

# Lab Scale Process Optimization for Manufacturing of Thin-Walled Hollow Shapes of Nickel by Electrodeposition

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## Research Article

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## ABSTRACT

Electroforming is an extension of electrodeposition process wherein one metal is deposited onto a cathode in the shape of a required geometry called a 'mandrel'. After deposition the mandrel is removed by preferential dissolution leaving behind a hollow thin-walled structure of the deposited metal. Electroforming is considered a strong contender for fabrication of lightweight, thin walled (few microns) components with high dimensional accuracy, intricate shape, precise reproduction of surface details with miniature geometry. This research was aimed to produce thin-walled complex shaped nickel components and to investigate the effect of process parameters including electrolytic solution composition, on surface morphology and mechanical properties of the product. Careful control of ingredients along with processing parameters resulted in wall thickness from 40 to 130 microns with tensile strength varying between 400 to 1100 MPa with a maximum hardness up to 750 Hv.

**Keywords:** Nickel; Electrodeposition; Electroforming; Grain size; Electroless plating; Microstructure; Mechanical properties; Electrochemical reactions

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## INTRODUCTION

Electroforming is an emerging manufacturing technique for producing thin walled metallic parts of desired size, shape and properties. The mainstay of electroforming theory relies upon the electrolytic deposition of certain metal over a conductive and removable substrate/mould called 'mandrel'. Electroforming is a modified electrodeposition technique originated from electroplating. Major components of the process include anode, cathode electrolyte, mandrel/substrate for plating and a power supply. The specific metallic salt solution is a source of metal anions that are compelled by the external electric field to migrate towards cathode and deposit as atoms after reduction over its surface. There exists no space between ions and the substrate, causing no damage to the surface. However, edges and breaks get thicker coats because of receiving larger currents <sup>[1]</sup>. The relative placements of electrodes at a suitable distance may overcome the thickness variation of electrodeposition during this process by conception of uniform current distribution over the model surface. The foremost usage of electroformed materials in capacity of tonnes, is the development of thin metallic foils. Interestingly printing plates for stamping bank notes also engage nickel electroforming, initially reported by Watson. Aerospace industry extensively infers electroforming usefulness, ranging from production of low weight precision parts for example antennas and wave-guides, to bigger rocket combustion chambers with built-in cooling channels. Pulse current technique and saccharin as additive in the sulfamate solution ((Ni(NH<sub>2</sub>SO<sub>3</sub>)<sub>2</sub>: 450 g/l, H<sub>3</sub>BO<sub>3</sub>: 30 g/l, NiCl<sub>2</sub>: 15 g/l and saccharin 3 g/l) to refine the grain structure of the electrodeposit of nickel; the researchers applied a high current density up to 20 A/dm<sup>2</sup> at 50 ±1 °C in order to reduce the deposition time <sup>[2]</sup>.

Experimental investigation was done by the improvement of the aspect ratio of the electroformed nickel mesh (the ratio of the growth of thickness to the reduction of microvia diameter) for which 2-aminoethanethiol and cysteine were used as additives in the electrolytic bath solution. Optical observation and electrochemical behaviours of these two additives were analysed by using optical microscopy, Linear Sweep Voltammetry (LSV) and galvanostatic measurements using Rotating Disk Electrode (RDE). Various concentrations (0 mg/l-20 mg/l) of 2-aminoethanethiol and cysteine were used in order to evaluate their performance to further enhance the aspect ratio <sup>[3]</sup>.

A very efficient equipment for mega sonic waves was developed keeping in view the acoustic radiation directions which were combined with the other functional modules in order to overcome the problem of uneven surface generation in the electroforming process. A few factors observed presumably leading to uneven electroform surface could be acoustic streaming, low cavitation effect and high sound intensity, which could be controlled using the mega sonic waves. To enhance the electroforming process based on HARMS<sup>®</sup>, use mega sonic waves, as a result of which the resist structure was observed to be little damaged, although it was an advantageous over the use of ultrasonic vibration in electroforming process. In the electrodeposition process with an aim to enhance ion transportation which further could produce deposits with high aspect ratio, and to remove unwanted bubble

