

# Chapter 5 The effect of Ultrasound on Electroless Plating of Nickel

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## **Abstract**

Ultrasound waves generate and enlarge gas cavities in an aqueous solution by compression and rarefaction cycles. When cavities have grown to a certain size they become unstable and collapse under external pressure. This process leads to a number of effects such as standing waves, microjetting, localized temperature increases etc., which can have a positive effect on electrochemical and chemical systems. In this chapter research studies concerning electroless nickel (Ni) deposition by ultrasound are reviewed. The main benefits of using ultrasound assisted electroless Ni deposition include (1) increased rate of deposition, (2) modification of coating morphology (3) modification of coating composition (4) dispersion of particles for composite deposition and formation of core-shell particles and (5) improved coating uniformity on complex structures.

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## 5.1 Introduction to Ultrasound/Sonochemistry

The potential for ultrasound to influence electrochemical processes has been realised for at least 60 years. In that time, the effects of ultrasonic irradiation on electroless systems in general and electroless nickel in particular have been widely studied and a number of benefits have been identified, at least at the laboratory scale. Before the various studies are discussed, a short introduction is given to the effect of ultrasound on a liquid medium *i.e.* sonochemistry.

When low frequency ultrasound is applied to a liquid medium, transient or inertial gas cavities (or bubbles) are created inside the liquid that gradually grow in subsequent compression and rarefaction cycles (Wood, Lee & Bussemaker, 2017). The temperature of gases inside the cavity has been calculated to reach  $\sim 5,000\text{ K} - 7,000\text{ K}$  (Crum & Suslick, 1995). The expansion of a gas cavity continues until it reaches a size where the vapour pressure inside the bubble becomes unstable whereupon it implodes (**Figure 5.1a**). When a cavity implodes very high temperatures and pressures occur locally depending on the frequency of the ultrasound. The surrounding liquid in close proximity to the imploding cavity reaches  $2,343.15\text{ K}$ , and the pressure on cavity implosion has been estimated to be close to 500 atmospheres (Suslick & Doktycz, 1990). After cavity collapse there is a rapid drop in temperature at rates faster than  $10^{10}$  degrees per second (Crum & Suslick, 1995) therefore the bulk solution temperature is lower than  $373.15\text{ K}$ . If a solid surface is present (for example an electrode) then microjetting can occur due to asymmetric bubble collapse as shown in **Figure 5.1b**, producing microjets which, again depending on the frequency and power of the ultrasound, can hit the surface at speeds of up to  $>100\text{ m/s}$ .

[insert: Fig 1a Intro Crum 2018]

[insert: Fig 1b - d]

**Figure 5.1:** Cavity collapse; (a) high-speed flash photomicrograph of an unstable imploding cavity with a diameter of  $150\text{ }\mu\text{m}$  (Suslick & Doktycz, 1990) in a liquid irradiated with ultrasound near a solid substrate surface; image provided by Lawrence Crum (copyright owner). Illustration of the (b) formation of a microjet from an imploding cavity, and

(c) a microjet striking the surface, (d) pressure wave and light emitted after cavity collapse.

### 5.1.1 Influence of Ultrasonic Waves on Chemical Systems

The factors that influence sonoelectrochemical processes that results in a variety of reactions have been briefly summarized in **Table 5.1**. Primary factors that directly influence an ultrasonic system are (Wood *et al.*, 2017):

1. *Power (pressure) amplitude*, determines number of cavities produced, including motion, coalescence and agglomeration of cavities by acoustic streaming.
2. *Frequency of sound field*, cavity size increases with decreasing applied frequency (< 100 kHz) and collapse of a cavity accelerates. May also affect cavity distribution and population, and extent of chemical reaction.
3. *Reactor design*, encompasses: transducer type (probe or plate), signal type (pulsed or continuous), liquid height, liquid temperature, reflective plate (lowers sonochemiluminescence activity), diameter of vessel : diameter of transducer ratio, flow of liquid.

The effect of ultrasound on a liquid can vary in different solutions because secondary factors have an influence on the effects of primary factors. Some examples of secondary factors include: solution temperature and pressure, solution viscosity, concentration of gases dissolved in solution, reactor geometry, mechanical stirring speed etc.

The aim of this chapter is to review and present results from research studies mainly focused on ultrasonic deposition of nickel (Ni) on solid surfaces from an electroless Ni solution. By comparing different methods and results from electroless Ni deposition research articles we intend to highlight trends and describe new recent developments in this field. Most sonochemical research for electroless Ni deposition has been conducted at a low frequency range of 20 Hz – 100 kHz, although some examples are provided where frequency is extended up to 1 MHz.

**Table 5.1:** Ultrasonic factors that affect a liquid solution and solid sample in an electrochemical system (Mason & Bernal, 2012; Suslick & Doktycz, 1990; Wood *et al.*, 2017).

