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

Rodrigo Alexandre Ferreira Raposo rodrigo.a.raposo@tecnico.lisboa.pt

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-butadiene-styrene (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 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

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.

2 – Theoretical Context

2.1 – Hollow Metallic Microlattice: A Man-Made Cellular Solid

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]. 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.

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 [17]. 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 [18].

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 stretchdominated [20]. 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 bendingdominated microlattices are known for. On the other hand, the most common stretch-dominated microlattices are closed-cell and some 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 [17,21,22]. *Figure 1* is a graphical comparison between the two compressive behaviours for two typical unit cell architectures.



Figure 1- Bending vs Stretch-dominated compressive behaviour generic charts [21].

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 their relative density.

2.2 – Production of Hollow Metallic Microlattices

2.2.1 – Production of Polymeric Templates

The most used AM process to produce polymeric sacrificial matrix for the manufacture of Ni-P microlattices is the Self-Propagating Photopolymer Waveguides (SPPW) [1,19,23,24]. 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. 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 [23]. SPPW is a very uncommon process, being only used for very specific applications.

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 pretended object. FFF has a layer hight 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) [24].

Even though FFF does not have as good resolutions, surface finishing, etc., as SPPW and technique, 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 right 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. 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 [25].

For ABS objects, cold vapour treatment has shown amazing results when using dimethyl ketone or acetone as the solvent. The process not only makes 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 [25].

2.2.2 - Metallization of Polymers using Electroless Process

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 [27,28]. 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,

$$M^{z+} + Red \to M^0 + Ox \tag{1}$$

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.(2)).

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

The redox potentials of Sn4+/Sn2+ and Pd2+/Pd are 0,15 V and 0.987 V, respectively, resulting in a flow of electrons from Sn4+/Sn2+ to Pd2+/Pd. 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 [29]. 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 [26]. This time a PdCl₂ and HCl solution is used, that allows the reduction of Pd²⁺ into Pd at the surface.

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 some other chemical agents, such as complexing agents, pH regulators, stabilizers, and buffers [30]. 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 [30,31]. 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 [33].

Starting by looking at the chemical reactions of nickel deposition by hypophosphite, there is one main anodic reaction (Eq. (3)) and one main cathodic reaction (Eq. (4)), where the adsorbed hydrogen reduces the nickel ions on the catalytic surface, promoting the growth of the coating.

$$H_2 P O_2^- + H_2 O \to H P O_3^{2-} + H^+ + 2H_{ads}$$
(3)

$$Ni^{2+} + 2H_{ads} \rightarrow Ni^0 + 2H^+ \tag{4}$$

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 (5), (6) and (7) 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.

$$2H_{ads} = H_2 \tag{5}$$

$$H_2 P O_2^- + H_{ads} \rightarrow H_2 O + O H^- + P_{ads} \tag{6}$$

$$3H_2PO_2^- \to H_2PO_3^- + H_2O + 2OH^- + 2P_{ads}$$
 (7)

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. Also, 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 hypophosphites the normal operating temperature is between 60 °C and 95 °C [34]. Although higher deposition rates are obtained for temperatures higher than 90 °C, the probability of bath instability and decomposition increases.

The pH of the *EN* bath not only influence 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 [35]. Figure 2 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.



Figure 2 Effect on solution pH on deposition rate and phosphorus content of the coating [34].

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 [36,35]. 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 (y 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 [38]. 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 [39].

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. Despite ABS is 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 not careful, the pressure from the expanding template may cause physical defects on the metallic structure. ABS has different organic solvents that are used for dissolution/reprecipitation techniques, such as acetone and dichloromethane [41].

2.2.4 - Properties of Ni-P Hollow Microlattices

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 3.(a); variation of the circular cross-section of the struts, tending more to an oval-shape (Figure 3.(b)); presence of cracking near the nodes (Figure 3.(c)); and, finally, cracking along the struts of microlattices (Figure 3.(d)). All of these defects can have direct impact in the mechanical properties of the hollow 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. It is easy to say that the more the production process evolves, and these defects get more and more rare, the greater the improvement on the microlattices' mechanical properties will be.



Figure 3- SEM images of common geometric defects observed in hollow metallic microlattice materials [19]

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 [42] 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 ration of the struts (t_S/D_S) of $2x10^{-4}$ [40]. 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 [19].

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.

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]. Their ability to massive reduce weight of structural parts has already caught the attention of the aeronautical industry, since companies like Boing 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 Procedure

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. Since the technique SPPW was not available for this work, 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 [43]. 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 nuzzle 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 template 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.

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. 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 or no progression in the dissolution process was observed. The used organic solvents where acetone, dichloromethane (DCM), tetrahydrofuran (THF) and N,N-dimethylformamide (DMF).

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. A $34.5 \times 25 \times 20$ 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. 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 effectiveness of the acetone surface treatment, a quantitative evaluation of the surface roughness of treated samples was done. 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).

The next step of the microlattices production is the surface activation of the polymeric templates. 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 SnCl_2 . 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 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.

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. 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. In this work 250 mL EN solutions were used, with a pH between 5 and 5.5. 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.

For microlattice templates 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. Fourteen microlattice samples were coated in this work, where 2 of them were coated with only 1 EN solution, another 5 were subjected to 2 EN baths, and the last 7 were coated with 3 EN solutions.

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. The chemical route was the 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.