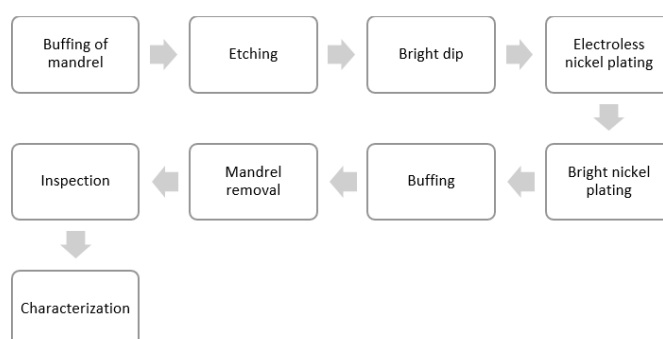
formation during the process, mega sonic waves were used. In the early 1980's the LIGA process was designed under the supervision of German FZK (Research Centre Karlsruhe). LIGA process is the combination of plastic moulding, electroforming and lithography, which has the advantage of producing micro components at relatively low cost. The manufacturing of micro components is feasible only if electroforming is combined with the lithography [4]. In the year 2016 the COMSOL® multiphysics software to check the effects of electrolyte convection on nickel ion concentration distribution and the flow field, within the micro/nano cavities. The bamboo leaf was used as the template in the electroforming experiment keeping in view the micro/nano hierarchical structures. The simulation performed for electroforming process showed that enhancement in the convection near the cathode surface increased the mass transfer. Performed electroforming experiment to investigate the microstructure of electrodeposited nickel by abrasive assistance concept. It was indicated by the results that horizontal cathode gave the homogeneous microstructure in the friction-induced electroforming process. With the increment in the linear velocity of the cathode, better surface finish and refined grain structure of the nickel electrodeposit were obtained. This paper explains step wise procedure of nickel electroforming using nickel sulfate and nickel sulfamate electrolytic solutions, along with the effect of process variables on the microstructure and the resulting mechanical properties of the nickel electroform [5].

## MATERIALS AND METHODS

### Nickel electroforming

A flow chart to manufacture complex shaped thin-walled nickel electroform as per ASTM standards, is shown in Figure 1. After buffing, the aluminium substrate was etched in a solution of Sodium Hydroxide (NaOH) and Sodium Carbonate (Na<sub>2</sub>CO<sub>3</sub>) using an optimized concentration maintained at 50 °C, for a period of 25-30 seconds. This step was performed to remove air formed aluminium oxide (Al<sub>2</sub>O<sub>3</sub>) layer from the surface. The etching was followed by bright dipping to neutralize the aluminium substrate. It was kept in the nitric acid (7% HNO<sub>3</sub>) solution for 90 seconds at room temperature. This dipping resulted in making the aluminium substrate bright and shiny [6,7].

Figure 1. Flow chart of the electroforming process.



After the bright dip, electroless nickel plating was performed by employing a primary electrolytic solution on the aluminium substrate, which generated a light greyish metallic coating of nickel. This very thin layer of nickel assisted in the development of the subsequent layer of nickel which was to be deposited by the secondary electrolytic solution; it also helped in removal of aluminium substrate from the finally developed nickel electroform, during the later stages. This electroless nickel plating was performed in a plating bath. The process temperature was kept to 85 °C ± 2 °C. The solution pH was maintained at 5, by using either nickel hydroxide or hydrochloric acid. The deposition time was 25 min. Table 1 shows the optimized composition of electroless plating solution [8].

**Table 1.** Composition and concentration of the primary electroless nickel plating solution.

Chemicals	Concentration
Maleic acid	34 g/l
Nickel sulfate	34 g/l
Thiourea	1 ppm
Sodium hypophosphite	35 g/l
Succinic acid	10 g/l

Once the primary nickel layer was developed on the aluminium substrate it was then dipped into the secondary or bright nickel-plating solution for a prolonged period of time depending upon the thickness of the nickel electroform required. Mi-151 bench type pH meter manufactured by MARTINI® was used to measure the pH of the solution; pH could affect the bright plating range, cathode efficiency, impurities, throwing power, stress and could also influence the physical properties of the coating. Under normal operating conditions the pH tends to rise which must be controlled by addition of dilute sulfuric or hydrochloric acid. If the pH falls this will indicate either drag-in of an acid (e.g. from an acid dip), abnormal anode behavior, or the use of insoluble anodes. Nickel hydroxide solution was used to increase pH [9].