Factor	Description	Beneficial effects	Adverse effects
<b>Acoustic Streaming</b>	Steady flow of solution. Controlled by the amplitude of power applied to solution. Asymmetry of cavities give rise to this.	<ul style="list-style-type: none"> <li>• Increase in mass transfer of active chemicals.</li> <li>• Reduces the diffusion boundary layer.</li> </ul>	<ul style="list-style-type: none"> <li>• Coalescence of cavitation bubbles at higher powers (W).</li> </ul>
<b>Turbulent Flow</b>	Disorderly movement of solution. Influenced by vessel designs.	<ul style="list-style-type: none"> <li>• Similar benefits to acoustic streaming.</li> </ul>	<ul style="list-style-type: none"> <li>• Induces cavitation on solid surface.</li> <li>• Cavitation bubbles are moving randomly.</li> </ul>
<b>Microjets</b>	Jet from collapsed cavity strikes the surface directly.	<ul style="list-style-type: none"> <li>• Enhances mass transport of active species to surface.</li> <li>• Prevents fouling at surface by cleaning.</li> <li>• Remove or thin oxides/coatings on solid surfaces.</li> </ul>	<ul style="list-style-type: none"> <li>• Erosion of materials when cavity forms close to surface of solid.</li> <li>• Depassivation of metal surface increases corrosion risk.</li> <li>• Non-uniform work hardening of extended metal surface.</li> </ul>
<b>Emission of Shock Waves</b>	Pressure wave follows violent collapse of cavity.	<ul style="list-style-type: none"> <li>• Increased mass transport.</li> <li>• Causes collisions of particles.</li> </ul>	<ul style="list-style-type: none"> <li>• Wave can damage surface if cavity collapses very close to it.</li> <li>• Particles colliding at high speeds may fragment or fuse.</li> </ul>
<b>Chemical Effects</b>	Changes in solution or solute chemistry.	<ul style="list-style-type: none"> <li>• Radicals are generated depending on solvent e.g. HO•, HO<sub>2</sub>•, O• from water, and recombine to form reactive molecules e.g. H<sub>2</sub>O<sub>2</sub>, O<sub>2</sub> and H<sub>2</sub> that lead to redox reactions.</li> <li>• Cracking of alkanes at ambient temperature to form acetylene.</li> <li>• Controlled polymer degradation.</li> <li>• Amino acids Alanine, Ethylglycine, Glycine form in acetic acid solutions or under CH<sub>4</sub> or CO<sub>2</sub> with N<sub>2</sub>.</li> </ul>	<ul style="list-style-type: none"> <li>• Adverse reactions occur from radicals.</li> <li>• Can cause agglomeration of high melting point metal particles.</li> <li>• Mechanisms not studied in detail.</li> </ul>
<b>Heat</b>	Cavity implosion releases heat that removes ligands on metal ion.	<ul style="list-style-type: none"> <li>• Heat dissipates quickly.</li> <li>• Solution is warmed &lt; 373.15 K.</li> </ul>	<ul style="list-style-type: none"> <li>• Deformation/softening of metals very close to imploding cavity.</li> </ul>
<b>Sonoluminescence</b>	Light is emitted when excited molecules return to ground state. This effect is more prominent in organic solvents.	<ul style="list-style-type: none"> <li>• Increases by 29% when TiO<sub>2</sub> powder (20 mg) added in water (100 cm<sup>3</sup>).</li> <li>• Intensity increases with salt concentration in solution to a certain limit, due to gas solubility change.</li> </ul>	<ul style="list-style-type: none"> <li>• Can destabilise or reorder ligands on an organometallic molecule to form cluster compounds.</li> <li>• Sonoluminescence quenched by long chain alcohols in solution at 515 kHz.</li> <li>• Absent in highly viscous liquids.</li> </ul>

## 5.2 Effect of Ultrasound on Electroless Ni Plating Rate/Amount

Acoustic streaming and turbulent flow of a plating solution agitated by ultrasound increases mass transport of ionic species to the electrode surface therefore increasing the rate of deposition. Many

studies have looked at measuring electroless Ni plating rates, a detailed analysis of this topic led Bangwei Zhang to conclude that insufficient data is available in the literature to derive a mechanism (Bangwei, 2016). This was due to the multitude of electroless solution composition or physical parameters (*e.g.* plating time, temperature, sonication power/frequency) used by various researchers and each time these are changed the plating rate also shifts (**Table 5.2**). Another complication is that some studies have rotated the substrate in the electroless plating solution while applying ultrasound (to reduce turbulent flow and cavitation on the substrate), while others have kept the substrate stationary.

A good example of how flow of electroless plating solution affects the deposit is the study (Sharifalhoseini & Entezari, 2015) where it was found that the Ni-P deposition rate onto mild steel was higher when the sample was positioned horizontally with respect to the ultrasonic probe as opposed to vertical (see **Table 5.2**). In addition to this, from the present literature survey no two papers using similar power (W) and frequency (kHz), and different plating solution conditions (*i.e.* pH, composition, concentration) have quoted a similar deposition rate/amount. The rate of deposit growth is thought to be influenced by the following factors when applying ultrasound:

1. Reduction of the diffusion layer, and increase in mass transport to/from electrode surface (Abyaneh, Sterritt & Mason, 2007).
2. Increase in crystal nucleation rate by increasing active sites (Cobley, Mason & Saez, 2011).
3. Sonochemical activation of inactive hypophosphite (Mallory, 1978).

