depositions. Two of each sample grades were compression tested, almost, until maximum strain, while the other four samples were cyclic compression tested, for 100 compression cycles, from 1 N up to 30% and 60% of their maximum loads, these being the minimum and maximum loads applied during said cycles. In the standard compression and cyclic compression tests, a 1 mm/min and a 14 N/min rate were respectively used. For both these tests, an *Instron 5544* tensile tester was used with a 100 N loading cell and an advanced video extensometer, that allowed the collection of strain values through the relative position of two aligned white dots. Normally, these two dots are placed on the sample's surface to obtain strain values directly for the studied sample, but the used extensometer had a minimum distance of 10 mm between dots, producing noise in the obtained signal for values lower than this limit. To avoid this problem, the dots were placed in the bases of the compressive system instead on the sample struts (*Figure 29*).



Figure 29-a) Dots placement in the samples external nodes that lead to noise in the signal. b) Adopted detection point placement on the compression plates.

Although the noise in the values was avoided with the placement of the detection points in the compression plates, it also led to a wrong value of strain presented in the results spreadsheets, since the initial height, L_0 , was not the height of the microlattices but the initial distance between dots. So, the values had to be corrected by, firstly multiplying the strain values by the initial test length, and then divided them by the true height of the microlattices, L_0 . To obtain the correct values of L_0 , a *Mitutoyo* 450 mm Dial Height Gauge was used, measuring the distance between compression plates before the tests started (with both plates in contact with the microlattice as showed in *Figure 30*).





Figure 30- a) Dial height gauge used and b) how it was used to obtain the real initial height of the microlattice samples.

All the compression tests were video recorded with the use of a *GoPro*. This allowed, with the image processing software *ImageJ*, the study of the strain recovery after compression, determined by:

$$\% Recovery = \frac{L_{after \ load \ release} - L_{before \ load \ release}}{L_0 - L_{before \ load \ release}} \times 100$$
(15)

Where the numerator represents the recovery in mm observed after the load is removed from the sample, and the denominator is the total length that the sample was compressed (*Figure 31*).



Figure 31- Ni-P microlattices strain recovery with the Lbefore load release on the left and Lafter load release on the right.

3.6.2 SEM/EDS Analysis

The topography and elemental information of the produced and compression tested metallic microlattices were obtained via Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray Spectroscopy (EDS). These analyses can examine and produce magnified images by accelerating electrons onto a small conductive area of the sample's surface. With the use of specific detectors, X-rays, backscattered and secondary electrons are collected, providing the desired data.

SEM and EDS analysis were made in a *Phenom ProX G6 Desktop SEM* with a cerium-hexaboride (CeB₂) electron source using 20 kV, and an integrated EDS detector. Three distinct sections of three axially compressed microlattices were analysed. The mentioned sections consisted of the top section of the unit cell, the node connecting top and bottom cells, and another node connecting side to side the metallic microlattice's octahedral cells, as shown in *Figure 32.a*). The samples were coated with a Gold-20wt%Palladium alloy, producing a conductive layer on top of all the samples surface, allowing for the observation and study of the metallic coating and remaining polymeric residues (*Figure 32.b*)).



Figure 32- a) SEM holders with all the different segmented sections attached with carbon conducing tape. b) Coated samples with the Au-Pd conductive alloy.

3.6.3 X-Ray Diffraction Analysis (XRD)

With the goal of identifying the phases present in the produced Ni-P microlattices XRD was used. This technique utilizes a monochromic x-ray beam that by interacting with the sample, diffracts at specific angles, providing information on the phases present.

XRD analysis was performed in a *D8 Advance Bruker diffractometer*, with a tube electric potential difference of 40 kV, tube electric current of 30 mA, using a Cu-K α anode having 1.54060 Å as characteristic wavelength. The studied samples were made by grinding into powder fractions of two compression-tested microlattices. A crystal Si, zero signal, XRD holder was used. The samples were scanned from 2θ =30° to 60°, with a step size of 0.04°, and 1 s of acquisition time per step.

4. Results and Discussion

The current chapter aims to discuss, analyse, and present the experimental results obtained from the previously described and developed production process of Ni-P microlattices. The first four subchapters, *3D Printing of the Polymer Templates*, *Optimization of the EN Deposition on Cylindrical Samples, EN deposition on Microlattice Templates*, and *Polymeric Matrix Removal*, aim to present and describe the results observed during the microlattices production stages, while the last subchapter, *Characterization of Metallic Microlattice*, aims to exhibit the results obtained from the characterization process of the final Ni-P microlattices.

4.1 3D Printing of the Polymer Templates

The idea that 3D printing is a manufacturing technique that has well-defined parameters for every single design, material, and application is not very accurate. For a template, the ideal production parameters may be found on the first try, while for another one it may take more attempts.