Once the aluminium substrate was coated with self-sustaining thick layer of nickel, it was post-treated by using buffing machine which provided the nickel deposited an extra lustre/shine. After the buffing of the nickel layer, the aluminium mandrel was removed from it chemically using sodium hydroxide solution (concentration: 150 g/l). In order to perform mechanical testing (i.e. micro hardness, % elongation and tensile testing) and to check surface roughness of the electrodeposit, samples were prepared as per the relevant ASTM standards. Chemical compositions of electrolyte used for bright nickel plating and the optimized process parameters are given in Tables 2 and 3, respectively [10].

**Table 2.** Bright nickel plating solution composition and concentration.

Chemicals	Concentration
Nickel Sulphate (NiSO <sub>4</sub> )	300 g/l
Sodium Sulphate (Na <sub>2</sub> SO <sub>4</sub> )	90 g/l
Sodium Lauroyl Sulfonate (C <sub>12</sub> H <sub>25</sub> SO <sub>3</sub> Na)	105 mg/l
Sodium Chloride (NaCl)	10 g/l
Butynediol (C <sub>4</sub> H <sub>6</sub> O <sub>2</sub> )	0.4 g/l
Boric acid (H <sub>3</sub> BO <sub>3</sub> )	40 g/l

**Table 3.** Optimized process conditions for bright nickel plating.

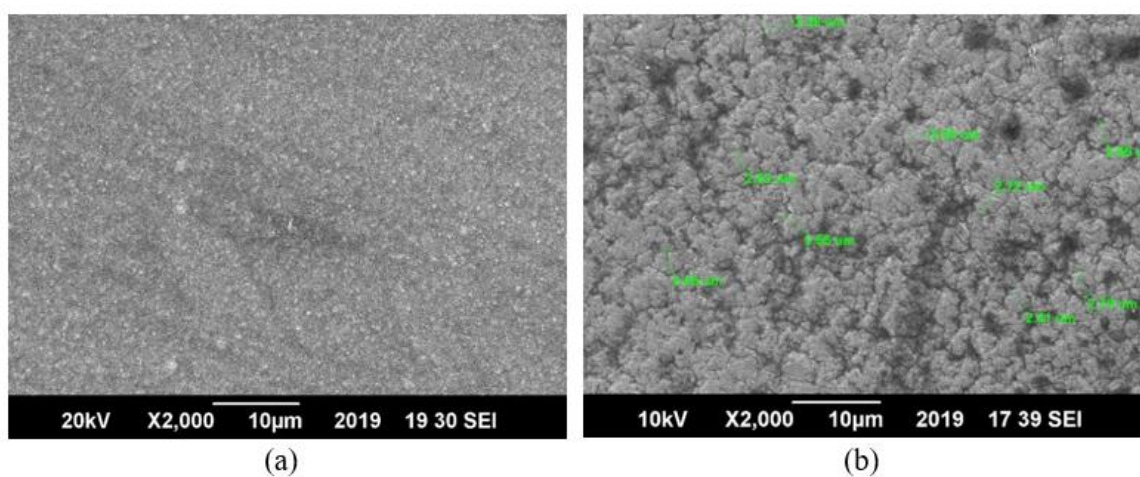
Parameters	Concentration
Volts	2-3 V
Current	1 Amp/dm <sup>2</sup>
Temperature	50 °C
pH	5
Air agitation	Continuous
Deposition time	4 hrs
Electroform thickness	150-200 μm

RESULTS AND DISCUSSION

Scanning Electron Microscopy (SEM) and Optical Microscopy (OM)

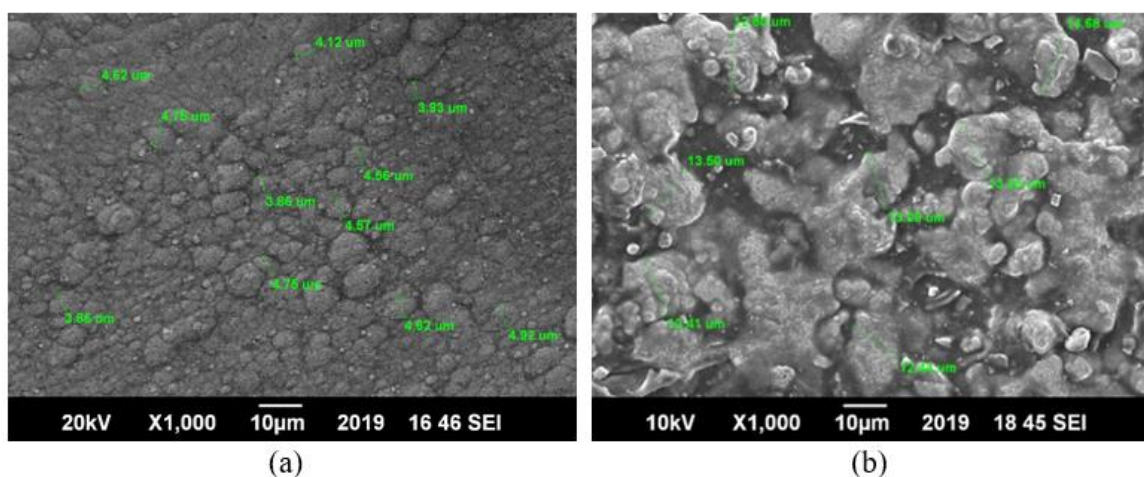
Figure 2 shows electrodeposited nickel surface using nickel sulphate electrolyte at two different current densities. It was observed that the grain size increased with increasing the current density, which in turn increased the over potential as well as the nucleation rate, resulting in larger grain sizes and enhanced surface roughness; it ultimately affected mechanical properties of the electroformed nickel.