There is no existing evidence on which route dominates and influences the process the most. Representative research articles from the past 50 years that describe Ni-P or Ni-B deposition (rate/thickness/weight) with and without ultrasound are listed in **Table 5.2**. The results show change,  $\Delta$  (%), in amount of Ni deposited is evident when using ultrasound.

$$\text{Change by ultrasound, } \Delta (\%) = \frac{\text{Thickness} - \text{Thickness at 0 kHz}}{\text{Thickness at 0 kHz}} \times 100$$

**Equation 5.1:** Calculation for change in thickness when applying ultrasound. Calculation is also used for change in mass, rate or composition.

The results clearly indicate that in the majority of cases, sonication causes the amount of Ni deposited to increase. As has been noted elsewhere in this book, a standard still or stirred electroless Ni electrolyte typically operates at 353.15 K to 368.15 K and reducing this temperature (~ 323.15 K to 343.15 K) would be beneficial from the perspective of overall process costs, reducing water consumption (due to evaporation) as well as bringing about environmental benefits. Sonication has been used as a means to enable the reduction in electroless Ni operating temperatures. For example, a copper substrate was electroless Ni-P plated using a constant solution temperature of 323.15 K with/without ultrasonication at 40 kHz frequency while the power was varied from 40 to 100 W (Hu *et al.*, 2011). A still or stirred solution failed to plate a copper surface at 323.15 K, but when sonication was applied Ni-P was deposited and the thickness increased with power. In a similar study (Cobley & Saez, 2012) Ni-P was deposited onto copper comparing different solution temperatures (323.15 to 363.15 K) at a constant ultrasonic frequency (20 kHz) and power (42 W cm<sup>-2</sup>). This work showed that the plating rate increased with temperature and that the application of ultrasound always brought about a higher deposition rate. In addition, it was found that at an electroless Ni solution temperature of 343.15 K the plating rate observed when ultrasound was applied was at least 1.5 X higher than the rate obtained from a ‘silent’ electroless Ni solution at 363.15 K (see **Figure 5.2a**). Although these results suggested sonication may enable low temperature electroless Ni deposition and therefore reduce energy consumption, it must be remembered that the application of ultrasound also requires energy. To our knowledge, no research has been conducted to calculate whether there is an overall energy benefit from the

application of ultrasound in this situation.

[insert: Fig 2a rate Cobley 2012]

[insert: Fig 2b rate Cobley 2012]

**Figure 5.2:** Effect of ultrasound (20 kHz) on the plating rate for an electroless Ni solution at different operating temperatures determined using (a) mixed potential theory, and (b) “weight gain”, on plated test coupons (Cobley & Saez, 2012).





Deposit Surface (Citation)	Label	Ultrasonic parameters kHz/Power	Results				Hardness (HVN)	$E_{corr}$ / V	$i_{corr}$ / $\mu\text{A}/\text{cm}^2$	Conditions		Solution concentrations (mol/dm <sup>3</sup> )		
			Thickness / mass / rate	$\Delta$ (%)	P % (B %)	P (B) $\Delta$ (%)				Temp/K (Time/s)	pH	Ni <sup>2+</sup> / Reduce agent	Chelate agent	Other
<b>Ni-P Mg-Li alloy</b> (Zou <i>et al.</i> , 2014)	34	0/0	20 $\mu\text{m}$		9.6		474	-0.72	18	353.15 (7200)	6.4 - 6.5	0.06 / 0.14	Sodium acetate (0.16)	NH <sub>4</sub> HF <sub>2</sub> (0.14) HF 40% v/v (12)
	35	40/100 W	20 $\mu\text{m}$	0	8.9	-7.3	556	-0.34	8	341.15 (7200)				
<b>Ni-P Mild steel</b> (Yang, Hou & Wu, 1997)	36	0/0	7.5 mg/cm <sup>2</sup> ·h		10.49		550	Not stated	Not stated	351.15 – 355.15	4.8	0.08 / 0.19	Sodium acetate (0.24)	Thiourea (1.31E-5)
	37	0.033/1 Wcm <sup>-2</sup>	10.3 mg/cm <sup>2</sup> ·h	37	8.39	-20.0	603			(Not stated)				
<b>Ni-P Copper</b> (Kobayashi, Chiba & Minami, 2000)	38	0/0	1.6 $\mu\text{m}/\text{h}$				Not stated	Not stated	Not stated	323.15 (3600)	7.0	0.15 / 0.33	Sodium Citrate Dihydrate (0.17)	Not stated
	39	28/3.15 Wcm <sup>-2</sup>	3.8 $\mu\text{m}/\text{h}$	138										
	40	45/3.15 Wcm <sup>-2</sup>	4.7 $\mu\text{m}/\text{h}$	194										
	41	100/3.15 Wcm <sup>-2</sup>	2.4 $\mu\text{m}/\text{h}$	50										
<b>Ni-Co-P Mild steel</b> (Sun, Guo <i>et al.</i> , 2011)	42	0/0	Not stated		6		Not stated 459	Not stated	Not stated	363.15 (3600)	6.4	Not stated	Not stated	Not stated
	43	0/0	5.38 $\mu\text{m}/\text{h}$		4.89		650			343.15 (3600)				
	44	28/not stated	14.87 $\mu\text{m}/\text{h}$	176	5.44	11.3								
<b>Ni-P Mild steel</b> (Sharifalhoseini & Entezari, 2015)	45	0/0			8.92		Not stated	-0.408	1.66	353.15 (7200)	4.8	9.5 / 29	Sodium citrate (5.1)	Sodium dodecyl sulfate (Not stated)
	46	Not stated (p:v)	7.8 $\mu\text{m}/\text{h}$	24	8.50	-4.7		-0.391	1.60					
	47	Not stated (p:h)	9.4 $\mu\text{m}/\text{h}$	49	8.66	-2.9		-0.326	1.02					
<b>Ni-P Mg AZ91D</b> (Ban, Shao & Wang, 2014)	48	0/0	17 $\mu\text{m}$		Not stated		Not stated	-1.2	13.1	353.15 (4500)	6.5	0.04 / 0.28	Citric acid monohydrate (0.04)	Thiourea (1.97E-5)
	49	530/5 W	15 $\mu\text{m}$ *	-12				-0.3	6.45					
<b>Ni-Cu-P Mild steel</b> (Sun, Liu <i>et al.</i> , 2011)	50	0/0	Not stated		11.61		655	Not stated	Not stated	343.15 (3600)	6.4	Not stated	Not stated	Not stated
	51	28/not stated			9.13	-21.4	765							
<b>Ni-P Mild steel</b> (Vasudevan, Narayanan & Karthik, 1998)	52	0/0	15 $\mu\text{m}/\text{h}$		Not stated		Not stated	Not stated	Not stated	366.15 (3000)	8.0 – 9.0	0.35 / 0.13	tri-Sodium citrate dehydrate (0.34)	Not stated
	53	25/400 W	45-50 $\mu\text{m}/\text{h}$	200 - 233										