The printing process of both polymeric templates suffered a few parameter adjustments while carrying out this experimental work.

The first set of parameters allowed the production of both polymeric templates, with the cylindrical template achieving decent quality and low noticeable defects. The same was not observed for the microlattice template though, since a lot of extra roughness and threading (polymeric threads across the template structure) were produced as seen in *Figure 33.a*). From there, the parameters were modified to achieve the best production quality of these templates.

Then a second set of parameters were applied, totally removing the produced defects from the first parameters, achieving templates without threading, deformation, or uncharacteristic roughness. Although the results achieved were ideal in terms of surface quality a last changed was made. These parameters produced 100% infilled templates, meaning that all the template's volume was filled with ABS polymer.

The last change in parameters was done to try and improve the removal of said templates from the metallic coating later in the experimental process. The removal of ABS with organic solvent promoted, even if in small quantities, the expansion of the polymeric template inside the Ni-P coating, damaging it by producing cracks and structure fractures. To mitigate this effect the last parameters were applied, producing templates with less than 100% infill by having small voids in the templates core. This later allowed the consistent production of the Ni-P microlattices, allowing the polymer to swell to the void's volume, applying less force on the Ni-P coating. As seen in *Figure 33.b*, the final microlattice template had less roughness and threading then the first one produced.

The main dimensional specifications of the microlattice template described in chapter 3.1 are summarized in *Table 2*.



Figure 33-a) Imaging of the first produced microlattice template vs b) the template with improved 3D printing parameters.

Specifications	Microlattice Template				
Size (mm)	32x32x29.23				
Unit cell	Octahedral				
Surface Area (mm ²)	2,05x10 ⁴				
Strut Diameter (mm)	2				
Strut Length (mm)	8				
Strut Angle, θ (º)	60				

Table 2- Microlattice template specifications summary.

4.1.1 ABS Solubility Tests

The need for an effective polymer matrix removal system was crucial to produce the Ni-P microlattices, since without it the process would always stop with an ABS/Ni-P coating composite.

The ABS solubility tests did not aim to present a direct translation for the final polymeric removal step in the microlattice's production, since the conditions were not the same. They aimed to provide information about the possibility of fully dissolution of the ABS template and about the best solvent for this role, by measuring the time needed for this task.

The results of the solubility tests are presented in *Table 3*. Starting by the most important result, the only solvent able to fully dissolve the ABS cylindrical template was dichloromethane (DCM), taking an average of 55 min to achieve it, while the other three were only able to partially dissolve identical samples.

Solvents	Polymer	Concentration (g/100 mL)	Nº of measurements	Average Time (h:min)	Dissolution Result	
ACE			1	4:00	Partial	
DCM		7		0:55	Total	
THF	ABS	5	2	3:30	Partial	
DMF			4	2:00	Partial	

Table 3- Results of the ABS solubility tests at room temperature.

When submerged in acetone (ACE), the templates suffered weight loss, decolouration and significant as seen in *Figure 34.a*). Not only the inability of total dissolution, but also the extra swelling produced during said dissolution made acetone an unfeasible option.

As for tetrahydrofuran (THF) and N,N-dimethylformamide (DMF), both were not as bad for said conditions as acetone, where both dissolve most of the ABS template. However, small ABS remains were present after long testing times (*Figure 34.b*)), making them a worse option than the selected DCM.



Figure 34- a) Comparison between an as-printed (top) and a cylindrical template after acetone solubility test (bottom); b) Remains of ABS after solubility tests using DMF; c) Repolymerization of ABS after DCM evaporation.

From the ABS/DCM solutions obtained during the template's dissolutions it would be possible to partially re-obtain both ABS and DCM, through the ABS re-polymerization process by solvent evaporation with solvent re-condensation and storage, making it one aspect to be further improved in future works. *Figure 34.c*) shows repolymerized ABS after the evaporation of DCM.

4.1.2 Surface Treatment of ABS Templates

The FFF process used to manufacture the polymeric templates has big surface roughness and waviness disadvantages when compared to its competitors. To improve these properties a cold vapour acetone surface smoothing system was developed and tested in the ABS templates. The analytical results are present in the following subchapter *4.1.2.1*.

The smoothing system showed improvements even when seen with the naked eye, making the surface acquire a shiny and glossy exterior for treatment times as low as 30 min (*Figure 35.a*)). However, with the increase of treatment times, besides the improvement previously described, the surface started to lose its hardness, to the point where even the sample holder promoted the indentation of the cylindrical ABS templates (*Figure 35.b*)). This restricted the time of sample exposure to a 60 min maximum, since it was the value from which this phenomenon started to happen.