Figure 2. SEM micrographs of the surfaces of electrodeposited nickel developed at two different current densities a) 1 A/dm<sup>2</sup>; b) 6 A/dm<sup>2</sup>.



The effect of temperature on the microstructure of the electroformed nickel is exhibited in Figure 3. It was observed that the grain size increased as the operating temperature increased. The grain size in Figure 3(a) was significantly smaller than the grain size shown in Figure 3(b). The grain size, in turn, strongly affected the mechanical properties of the electroformed nickel, as evident by the Hall-Petch effect.

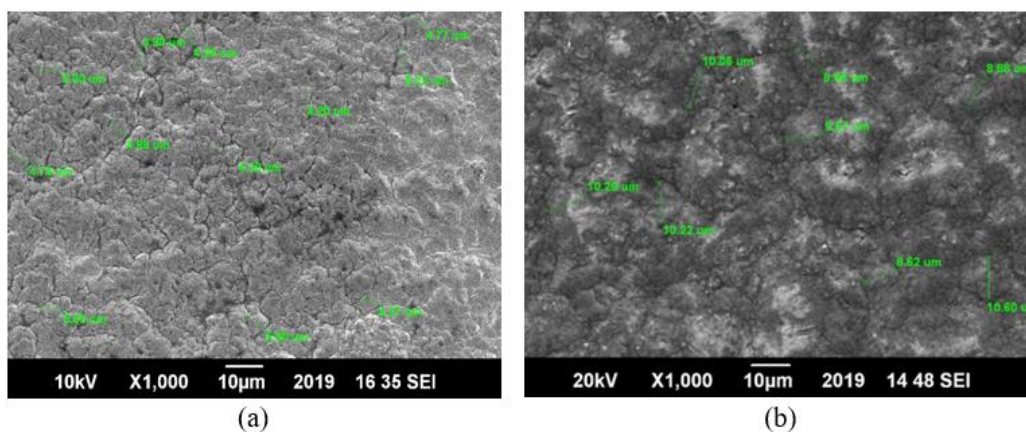
Figure 3. SEM micrographs of the surfaces of electrodeposited nickel developed at two different temperatures a) 30 °C; b) 60 °C.



SEM micrographs Figure 4 demonstrate the effect of pH on grain size of the electrodeposited nickel; it was observed that increasing pH from 4 to 6 had mild effect on the grain size of the electrodeposit *i.e.* the grain size

increased with higher pH. Noticeable effect on the mechanical properties was observed; tensile strength and hardness decreased with alkalinity, and vice versa. The possible reason of this peculiar change could be the hydrogen embrittlement of the pure nickel metal which led to provide more hardness and tensile strength. However, as evident from Figure 4, the effect on the grain size by increasing temperature and current density, was more prominent compared with the effect of pH [11].

**Figure 4.** SEM micrographs of the surfaces of electrodeposited nickel developed at two different pH values a) pH=4; b) pH=6.



Effect of deposition time on thickness of the deposited layer is shown in Figure 5. A variation of 32 µm to 118 µm was obtained by varying time from 1 to 5 hours. Figures 6 and 7 show Energy Dispersive X-ray (EDX) spectrum of the nickel electroformed sample prepared using both nickel sulfamate and nickel sulphate solutions, respectively and corresponding elemental compositions are given in Tables 4 and 5. The data revealed nickel as the base materials along with small traces of impurities like carbon and oxygen; oxygen was presumably due to the atmospheric exposure whereas the possible reason of carbon contents could be the presence of additives used in the nickel-plating solution. The amounts of impurities were relatively higher in case of nickel sulfate solution [12].