p = transducer is a probe/horn.

v or h = sample was held vertical or horizontal with respect to probe, p (respectively).

$E_{corr}$  and  $i_{corr}$  derived from electrochemical polarization curves where NaCl (aq) is an electrolyte.

\* = thickness not including transition layer (17  $\mu\text{m}$ ).

As indicated in **Table 5.2**, there is no accepted value as the optimum ultrasonic frequency to get the maximum benefits from sonication. However, some researchers have suggested that the optimum electroless Ni-P plating frequency is 40 kHz using the weight gain method (Park *et al.*, 2002) since they found that at 28 kHz or 68 kHz the deposition rate becomes slower than using no ultrasound (**Table 5.2**). An earlier study (Kobayashi *et al.*, 2000) concluded that optimum electroless Ni plating frequency is 45 kHz in a solution containing a citrate complexing agent, but they found that the plating rate at 28 kHz and 100 kHz is still higher than with no ultrasound. They also reported that an ultrasound agitated electroless Ni is less stable at pH > 8 or temperatures > 333.15 K than under silent conditions. There is no accepted value as the optimum plating frequency even after the studies by Park *et al.* and Kobayashi *et al.* researchers have continued to use lower/higher frequencies than 40 – 45 kHz (**Table 5.2**). Inconsistencies are noticed when comparing papers that indicate electroless Ni plating is not primarily influenced by ultrasonic parameters and other factors (*i.e.* pH, solution temperature and composition) influence deposit thickness, compactness, and composition.

Experiments have been conducted (Mallory, 1978) where only the complexing agent for Ni<sup>2+</sup> was varied; sonication power/frequency, time of exposure and solution composition were not changed. Results of this study demonstrated that plating rate can increase or decrease when the type of complexing agent is changed (**Table 5.2**, labels 24 - 33) but in all cases (except when citric acid is used as a complexing agent) the application of ultrasound increased the amount of Ni deposited. However, this and other studies also showed that increasing the amount of chelating agent in the Ni<sup>2+</sup> electrolyte stabilises the plating solution, and the deposition rate drops when applying ultrasonication (Abyaneh *et al.*, 2007; Mallory, 1978). **Figure 5.3** is an example of this effect, where the deposition rate dropped in the presence of ultrasound in a Ni<sup>2+</sup> electroless electrolyte

containing  $\text{CH}_3\text{COONa}$  (0.24 M) chelating agent whereas at low chelate concentrations (0.04 M) sonication had a positive effect. This effect was explained by an increase in solution stability when higher a concentration of chelating agent was present.

[insert: Fig 3a rate Abyaneh 2007]

[insert: Fig 3b rate Abyaneh 2007]

**Figure 5.3:** Rate of Ni-P deposition vs.  $\text{NiCl}_2$  concentration for a silent and ultrasonic solution (35 kHz / 0.80 W/cm<sup>2</sup>) containing 0.19 M sodium hypophosphite and (a) 0.04 M sodium acetate, (b) 0.24 M sodium acetate. Plating at 363.15 K and 15 minutes (Abyaneh *et al.*, 2007).

The molar ratio of the reducing agent to  $\text{Ni}^{2+}$  is also an important factor; Abyaneh and co-workers (Abyaneh *et al.*, 2007) demonstrated that an increase of 89 % in Ni-P deposition rate can achieved (**Figure 5.3a**) using  $\text{NiCl}_2$  (0.13 M) and  $\text{NaPO}_2\text{H}_2$  (0.093 M). However, the solution was unstable because the complexing agent concentration was too low. This group investigated how plating rate is affected by amount of thiourea stabiliser at different pH values (**Figure 5.4**). No Ni-P plating was deposited below pH 3.6, which is in agreement with other studies listed in **Table 5.2**, and the most significant increase in plating rate with pH was using 2 ppm thiourea. An optimum pH of 5.25 (**Figure 5.4**) for plating rate is in close agreement with pH 5.5 selected using a statistical analysis modelling method in a separate study (Park *et al.*, 2002).