Figure 35-a) Result of a 30 min acetone surface treatment on a microlattice template; b) 75 min treated cylinder template with noticeable indentation from the plastic holder.

4.1.2.1 Roughness Analysis of Surface Treated 3D Templates

In order to analytically validate the observable results from the cold vapor acetone surface treatment, *Ra* measurements were performed on treated cylindrical samples with different exposure times.

In relation to the waviness of the samples, it was possible to observe a great reduction from the increasing treatment times, being justified by looking at *Figure 36*. For untreated ABS cylindrical samples (*Figure 36.a*)), the optical profilometer was not able to analyse all the sample's surface having a lot of unregistered values, especially in the valleys of the 3D printed layers. This means that the profilometer did not had the resolution to obtain values with such height difference.

However, for treated samples with just 15 min of exposure (*Figure 36.b*)) an increase in obtained values was observed, implying a reduction of the surface waviness. The increase in treatment time proved to promote better surface recognition, with the 120 min samples having almost all the surface values detected (*Figure 36.c*)).



Figure 36- Difference between the surface roughness attained results for: untreated sample a); 15 and 120 min surface treated samples, respectively, b) and c).

For the roughness analysis of the ABS samples, analytical values were obtained and are presented in *Figure 37*. It is possible see that a decrease from 0.39 down to 0.24 μ m of Ra values was observed by increasing the exposure time from 15 to 120 min. A noticeable difference between Ra values is observed between 15 and 30 min of treatment times, but the same does not happen between 30 to 120 min, where the Ra values stay within the same magnitude.

As said in the beginning of this subchapter a value for untreated samples could not be found with the available equipment. However, a 19 μ m Ra was experimentally obtain by A. Colpani in 2019 [41]. Having this value as a reference for untreated samples, it is possible to say that a big reduction in roughness was promoted with this smoothing system.



Surface Roughness of Cold Acetone Treated Samples

Figure 37- Influence of cold vapor acetone surface treatment times on the surface roughness (Ra) of ABS cylinders.

The difference between Ra values for 30 and 45 min treatments were not high, since for longer exposure times the mechanical properties of the treated surface tend to decay. From this point forward, a 30 min exposure time was chosen to treat the samples.

4.2 Optimization of the EN Deposition on Cylindrical Samples

After the production of the polymeric templates, the study of the EN deposition parameters in cylindrical polymeric templates followed.

In total 9 cylindrical samples were EN coated with one 250 mL solution. The samples varied in the EN deposition temperature (ranging from 55 to 80 °C) and if they were or not surface treated for 30 min in the cold vapor acetone system. *Table 4* and *Figure 38* present the samples' nomenclature, their production parameters and provide illustration of the produced samples.

Table 4- Summary production parameters and results of cylindrical ABS templates.

	EN Depositi	on	Acetone	
Samples	Temperature Time (ºC) (h)		Surface Treated	Observations
CS_55_ST	55		Yes	Unable to coat all the sample surface due to low deposition rates
CS_60_ST	60		Yes	Unable to coat all the sample surface due to low deposition rates
CS_65_ST	65		Yes	Unable to coat all the sample surface due to low deposition rates
CS_70_ST	70		Yes	Unable to coat all the sample surface due to low deposition rates
CS_75_ST	75	1	Yes	Full coating achieved, with major deformations on the geometric shape of the polymeric template
CS_80_ST	80		Yes	Full coating achieved, but with major deformations on the geometric shape of the polymeric template and irregular deposition occurred
CS_70_AP	70		No	Unable to coat all the sample surface due to low deposition rates
CS_75_AP	75		No	Full coating achieved, without any deformation on the template geometry
CS_80_AP	80		No	Full coating achieved, without any deformation on the template

Note: The sample nomenclature consisted in the type of template used, cylindric sample (CS), followed by the EN temperature deposition, ending with surface treated (ST) or as-printed (AP).



Figure 38- Imaging results of the different production utilised for cylindrical ABS templates.

The polymeric template surface activation step was the same across all the samples and seemed like promoting a complete coating of the template's surfaces when the EN deposition conditions were adequate.

For deposition temperatures less than or equal to 70 °C, incomplete coatings were produced for both as-printed (AP) and surface treated (ST) samples, meaning that for the selected EN solution not enough thermal energy was provided to achieve adequate deposition rates for a full coating of the samples. While for deposition temperatures of 75 and 80 °C high enough deposition rates were achieved, fully coating the polymeric surface. However, for a deposition temperature of 80 °C, the deposition process of the EN bath started to coat in large quantities on the glass walls of the bath container and not only on the polymer sample. To ensure that this heterogeneous deposition did not influence the outcome of the Ni-P alloy the temperature of 75 °C was considered to be the safest option.