**Figure 5.** SEM micrographs showing cross section of the nickel-plating samples at various deposition time durations: (a) 1hour (b) 2 hours (c) 3 hours (d) 4 hours (e) 5 hours

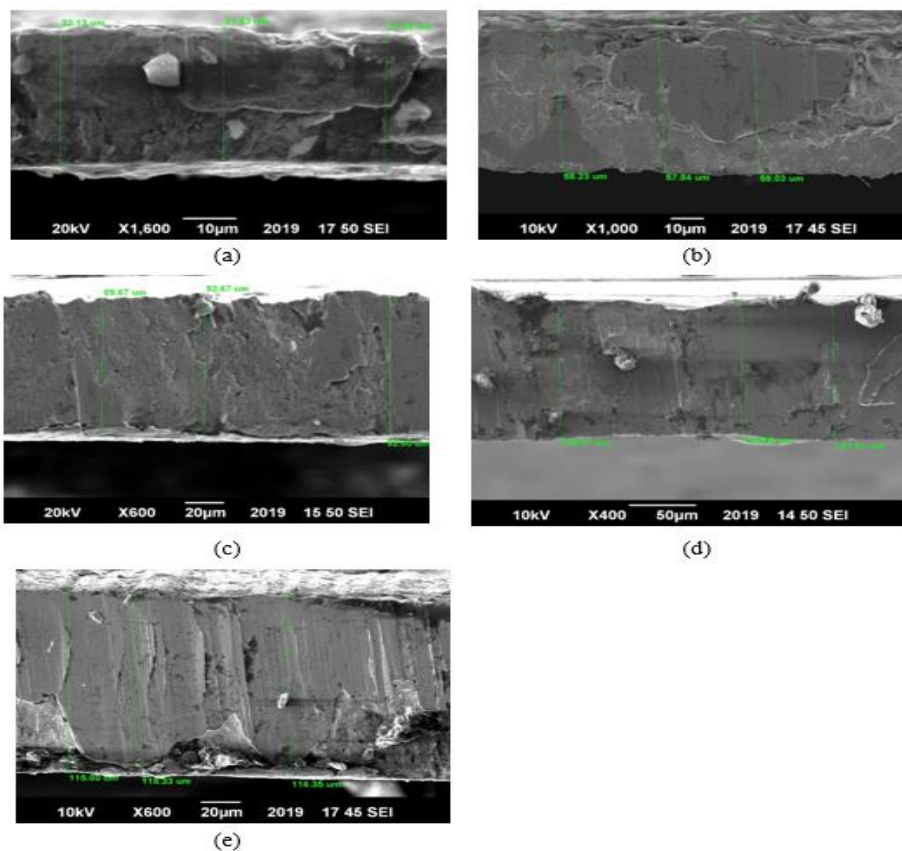


Figure 6. SEM image and EDS result of nickel sulfamate sample.