[insert: Fig 4 rate Abyaneh 2007]

**Figure 5.4:** The effects of pH on the plating rate of Ni-P in the presence of ultrasound at a series of various thiourea concentrations, 0-3 ppm (Abyaneh *et al.*, 2007).

Another influence to consider is the use of surfactants in an ultrasonic solution. Surfactants will influence the surface tension of the electrolyte and will therefore have an impact on cavity growth and stability, which in turn affects the rate. A detailed review was compiled about studies on parameters that influence ultrasonic cavitation (Wood *et al.*, 2017) and the use of surfactants (among other chemicals) is considered as a parameter that enhances the effects of a sonochemical system. Some findings of Wood *et al.* are detailed in **Table 5.3**. Effects of transient cavitation

and resistance to mass transport are carefully balanced by surfactant and salt concentration in solution. There is evidence that higher concentrations of surfactants in solution form micelles and reduce mass transport.

**Table 5.3:** Effect of different types of surfactants on cavitation (Wood *et al.*, 2017).

Characteristic	Surfactant	Effect on cavitation
<b>Bulky head group</b>	Dodecyl dimethyl ammonium propane sulfonate (DDAPS)	<ul style="list-style-type: none"> <li>• Induce bubble surface instabilities.</li> <li>• Increase rectified diffusion.</li> </ul>
<b>Long chain tail</b>	Dodecyl trimethyl ammonium chloride (DTAC)	<ul style="list-style-type: none"> <li>• Reduces resistance to mass transfer.</li> <li>• Chance surfactant will adsorb to cavity surface decreases with increasing chain length.</li> </ul>
<b>Ionic head group</b>	Sodium dodecyl Sulfate (SDS)	<ul style="list-style-type: none"> <li>• Reduces bubble coalescence by electrostatic repulsion.</li> <li>• Electrostatic interaction of surfactant is inhibited by salts.</li> </ul>
	DTAC	<ul style="list-style-type: none"> <li>• Increase in cavity growth rate and cavity surface instability.</li> </ul>
	Perfluorocarboxylic Acid (PFOA)	<ul style="list-style-type: none"> <li>• Surface tension rises on cavity.</li> </ul>

Chiba *et al.* electroless Ni-B plated copper substrate with/without ultrasonic waves, and compared the plating rate to an alternative method where the plating solution is still but the Cu sheet substrate is vibrated while plating. Their results show that the thickest coating and therefore the fastest deposition rate was achieved by ultrasonication (45 kHz, 100 W). Deposition rate by mechanical agitation (without ultrasound) was faster than vibration of substrate (Chiba *et al.*, 2003).

### 5.3 Influence of Ultrasound on Structure, Morphology and Properties of Electroless Ni Coatings

#### 5.3.1 Effect of Ultrasound on Ni Deposit Composition

Control of phosphorus or boron content in Ni coatings is very important because composition influences the properties of the coating. ASTM B733-15 standard (ASTM Committee, 2015) definitions of changes in coating properties with changing P (%) are summarised in **Table 5.4**.

**Table 5.4:** Ni deposits containing different levels of P content, and applications that match their properties. ASTM B733-15 (ASTM Committee, 2015).

Type	P (%)	Microstructure	Applications	Properties of Ni-P
Lower	1 - 3	Crystalline	Electronics	Solderability, bondability, increased electrical conductivity, and resistance to strong alkali solutions.
Low	2 - 4	Crystalline	Abrasion and wear resistance	High as-plated hardness (620 - 750 HK 100).
Medium	5 - 9	Mixture of crystalline and amorphous	General purpose	Wear and corrosion resistance.
High	> 10	Amorphous	Beryllium and titanium parts for low stress	Longer salt-spray and acid resistance. Considered non-ferromagnetic.

It is generally accepted that ultrasonication of the plating solution tends to cause a drop in P (%) in the deposited coating at higher temperatures compared to a similar silent plating solution (Cobley *et al.*, 2011). For example (Cobley & Saez, 2012) a decline P (%) content was observed with increasing temperature (323.15 K to 363.15 K) using a 20kHz / 42Wcm<sup>-2</sup> probe, and the difference between silent and ultrasonic deposition increases as temperature is lowered. The content of P (%) in **Figure 5.5** is much higher than the standard 4 % – 15 % reported by most studies (**Table 5.2**).

[insert: Fig 5 composition Cobley 2012]

**Figure 5.5:** P content (%) in Ni-P deposited using 1 Ni<sup>2+</sup> : 1.33 NaH<sub>2</sub>PO<sub>2</sub> (323.15 K to 363.15 K) at 20 kHz / 42 W/cm<sup>2</sup> electroless plating solution (Cobley & Saez, 2012).