Regarding the use of the acetone surface treatment, it was observed that for deposition temperatures of 70, 75 and 80 °C the produced coating did not maintain the geometrical shape of the polymeric matrix, creating bulges and fractures on the deposited coating. This made the surface treatment for 30 min (as it was) and the EN deposition not compatible for the production of stable and regular coating. From these results it was chosen not to use the acetone surface treatment for the metallization of the microlattice templates.

Taking all of this into account, the most plausible sample to lead into a hollow metallic structure was the sample CS_75_AP. Consequently, this sample was broken in half and submerged in DCM at 35 °C and, finally, the first hollow Ni-P structure was produced (*Figure 39*)



Figure 39- First hollow metallic structure produced from half of the CS_75_AP sample after template removal with DCM.

The simultaneous use of the acetone surface treatment and the EN deposition was not achieved during this work. This does not mean that with some alterations and improvements in either or both processes it would not be possible be combine them to achieve even better coatings.

4.3 EN deposition on Microlattice Templates

After the optimization of the EN deposition parameters on the simpler cylindrical templates, the EN deposition on the microlattice templates followed.

The activation step of all the samples proved to be effective, always promoting a full coating of all the microlattice's surfaces. The deposition conditions were the same for all the produced samples, with a deposition temperature of 75 °C, 30 min of deposition for each immersion step done, and a pH between 5 and 5,5. The pH values may have had some fluctuations across different samples, since it was used pH paper strips indicator for the pH adjustment.

Due to the collaboration with the IST Product Development Lab the produced microlattice templates used different coloured ABS, using the available spool at the time.

Once the EN deposition time was finished the samples were removed from inside the EN bath and left to cool at room temperature before being water rinsed. In the end, no relevant differences were seen between Ni-P coatings as it was expected, since the depositions parameters and solutions were identical, with the only anticipated difference being the mass of samples produced with 1, 2, or 3 immersions in 250 mL EN solutions. The produced samples, their deposition parameters, polymer removal result, density values, and mechanical compressive values are presented in *Table 5*.

	Temp	late	EN	EN Deposition		Matrix Removal				Relative		Max	Compressive	Deformation			
Samples	ABS Filament	Infill %	№ of 250 mL solutions	т (ºС)	Time per EN solution (min)	рН	DCM T (mL) (ºC)	Time (h)	Mass (g)	Density (kg/m ³)	Density (%)	Compressive Test	Compressive Stress (kPa)	Modulus, E (MPa)	Recovery (%)	Observations	
MS_1_2x250	Red	100	2			~5- 5.5	200 45	1	-	-	-	-	-	-	-	Structural damage on the hollow microlattice	
MS_2_3x250	Red	100	3					400 45	5	-	-	-	-	-	-	-	Structural damage on the hollow microlattice
MS_3_3x250	Red	100	3					450 45	6	-	-	-	-	-	-	-	Structural damage on the hollow microlattice
MS_4_3x250	Blue	<100	3				400 45	4	1.4055 ± 0.0001	41.6	0.47	Total Compression	18.1	0.168	21.0	-	
MS_5_3x250	Blue	<100	3				300 35	16	1.381 ± 0.0001	40.9	0.46	Cyclic 30% Max Load	6.9	-	81.5	-	
MS_6_1x250	Blue	<100	1				200 45	1	-	-	-	-	-	-	-	Structural damage on the hollow microlattice	
MS_7_1x250	Grey	<100	1				300 35	16	-	-	-	-	-	-	-	Structural damage on the hollow microlattice	
MS_8_2x250	Blue	<100	2	75	30		400 45	4	1.1705 ± 0.0001	34.6	0.39	Total Compression	11.3	0.077	30.3	-	
MS_9_3x250	Black	<100	3				400 45	4	1.386 ± 0.0001	41.0	0.46	Total Compression	31.3	0.212	29.7	Small cracks detected	
MS_10_3x250	Black	<100	3				300 35	16	-	-	-	-	-	-	-	Structural damage on the hollow microlattice	
MS_11_2x250	Blue	<100	2					400 45	4	1.232 ± 0.0001	36.5	0.40	Total Compression	12.1	0.075	46.5	-
MS_12_2x250	Blue	<100	2				350 45	5	1.2584 ± 0.0001	37.2	0.41	Cyclic 30% Max Load	3.6	-	89.2	-	
MS_13_2x250	Blue	<100	2				400 45	1.022 Cyclic 00 45 4 ± 30.2 0.34 60% Max 7.0 0.0001 Load Load 1000000000000000000000000000000000000		7.0	-	49.3	-				
MS_14_3x250	Blue	<100	3				350 45	4	1.4352 ± 0.0001	42.5	0.48	Cyclic 60% Max Load	12.5	-	48.5	-	

Table 5- Final Ni-P microlattices production parameters and relevant properties.