After the production of Ni-P microlattices, the characterization of its metallic structure was carried out. Axial compression tests, SEM/EDS and XRD analysis were used to obtain qualitative and quantitative results. to study the mechanical behaviour of the Ni-P microlattices under compressive loads and to obtain the most data, 8 Ni-P microlattice samples were tested, 4 of them being produced with 3 x 250 mL EN depositions and the other 4 with only 2 x 250 mL 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.

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). 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.

With the goal of identify the phases present in the produced Ni-P microlattices XRD was used. The XRD analysis were performed in a *D8 Advance Bruker diffractometer*, with a tube electric potential difference of 40 kV and the samples were scanned from $2\theta=30^{\circ}$ to 60°, with a step size of 0.04°, and 1 s of acquisition time per step.

4 – Results and Discussion

4.1 – 3D Printing of the Polymer Templates

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. 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.

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.

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.

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

	Template		E	Matrix Removal								Maria					
Samples	ABS Filamen	Infill t %	Nº of 250 mL solutions	T (°C)	Time per EN solution (min)	рН	DCM (mL)	T (°C)	Time (h)	Mass (g)	Density (kg/m ³)	Relative Density (%)	Compressive Test	Max Compressive Stress (kPa)	Compressive Modulus, <i>E</i> (MPa)	Deformation 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	$1.4055 \\ \pm \\ 0.0001$	41.6	0.47	Total Compression	18.1	0.168	21.0	-
MS_5_3x250	Blue	<100	3	75	30		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				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	$1.232 \\ \pm \\ 0.0001$	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	4	1.022 ± 0.0001	30.2	0.34	Cyclic 60% Max Load	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 1 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.

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, making them a worse option than the selected DCM.

4.1.2 - Surface Treatment of ABS Templates

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. 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. This restricted the time of sample exposure to a 60 min maximum, since it was the value from which this phenomenon started to happen.

4.1.2.1 – Roughness Analysis of Surface Treated 3D Templates

In relation to the waviness of the samples, it was possible to observe a great reduction from the increasing treatment times. For untreated ABS cylindrical samples, 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.

For the roughness analysis of the ABS samples, analytical values were obtained. 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.

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

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.

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 enough deposition rates for a full coating of the samples. While for deposition temperatures of 75 and 80 °C high adequate 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.

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

4.3 – EN deposition on Microlattice Templates

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 250 mL of EN solution used, 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.

In the end, no relevant differences were seen between Ni-P coatings as it was expected, since the depositions parameters and solutions were identical.



Figure 4- Produced Ni-P metallic hollow microlattice.

4.4 – Polymeric Matrix Removal

The removal process of the polymeric matrix developed allowed the production of 8 final Ni-P microlattices with structural integrity, however some samples were heavily damaged during this step, existing 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.

-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.

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

4.5 – Characterization of Metallic Microlattice

4.5.1 - Axial Compression Tests

The standard compression curves, illustrated in Figure 5, show similar mechanical behaviours between 3x250 and 2x250 samples. For a better understanding and visualization, Figure 5 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 %.

Moving now to the analysis of the cyclic compression tests (Figure 6). 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 the samples (although being the less deformed to), with values of 81.5 and 89.2 %. The results of the samples tested 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.

4.5.2 - SEM Observation of Ni-P Microlattices

There are some shared features present across all the samples (Figure 7). 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



Figure 6- Compressive stress vs strain curves for 4 cycl compression tested samples (100 cycles)

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 [44]. The concentrated existence of these structures in some 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.

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 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. Some 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 identifiable the presence of pores in the metallic coating.



Figure 7- 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).4.5.3 – EDS Analysis of Ni-P Microlattices



Figure 8- EDS analysed regions for the acquired values in Table 2.

 Table 2 - EDS analysis results for 4 different regions of the produced

 Ni-P microlattices.

Element		Region	1	Region 2				
Symbol	Atomic %	Weight %	Wt.%P (Ni-P alloy)	Atomic %	Weight %	Wt.%P (Ni-P alloy)		
С	90.1	71.4		61.1	25.0	9.2		
0	7.6	8.0		3.6	2.0			
Р	1.1	4.1		5.6	5.7			
Ni	1.3	16.5		28.0	56.1			
Au	.1.3	16.5		1.6	11.2			

Region 1 was selected to verify and validate the presence of ABS residues on the microlattice surface already observed in SEM, while Regions 2 aimed at a regular section of the microlattice surface to obtain information on the composition of the Ni-P coating (Figure 8). 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 2*.

The EDS analysis on region 1 revealed a high weight percentage in 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.

When it comes to regions 2 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 weight percentage of P in the final alloy is 9.2. This value is in line with EN bath pH selection of 5 to 5.5, that is supposed to produce coatings with wt.%P between 7 and 9 % [34]. 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)

For both analysed samples the XRD diffractograms are identical (Figure9), showing a broad peak at 44.7° corresponding to the Ni(111) diffraction plane [45]. 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.



Figure 9- XRD diffractograms of two Ni-P microlattice powdered samples with the reference pattern of Ni at the bottom (ICSD no. 43397)[45].

Also as expected, there are no other relevant peaks identifiable in both diagrams, assuring that no formation of the Ni_3P phase was promoted (peaks at 41.90° and 46.79° [46]).

5 – Conclusion

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.

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.

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.

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.

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 obtain 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 some extra localized cauliflower structures on some 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). 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.

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.

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