A plot of P (%) vs. rate of deposition (μm/h) comparing four different research articles shows that generally, ultrasonically assisted electroless Ni-P coatings tend to have higher deposition rates and lower P content (**Figure 5.6**). However, there are some exceptions where P (%) is higher than the deposit P content from the silent solution due to secondary factors.

[insert: Fig 6 P vs Rate SBegum 2018]

**Figure 5.6:** Plot of P (%) vs. Rate of deposition of electroless Ni-P coating (μm/h). Ultrasonic and corresponding silent electroless plating solutions indicated by u and s labels (respectively). Data taken from four separate research articles (see **Table 5.2**).

In the present literature survey only two articles were found that showed increases in

coating P content when comparing ultrasonic to silent agitation methods (Mallory, 1978; Sun *et al.*, 2011). Mallory noted that P content in Ni-P deposit is higher (P 5.6 %), than in a silent solution deposit (P 4.9 %), only when using glycine chelating agent and applying ultrasound: 49 kHz / 30 W (Mallory, 1978). From this evidence, Mallory concluded that the drop in P content when using ultrasound is not only caused by increase in solution temperature but also type of chelating agents in the solution. In parallel experiments, Mallory observed a decrease of P (%) in the coating deposited when using the same ultrasound settings and chelating agents containing only oxygen functional groups *i.e.* citric acid, lactic acid or glycolic acid (**Figure 5.7a - c**). In addition to this, all Ni-P depositions listed in **Table 5.2** from separate studies have used chelating agents with only oxygen functional groups at acidic pH. Although no theory/mechanism has been proposed to explain how glycine (**Figure 5.7d**) chelating agent increases P content in a binary Ni-P coating deposited by ultrasound at pH 4.8. Other studies have shown that glycine cannot form a stable complex with Ni<sup>2+</sup> in an acidic pH range (Sotskaya & Dolgikh, 2008). However, when glycine is mixed with other complexing agents, *i.e.* alanine and citric acid at pH 5.4, to form a composite coating of Ni-P-SiC by ultrasound (Ashassi-Sorkhabi & Es'haghi, 2013) the P content decreases (see **Table 5.5**, page 29).

[insert: Fig 7a - d]

**Figure 5.7:** Chemical structures of (a) Citric acid, (b) Lactic acid, (c) Glycolic acid, and (d) Glycine.

Sun *et al.* also reported higher P content when deposited from an electroless Ni-P electrolyte under ultrasonic irradiation (28 kHz / power not stated) compared to a silent solution (Sun *et al.*, 2011), but did not indicate the type of chelating agent used, and their electroless solution temperature was lower (343.15 K) than Mallory's study (Mallory, 1978). However, a recent study (Zou *et al.*, 2014) using a similar temperature (341.15 K) to Sun *et al.* has shown sodium acetate chelating agent is utilized a -7.3 % drop in P (%) content is observed when sonication is applied. Therefore, in the

study by Sun and co-workers, it is likely P content was affected by cobalt sulfate concentration as Co was co-deposited in Ni with phosphorus (Sun *et al.*, 2011). They also showed that the Co content in the coating was higher when deposited under ultrasound compared to those coatings deposited from a silent electrolyte. A similar trend was shown in a study (Qian *et al.*, 2017) that co-deposited Ce in Ni-B (**Table 5.2**, labels 4-7) where the Ni-B-Ce deposited by sonication contained more B than the binary Ni-B deposit prepared using the same ultrasonic parameters (60 kHz / 150 W at 358.15 K). The Ce content in this study was also higher than the Ce deposited using a still solution.

On the other hand in a separate study (Sun *et al.*, 2011) Cu was co-deposited with P from a Ni-P electroless solution using the same electroless plating parameters as in the study for Ni-P-Co; a trend where P content decreases (compared to binary Ni-P) as Cu content increases in Ni-Cu-P when using ultrasound was observed. Matsuoka and Hayashi reported that increasing the concentration of thallos nitrate stabilizer in the solution (2 – 22 wt%) and pH (5 to 9) causes a decrease in the amount of P in a Ni-P coating deposited by ultrasound (25 kHz / 150 W) at 353.15 K (Matsuoka & Hayashi, 1985). This was due to co-deposition of thallium in the Ni coating, and the thallium content increased in the deposit whilst the P content decreased.

### **5.3.2 Changes in Ni Deposit Microstructure via Ultrasound**

Many authors have reported that the Ni-P deposit has a somewhat rounded nodular surface morphology (**Figure 5.8a**), while a Ni-B coating has cauliflower type structures on the surface (*e.g.* **Figure 5.9**). It has been found Zou *et al.*, 2014) that the nodule size on the surface of an electroless Ni-P coating decreases when ultrasound is used during deposition **Figure 5.8b**, and this can increase the hardness and wear resistance of the coating. In this example it was also observed that without sonication there were pores at the Ni-P and substrate interface. It was proposed that



the use of ultrasound during electroless deposition minimizes pin-hole gaps in the Ni deposit surface by efficient removal of hydrogen gas formed during the deposition reaction. Difference in coating porosity through the thickness of the coating is evident when applying ultrasonication. For example the morphology of a sectioned crystalline Ni-B coating is columnar and porous (*e.g.* **Figure 5.10a**); whereas a coating deposited with ultrasonication is columnar and compact, *e.g.* **Figure 5.10b** (Bonin *et al.*, 2017).