Note: The microlattice sample's nomenclature in this work consisted in the type of template used (*MS* for microlattice structure), followed by the number of the produced sample, ending with the number of EN 250 mL solutions used.

4.4 Polymeric Matrix Removal

The final step in the production of Ni-P microlattices consisted of the removal of the sacrificial polymer matrix by chemical dissolution of ABS with DCM. Before this step, the top supports from the ABS template coated with Ni-P alloy were removed, exposing the inner polymeric template. To increase the contact area between template and solvent even more, all the top and bottom faces of the structure were sanded until the polymer template was exposed. After the samples preparation, the removals were performed at 45 °C for approximately 4-6 hours while controlling the volume of DCM, or at 35 °C for longer dissolution times without the need to be so careful with the DCM volume, since the evaporation rate was lower. Both sets of parameters worked fine for most of the samples.

Although a few samples were heavily damaged during this identical polymer removal step, there was a plausible reason for all of them:

- For samples MS_1_2x250, MS_2_3x250 and MS_3_3x250 the problem was associated with the first set of microlattice template's printing parameters used, having a 100 % infill structure. The submersion of the ABS coated template in DCM led to the swelling of the template, causing internal forces on the Ni-P coating, since the only way for the polymer to expand was outwards. This produced catastrophic damage on the final microlattices with the formation of cracks, and strut and node fractures, as is illustrated in *Figure 40.MS_3_3x250*.
- Other samples, that could not be produced, were MS_6_1x250 and MS_7_1x250. The explanation for these samples is that even for the used <100 % infill templates, the polymer expansion was enough to fracture the microlattice. Adding, as well, the fragility of such thin coating that needed to be moved/removed from a high viscous ABS/DCM solution that offered resistance on the microlattice walls, causing the fracture of struts and nodes. It might be possible to produce these thinner and lighter samples if the 3D printing parameters are improved to achieve even lower percentages of infill templates, or if the polymer removal system promotes a less aggressive handling of the microlattice.</p>
- The last samples that showed problems during the polymer template removal were sample MS_9_3x250 and, specially, MS_10_3x250. At the time of the event, no logical reason was at sight, since the template used and EN deposition parameters were the same as previously successfully Ni-P microlattices produced (like MS_5_3x250). But after some ponderation, a connection with the ABS type used appeared. For these two samples Black ABS was used instead of the previously used Blue and Grey ABS variants. Since the manufacturing company of these ABS filaments do not provide a full insight into the chemical differences between coloured filaments, it was assumed that the Black ABS filament must contain some additive that causes greater volume expansion when submerged in DCM. This results in cracking formation in the final Ni-P coatings (*Figure 40.MS_10_3x250*).



Figure 40- Contrast between Ni-P microlattices metallic structures using: a) a 100% infill ABS template; b) a <100% infill Black ABS template; and c) a <100% infill Blue ABS template.

The best overall set of production parameters observed in this work were: less than 100 %infill polymeric templates, with the immersion in 2 or 3 EN solutions at 75 °C and pH values between 5 and 5.5, followed by the chemical removal of the polymeric template with DCM at 45 °C for 4 hours.

In the end, eight structurally solid Ni-P microlattices were produced. These Ni-P Microlattices had mass, densities and relative densities ranging from 1.022 to 1.4352 g, 30,2 to 42.5 kg/m³ and 0,34 to 0.48 %, respectively, just missing the ultralight regime classification (<10 kg/m³).

4.5 Characterization of Metallic Microlattice

After the final Ni-P microlattices production, the metallic structures were mechanically tested and characterized through axial compression tests, SEM and EDS analysis and, finally, XRD analysis.

4.5.1 Axial Compression Tests

To evaluate the compressive mechanical behaviour and properties of the produced Ni-P microlattices, both standard and cyclic compression tests were performed. From these tests, eight compressive stress vs strain curves were obtained (*Figure 41* and *Figure 43*), with the most important values being summarized in *Table 5*.

The standard compression curves, illustrated in *Figure 41*, show similar mechanical behaviour between 3x250 and 2x250 samples. For a better understanding and visualization, *Figure 42* provides a visual sequence of the Ni-P microlattice during the compression test. First, the stress increases almost linearly until a first peak is reached around 12 % strain. Then, a subtle decrease follows, most likely associated with the first appearance of strut and node cracking. Then again, the stress increases into a maximum value, at around 22 % strain. It is at this point that 3x250 and 2x250 samples differ. While the first ones tend to suffer a decrease in stress until the densification stage occurs, the second ones tend to plateau around the maximum stress value until the densification of the structure (around the 70%), ending, in both cases, with a highly fractured microlattice. These results met the idea that thinner Ni-P microlattices are able to sustain more deformation strains and get higher strain recovery properties,

whilst thicker microlattices have higher maximum compression and compressive modulus values but suffer more permanent structural damaged for the same applied strain. The analysis of the compression plots presented values for maximum compressive stress and Compressive Modulus ranging from 11.3-31.3 kPa and 75-212 kPa, respectively. As predicted, the strain recovery values for the 2x250 were higher than for the 3x250 samples, being respectively 30.3-46.5 % and 21.0-29.7 %.