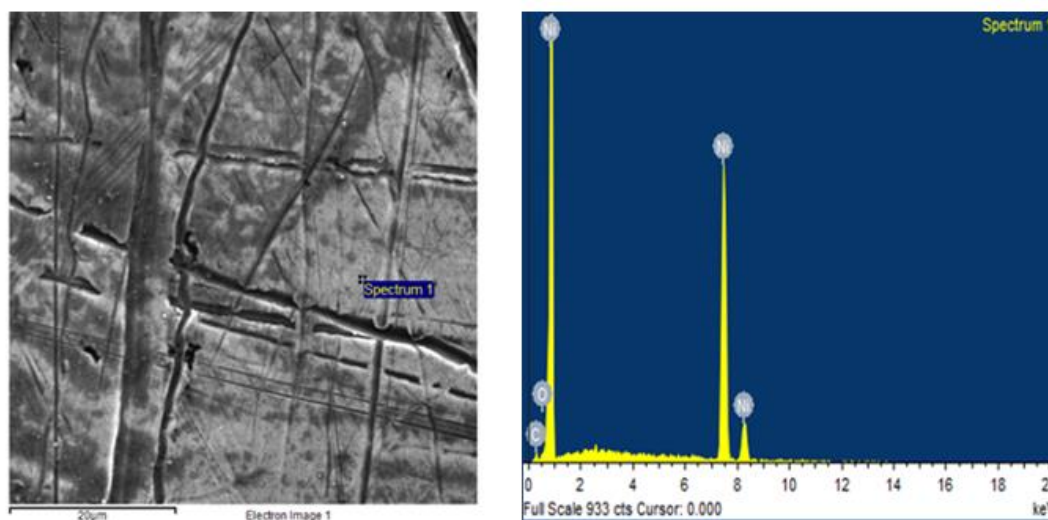
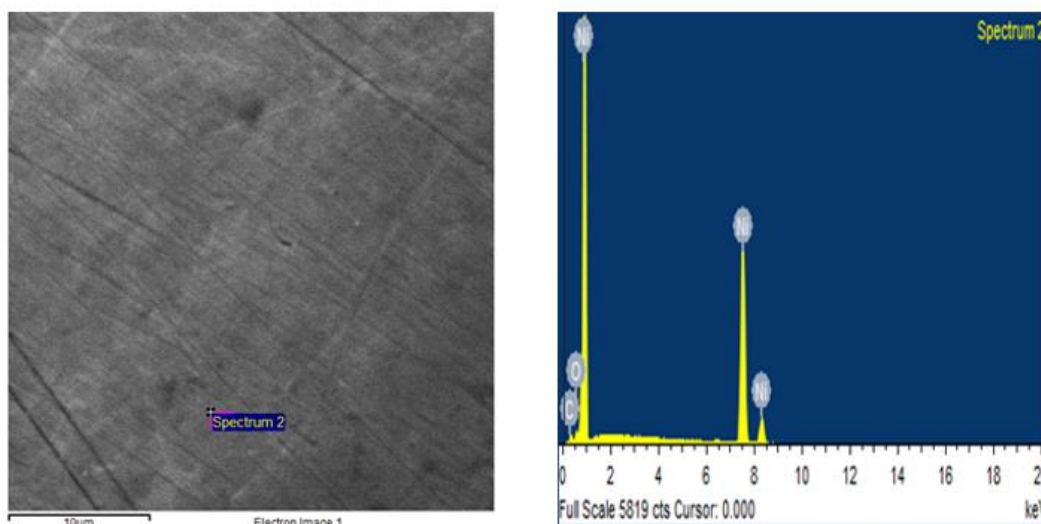


Figure 7. SEM image and EDS result of nickel sulfamate sample.



**Table 4.** Elemental composition of nickel electroform using nickel sulfamate solution.

Element	Weight %	Atomic%
C	4.56	18.51
O	0.98	2.98
Ni	94.47	78.51

**Table 5.** Elemental composition of nickel electroform using nickel sulphate solution.

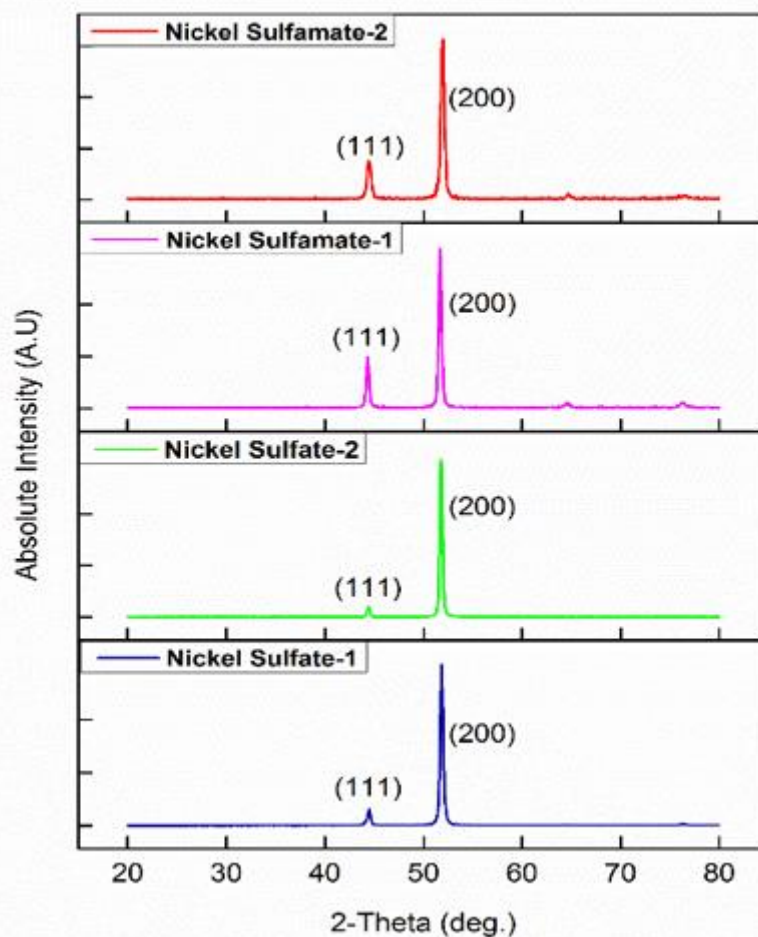
Element	Weight %	Atomic%
C	7.87	28.47
O	1.67	4.54
Ni	90.47	66.99