[insert: Fig 8a microstructure Zou 2014]

[insert: Fig 8b microstructure Zou 2014]

**Figure 5.8:** SEM showing change in surface morphology and nodule size of Ni-P deposit from an electroless Ni solution that is (a) silent and (b) agitated by ultrasound, 40 kHz / 100 W, (Zou *et al.*, 2014).

[insert: Fig 9 microstructure Niksefat 2015]

**Figure 5.9:** SEM showing cauliflower type surface morphology and nodule size of Ni-B deposit from a silent electroless Ni solution with agitation by rotation of the sample at 300 rpm (Niksefat & Ghorbani, 2015).

[insert: Fig 10a microstructure Bonin 2017]

[insert: Fig 10b microstructure Bonin 2017]

**Figure 5.10:** SEM cross section morphology of electroless Ni-B coating deposited (a) without ultrasound, and (c) with ultrasound (35 kHz / 0.065 W/cm<sup>3</sup>) energy density ultrasound (Bonin *et al.*, 2017).

XRD of ultrasonically deposited Ni coatings shows a strong broad single Ni [111] peak for an amorphous structure, and ultrasound may result in some crystalline phases appearing.

Mallory *et al.* reported crystal sizes from Ni [111] peaks from Ni-P plating deposited from silent and ultrasonic solutions were similar: 1.7 nm and 1.9 nm respectively. Both deposits were amorphous and the two deposits were distinguished by a minor Ni [200] shoulder on Ni [111], which was absent in as-plated Ni-P from a silent solution (Mallory, 1978).

Ban and co-workers deposited Ni-P onto Mg alloy from an ultrasonic (530 kHz / 5 W)

electroless Ni solution, and the coating had a dendritic transition layer (17  $\mu\text{m}$  thick) where the Mg and Ni-P were intermixed, **Figure 5.11** (Ban *et al.*, 2014). A transition layer formed when high frequency ultrasonic irradiation deformed the Mg alloy surface while the electroless Ni solution penetrated and deposited Ni-P in the deformed Mg layer. The XRD pattern of Ni-P coating deposited from a silent solution was amorphous and when ultrasound irradiation used the Ni phase was crystalline, indicating ultrasound at 530 kHz frequency caused a phase transformation.

[insert: Fig 11 microstructure Ban 2014]

**Figure 5.11:** SEM image of a sectioned Ni-P plating deposited on Mg alloy AZ31 at a constant frequency of 530 kHz / 5 W (500 mL electroless solution, pH 6.5) for 75 minutes (353.15 K) (Ban *et al.*, 2014).

Sharifalhoseini and Entezari deposited Ni-P onto mild steel by positioning the sample vertically or horizontally with respect to the ultrasonic probe in electroless Ni (Sharifalhoseini & Entezari, 2015), and they concluded that placing the sample horizontally below the probe tip gave an improved surface finish by comparing SEM images (**Figure 5.12**).

[insert: Fig 12a - c microstructure Sharifalhoseini 2015]

**Figure 5.12:** SEM micrographs of electroless Ni deposits from: (a) silent solution, (b) sample is vertical vs. ultrasonic probe, and (c) sample is horizontal vs. ultrasonic probe (Sharifalhoseini & Entezari, 2015).

### **5.3.3 Effect of Ultrasound on Ni Deposit Mechanical/Physical Properties**

Ni coatings are removed by adhesive or scratch wear; spall wear is usually observed when the Ni coating is a composite containing particles. Important factors in reducing wear are strong adhesion to substrate, high hardness and low friction coefficient. Very few articles were found where the wear of Ni-P or Ni-B coating deposited by ultrasonication were reported because wear resistance tends to increase with hardness (Bonin *et al.*, 2017; Sun *et al.*, 2011). Most studies assume a coating with high hardness has excellent resistance to wear.

However, the mechanism of wear can vary depending on type of ultrasonic agitation method/parameters. Bonin *et al.* deposited Ni-B using an (i) silent mechanically agitated solution, (ii) ultrasonic cleaner (35 kHz/0.065 W mL<sup>-1</sup>) and (iii) probe (20 kHz/0.058 W mL<sup>-1</sup>). They established that Ni-B is removed *via* abrasive and adhesive wear for Ni-B deposited by silent and 35 kHz solution (Bonin *et al.*, 2017). Whereas, for Ni-B deposited using a 20 kHz probe the adhesive wear mechanism dominated. In their study they did not see a significant improvement in hardness and wear when using ultrasound during electroless plating.

Electroless Ni plating deposited in the presence of ultrasound has been shown to increase hardness of Ni coatings due to (1) increase of crystalline phases, *i.e.* Ni<sub>2</sub>P<sub>5</sub>, Ni<sub>3</sub>P and Ni<sub>2.55</sub>P (Yang *et al.*, 1997), (2) a decrease in the phosphorus or boron content, and (3) smaller Ni crystal grains.