Figure 41- Compressive stress vs strain curves for 4 compression tested samples using a 1 mm/min compression rate.



Figure 42- Deformation sequence of sample MS_8_2x250 at different strain percentage points.

Moving now to the analysis of the cyclic compression tests (*Figure 43*). The two samples (MS_5_3x250 and MS_12_2x250) which endured 100 cycles at 30 % of the maximum load (7 and 3.5 N, respectively) showed identical compression paths, with low strain propagation between cycles. Their strain recoveries were the highest of all samples (although being the less deformed to), with values of 81.5 and 89.2 %. The results of the samples for 100 cycles at 60 % of the maximum load, were not as similar between them. While sample MS_13_2x250 endured the 100 cycles following very identical

compression paths and with very low strain increase, sample MS_14_3x250, although having similar compression paths, suffered an increase in strain of 21 % from the first to the last cycle (from 0.43 to 0.64). The samples reported strain recoveries of 49.3 and 48.5 %, respectively, but is important to notice that the structural integrity of sample MS_13_2x250, after the compression tests, was better than the sample MS_14_3x250, due to higher deformation and damage to the structure of this last one.



Figure 43- Compressive stress vs strain curves for 4 cyclic compression tested samples (100 cycles).

The results were in line with the expectations observed in the literature (presented in *chapter 2.2.4*), with the lighter and thinner samples to exhibit better strain recoveries, better cyclic behaviours, and better energy absorption properties.

4.5.2 SEM Observation of Ni-P Microlattices

To study the Ni-P microlattices surface topography and defects produced during the cyclic compression tests, three samples were observed in three different microlattice sections, as showed in *Figure 44*.

There are some shared features present across all sample images. All the samples share the same topology and surface structures. It is possible to see, in all of them, the additive manufactured layers produced in the 3D printing process that directly translated to the final Ni-P microlattice. Also, the metallic features at the surfaces are the same across the three samples. This is the typical morphology of the Ni-P coatings, where spherical grains arrange themselves side by side, originating what is called cauliflower morphology [81]. The concentrated existence of these structures in localized areas of the microlattice surface can be justified by the cooling of the microlattice after EN deposition. When removed from the EN bath, the microlattice was let to cool down at room temperature before being water rinsed,

finally removing the EN solution from the coating surface. However, during this cool down process, the remaining solution, wetting the coating, was still able to deposit the last nickel particles on the coatings surface, promoting the formation of the same cauliflower morphologies, but not as evenly distributed. In the images it is possible to observe ABS remains from the polymer removal step.



Figure 44- SEM imaging of three microlattice samples in three different regions, highlighting: extended cracking with (yellow boxes); small cracking (red boxes); polymer residues (orange boxes); localized cauliflower morphologies (green circles); and coating pores (blue circles).

The top section images of the cyclic compressed samples MS_12_2x250 and MS_13_2x250 show the local buckling of the coating top wall, being the result of the applied forces from the compression plates in these areas. The same is not present in the untested sample MS_3_3x250 image, where no bent of the wall is observed.

The other two sections, the top-to-bottom and side-to-side nodes, shared the same type of information. In the images of the compressed samples, it is possible to identify big cracks across the metallic surfaces, these being more prominent in the MS_13_2x250 sample because of compression cycles of 60 % of its maximum load. Small cracking across all the samples' images is detected. These are most likely associated with the cool down process, being advisable to promote a slower cooling for future works. Finally, it is also easily detectable the presence of pores in the metallic coating (especially in the tested samples images). These defects may act as stress concentrators, leading to the growth of fractures and damage of the mechanical properties.

Overall, with this analysis it is possible to say that: similar coatings were promoted across all samples in terms of morphology; the morphology seen is typical for Ni-P electroless coatings; the main defects produced during cyclic testing were the buckling of the Ni-P coating top and the extensive cracks across the coatings surface; other defects like small thermal cracking and pores were detected; and, finally, there was still ABS residues at the outer surface of the microlattice, implying that an extra cleaning with a small fresh DCM volume might be needed to avoid their presence in the final structures.