**X-Ray Diffraction (XRD)**

XRD patterns of the electroformed nickel using nickel sulfate and nickel sulfamate electrolytes is shown in Figure 8. An analysis using the standard PDF card acquired by using X-pert high score software, (Card No.01-087-0712), revealed the strongest diffraction peaks at 45° and 53° corresponding to (111) and (200) crystal planes indicating fcc structure of Ni; other diffraction peaks were not visible [13].

**Figure 8.** The XRD patterns of Nickel deposits using nickel sulfate and nickel sulfamate electrolytes.



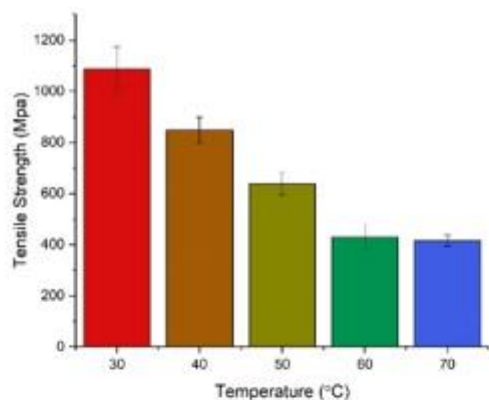


### Tensile testing

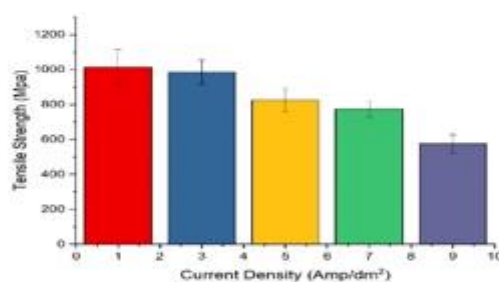
Tensile testing of pure nickel electrodeposits was carried using various electrolytic bath operating conditions *i.e.* temperature, current density and pH by using SHIMADZU AGS-X series precision UTM with a 20 kN load cell at a strain rate of 0.5 mm/min, following ASTM E8 standard.

Effects of various parameters on tensile strengths of electroformed nickel have been summarized in Figure 9. Multiple samples were tested for consistency as indicated by error bars in the Figure. It was observed that increase in the current density and temperature resulted in an increase in grain size of the electrodeposited nickel as shown in the SEM and optical micrographs, which correspondingly decreased the strength of the electroforms. It was further noticed that a high current density caused increased hydrogen evolution which was held responsible for enhanced surface roughness, larger crystal size and lesser elongation, as supported by the Hall-pitch effect. Furthermore, as evident from Figure 9(c), increasing the pH value from 4-6 resulted in a decrease in the tensile strength of the nickel deposits, as higher acidic concentration (low pH) of the solution would cause hydrogen inclusion in the deposits resulting in hydrogen embrittlement of the sample having higher tensile strength values [14].

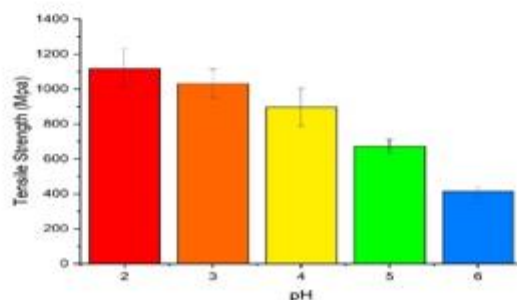
**Figure 9.** Tensile strengths of electroformed nickel as result of variation in a) temperature; b) current density; c) pH of the electrolyte.