4.5.3 EDS Analysis of Ni-P Microlattices

In addition to SEM, EDS analysis was also preformed to chemically characterize the Ni-P microlattices, obtaining information on their elemental constituents. Four regions were analysed and are represented in *Figure 45*.

Region 1 was selected to verify and validate the presence of ABS residues on the microlattice surface already observed in SEM. Regions 2 and 4 aimed at a regular section of the microlattice surface, while region 3 aimed to obtain information on the irregular morphologies observed across the samples, to see if their composition matched the rest of the Ni-P coating, validating the idea suggested in the SEM analysis. The obtained values of element atomic concentration, element weight concentration, and determined weight percentage of P in the Ni-P coating are presented in *Table 6*.



Figure 45- EDS analysed regions for the acquired values in Table 6.

Element		Region	1		Region	2	Region 3			Region 4		
Symbol	Atomic %	Weight %	Wt.%P (Ni-P alloy)	Atomic %	Weight %	Wt.%P (Ni-P alloy)	Atomic %	Weight %	Wt.%P (Ni-P alloy)	Atomic %.	Weight %	Wt.%P (Ni-P alloy)
С	90.1	71.4		61.1	25.0		46.7	16.0		39.4	12.2	
0	7.6	8.0		3.6	2.0	9.2	5.0	2.3	7.9	2.9	1.2	8.7
Р	1.1	4.1		5.6	5.7		6.4	5.7		8.6	6.9	
Ni	1.3	16.5		28.0	56.1		39.5	66.3		47.5	71.9	
Au	1.3	16.5		1.6	11.2		1.6	9.0		1.5	7.8	

Table 6- EDS analysis results for 4 different regions of the produced Ni-P microlattices.

The EDS analysis on region 1 revealed a high weight percentage of Carbon. Since the only carbon containing material/component in all this experimental work is the ABS polymer, it is concluded that these are residues produced and attached during the sacrificial template removal stage.

Regarding the other three regions it is right to say that some vestigial polymer is still being detected, even if in way smaller quantities. It is also observed that the composition of region 3 is similar to regions 2 and 4, meaning that these bulging structures are made of the exact same components as the rest of the Ni-P coating. A weight percentage of 7.9, 8.7 and 9.2 in P was obtain for these three regions. These values are in line with EN bath pH selection of 5 to 5.5, that is supposed to produce coatings with wt.%P between 7 and 8.5 % [56]. This means that the goal of producing Ni-P microlattices with wt.%P between 7 and 10 % was met with the used EN bath conditions and solutions.

4.5.4 X-Ray Diffraction Analysis (XRD)

To study and identify the phases produced during the EN deposition of the Ni-P microlattice structures, XRD analysis was carried out in powder samples obtained from microlattices MS_11_2x250 and MS_9_3x250. The obtained values and a Ni reference pattern (ICSD no. 43397 [82]) are presented in *Figure 46*.



Figure 46- XRD diffractograms of two Ni-P microlattice powdered samples with the reference pattern of Ni at the bottom (ICSD no. 43397)[82].

For both analysed samples the XRD diffractograms are identical, showing a broad peak at 44.7° corresponding to the Ni(111) diffraction plane. This indicates that the Ni-P alloys, present in the produced microlattices, are mainly amorphous with some cfc crystalline structures identical to Ni- α . By matching this result with the metastable phase diagram of Ni-P, it is possible to say that the present phases in the Ni-P microlattices are the amorphous γ and the fcc crystalline β phase. The similar results between samples MS_11_2x250 and MS_9_3x250 prove that the deposition conditions and solutions

used promote identical crystallographic results across the microlattice samples, not being affected by the number of EN solutions used.

Also as expected, there are no other relevant peaks identifiable in both diagrams, assuring that no formation of the Ni₃P phase was promoted (peaks at 41.90° and 46.79° [83]). These are great news, since the microlattices obtained from the selected production processes can be thermally treated without the presence of initial ductility reducing phases like Ni₃P. In the future, thermal treatments, such as annealing, can be studied, since it normally promotes the recrystallization and grain growth of the microlattice microstructure, that could lead to even better ductility and better strain recovery results in the mechanical compression tests. It can not be guaranteed that this would happen for the Ni-P alloy produced, since the formation of Ni₃P might be promoted during set thermal treatment, need further investigation on the subject.

5. Conclusions and Future Work

The main goals of this work were to produce and characterize ultralight Ni-P microlattices. Although the produced microlattices did not achieve the ultralight classification (not having densities below 10 kg/m³), it is safe to say that the experimental techniques used allowed production and characterization of good quality Ni-P microlattices.

The production parameters, selected for the FFF manufacture method of ABS sacrificial template used in the first stage of this work, proved to develop templates with enough quality to produce Ni-P microlattices. There was no need for the use of support material and the improvement of templates with infill percentages lower than 100 % demonstrated to help a lot in the polymer template removal stage. The further reduction of the infill percentage by improving the 3D printing parameters even more, could allow the production of even thinner and lighter microlattices.

When it came to the polymer surface treatment by the cold acetone vapour technique, a reduction of the waviness and the roughness of the polymeric samples were observed, obtaining Ra values of 0.39 and 0.24 μ m for respective treatment times of 15 and 30 min. Even though the goal of reducing the polymeric sample roughness was met, the pairing of this technique and EN deposition process was not possible throughout this work. Since the results of both techniques were positive, it would be interesting to test different treatment times and EN bath parameters, or even a study of a proper drying system for treated samples with the goal of allying both techniques.

The metallization stage of the ABS templates showed to be effective, with both the activation and EN deposition process proving to promote consistent and solid Ni-P coatings/microlattices. The activation promoted the full coating of all the different samples in all their areas. The EN deposition bath parameters of 75 °C and pH between 5-5.5, the selected ratios of the chemical agents and bath composition promoted reasonable deposition rates and the right weight percentage of P in the final microlattice.

Closing the production stages was the removal of the polymeric templates. From the executed solubility tests, the only solvent that proved to be able to perform the total dissolution of the ABS templates was DCM. The removing process of the final microlattice was effective, requiring around 500 mL of DCM and removing times of 5 to 16 h for removing temperatures of 35 °C and 45 °C, respectively. Although the majority of the polymer was removed, the EDS analysis showed the existence of vestigial polymer on the final structures, resulting from the repolymerization of the ABS after their removal from the concentrated solvent. It is still possible to improve this production stage by, again, producing polymer templates with less infill percentage, by promoting a last removal with fresh DCM solvent, and by promoting a better sample handling system, reducing the risk of accidental damage to microlattices.

With the compressive tests done to the produced Ni-P microlattices, it was possible to observe their mechanical behaviour. For heavier and thicker samples, a less ductile behaviour and lower strain recoveries were observed during the standard compression tests, though they presented higher values of maximum stress and compression modulus when compared to the lighter and thinner samples. These last ones showed high strain recoveries and a typical ductile behaviour expected for ultralight Ni-P

microlattices. In the cyclic test the same trend was observed, with the thinner samples being able to recover and to endure the compression cycles better than the thicker microlattices. For the standard compression tests values of maximum compressive stress, compressive modulus and strain recoveries ranged from 11.3 -31.3 kPa, 75-212 kPa, and 21.0-46.5 %, respectively. For cyclic tests, strain recoveries of 81.0-89.2 % and 48.5-49.3 % were obtained for samples test with 30 % and 60 % of their maximum load.

The EN deposition coatings are known to form spherical particles that assemble into a microstructure called cauliflower. Through SEM surface observation of the produced Ni-P microlattices it was possible to observe that the same type of arrangement and microstructure was promoted, with several extra localized cauliflower structures on different surface areas. It was also possible to identify cracks and nodes on the observed samples, associated with the cooling of the microlattices after EN deposition (small cracks) and with the loads applied during the cyclic tests (large cracks). To reduce the presence of these extra microstructures on the nickel surface and the existence of thermal cracking, the microlattices should be washed with clean water at the EN deposition temperature right after the deposition and should be cooled down slowly afterwards.

The pH values of the EN bath aimed to produce Ni-P alloys with P weight percentages between 7 and 10 %, this range being the one that presented better mechanical properties for the coating. The EDS analysis showed percentages between 7.9 and 9.2 wt.%P for the analysed samples, meaning that the EN parameters produced the desired Ni-P alloy. This technique also proved the existence of polymer remains on the microlattice surface, suggesting that a last cleaning of the surface with fresh DCM might be required before the samples analysis.

Finally, with XRD analysis the expected results were also confirmed, where the obtained diffractograms showed that the Ni-P alloy was mainly constituted by an amorphous phase (γ -metastable phase) and a cfc crystalline phase (β -metastable phase). No other peak was detected apart from the big broad one, centred around the Ni(111) diffraction plane (at 44.7°), also ruling out the possibility of the formation of the ductility harmful Ni₃P phase.

As an overall conclusion, it can be said that the process of FFF using ABS proved to be a viable option for the production of Ni-P microlattices, where, in this work, it was possible to produce microlattices with densities and relative densities ranging from 30.2-42.5 kg/m³ and 0.34-0.48 %. Besides all the improvements suggested during this entire work, a last and, possibly, the most important suggestion is to perform/study the annealing treatment of the Ni-P microlattices, since it is expected that this can improve the ductility and the strain recovery ability of said microlattices.

6.Bibliography

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