(a)



(b)



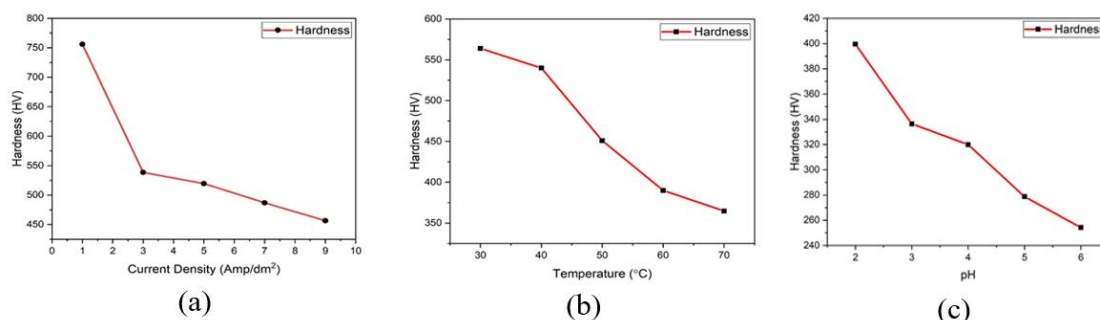
(c)

**Micro hardness test**

Microhardness testing of electroformed nickel surface was performed at various electrochemical processing parameters using Vickers microhardness machine. Figure 10 (a-c) exhibits the varying trends in the three major parameters of current density, temperature and pH. Although complete processing parameters have not been described with the Figure 11, however, a decreasing trend in hardness was observed by increasing the individual parameter. The trend in varying microhardness was also supported by other characterizing techniques since the processing conditions were mainly affecting the grain size which resultantly caused corresponding variation in mechanical properties. For example, by increasing the temperature and current density the grain size increased and consequently the hardness of the nickel electrodeposits decreased. Moreover, as a result of higher current density, enhanced evolution of the hydrogen was observed which also contributed towards higher hardness of the

deposits. A similar result for pH and microhardness was observed as higher acidity of the electrolyte increased hardness and brittleness in the electroformed nickel, as shown in Figure 10 (c).

**Table 10.** Effect of increasing a) current density; b) processing temperature; c) pH of the electrolyte on microhardness of electroformed nickel.



A detailed literature survey was done to fill the gaps in the research area of electroforming. In 1994 Michael discussed about the methods, materials and merchandise of the electroforming and highlighted important electroforming solutions and properties of the deposits; e.g. tensile strength was found in the range of 415 MPa-620 MPa, whereas microhardness was noticed to be 170 HV-230 HV (300 g load) for electrodeposited nickel using nickel plating salts and boric acid. High quality nickel films with fine grain morphology using a new electroplating method involving the emulsion of a supercritical carbon dioxide, an electroplating solution and a surfactant. The plated films using this method had Vickers hardness in the range 550 HV-705 HV (100g load). The properties and the effect of operating parameters on nickel plating was reviewed by the tensile strength values reported were in the range 345 MPa-485 MPa and microhardness range was 130 HV-200 HV (100 g load) for the electrodeposited Nickel using nickel sulfate as the electrolytic solution. Hardness measurements of the electrodeposit nickel was done in the year 2018 and it was found in the range of 476-496 (200 g load). The microhardness value of nickel deposits to be 568 HV. Moreover, they expanded their work to electrodeposited Ni-Co alloy, composite coatings in order to investigate their microstructure, properties and applications. Compared with the literature for mechanical testing of electrodeposited nickel, the current research provides enhanced and wider ranges of mechanical properties i.e. tensile strength (414 MPa-1117 MPa) and Microhardness (254-756: 300 g load). However, the wide variation was based on changing various processing parameters for the purpose of optimization the processing. The quest for electrodeposition of nickel etc. is still continuing leading to further useful applications.

## CONCLUSION

During the investigation a prominent effect of temperature on grain size of Nickel deposits was observed e.g. maximum grain size (13  $\mu\text{m}$  -14  $\mu\text{m}$ ) at 60°C. Enhanced evolutions of hydrogen gas and higher deposition rate at high current densities i.e. 6 Amp/dm<sup>2</sup> were also observed. Poor mechanical properties at larger grain sizes were verified by the tensile and microhardness testing. Inadequate mechanical agitation and fluctuating voltages resulted in pits formation. Dull nickel plating was observed at temperature above 60°C and pH value of 5.5. Hence by controlling all these parameters, the mechanical properties i.e. tensile strength and microhardness were enhanced. For example, depending on the process parameters, the tensile strength of the electroformed nickel varied between 411 MPa-1117 MPa and microhardness was in the range of 254 HV-756 HV.

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