Usually the hardness is higher when a lower amount of B or P in the coating is present (Cobley *et al.*, 2011). **Figure 5.13** is a plot of hardness *vs.* composition, from research articles summarised in **Table 5.2**, and from this plot it is evident that when Ni-P is deposited under ultrasound the hardness is higher than equivalent silent conditions, and as has already been stated the P % is lower (**Figure 5.13**). There is only one article (Sun *et al.*, 2011), see **Figure 5.13** (■ 28 kHz / power not stated), that shows an increase in hardness with P content; in this study the coating is Ni-P-Co. An increase in hardness can be explained by increase in Co 1.91 % (silent) to 3.27 % (28 kHz ultrasound) and this means more Co atoms are in the Ni crystal lattice (Srinivasan *et al.*, 2011). A similar trend of increasing hardness with B % is seen for Ni-B-Ce coatings (Qian *et al.*, 2017) when B 5.9 % and Ce 6% (silent) is increased to B 6.2 % and Ce 6.6 % when applying ultrasound (60 kHz/150 W).

Interestingly, when copper is co-deposited in a Ni-P coating (Sun *et al.*, 2011) the hardness is not affected in the same way as when using Ce or Co (**Figure 5.13**, ● 28 kHz), and the same applies

to the Ni-B coating (Bonin *et al.*, 2017) containing trace amounts of Pb (see **Table 5.2**, labels 1 - 3).

The deposition method, and not just composition, affects hardness. One study described Ni-B (25  $\mu\text{m}$  thickness, B 5.47 wt%) deposited at 368 K (pH 12) by ultrasound (35 kHz / 0.065  $\text{Wcm}^{-3}$  by probe) with no stirring (Bonin *et al.*, 2017). In a separate study, Ni-B (30  $\mu\text{m}$  thickness, B 6.6 wt%) was deposited from a silent solution (358.15 K, pH 14) while rotating (300 rpm) the substrate (Niksefat & Ghorbani, 2015). The hardness from Niksefat & Ghorbani method was higher (890  $\text{Hv}_{100}$ ) compared to Bonin *et al.* (844  $\text{Hv}_{100}$ ).

[insert: Fig 13 Hardness vs P SBegum 2018]

**Figure 5.13:** Hardness vs. P (%) content in electroless Ni-P coating. Ultrasonic and corresponding silent electroless plating solutions indicated by u and s labels (respectively). Data taken from six separate studies (see **Table 5.2**).

#### 5.3.4 *Effect of Ultrasound on Ni Deposit Adhesion to Substrate*

There are few papers on the effect of ultrasonic irradiation on adhesion of electroless Ni coatings. Adhesion strength of Ni-P to a magnetic substrate (Nd-Fe-B) from an electroless alkaline solution (pH 8 and 353.15 K) improves from 12 MPa (silent solution) to a maximum of 56 MPa when ultrasound (40 kHz / 150 W) is applied (Yan, Ying & Ma, 2009). **Figure 5.14** is a plot of adhesion strength vs. ultrasonic power (W) at 40 kHz, and this shows that power affects adhesion; 150 W is optimum for a Nd-Fe-B magnet surface.

[insert: Fig 14 adhesion Yan 2009]

**Figure 5.14:** Adhesion strength of electroless Ni-P coating to Nd-Fe-B magnets deposited at 40 kHz and different ultrasonic powers (W). Solution pH = 8.5, temperature = 353.15 K (Yan *et al.*, 2009).

Zhu *et al.* conducted thermal shock tests on Ni-P plated Mg-Li alloy to show that Ni-P deposited *via* ultrasonic assistance, 40 kHz/100 W (341.15 K, 7200 s), exhibits no evidence of poor adhesion

*i.e.* blistering, delamination, cracking, peeling. Whereas, the Ni coating prepared without ultrasonic irradiation delaminated. The differences in the two coatings were noted by visual inspection only (Zou *et al.*, 2014).

### 5.3.5 Corrosion Resistance of Ni Coating Deposited by Ultrasound

Data from all articles about electroless Ni deposition by ultrasound indicates that the key to very good corrosion resistance in salts and acids is that the coating structure has the following features:

1. Amorphous phase (very little or no crystals).
2. Compact with little or no porosity/voids.
3. Lower surface area (or roughness).
4. Uniform thickness.

Polarisation curves are often used to characterise corrosion resistance of Ni plated samples by ultrasound because they can be used to derive the rate of corrosion. In all cases (**Table 5.2**) very low  $i_{\text{corr}}$  values in NaCl (aq) are reported because Ni forms a thin passive film that slows the corrosion process;  $E_{\text{corr}}$  increased and  $i_{\text{corr}}$  decreased when comparing Ni coatings deposited under ultrasound to those deposited under silent solutions (Ban *et al.*, 2014; Bonin *et al.*, 2017; Chiba *et al.*, 2003; Qian *et al.*, 2017; Sharifalhosseini & Entezari, 2015; Yan *et al.*, 2009; Yang *et al.*, 1997; Zou *et al.*, 2014). For ultrasonically deposited Ni-P,  $E_{\text{corr}}$  is at -0.3 to -0.35 V and for Ni-B  $E_{\text{corr}}$  is at lower potentials  $\sim$  -0.65 to -0.75 V (**Table 5.2**).

Yang *et al.* prepared a Ni-P coating using mild ultrasonic agitation (0.033 kHz/1 Wcm<sup>-2</sup>) which contained crystalline phases, and it was found that the deposit was less corrosion resistant to 0.2 mol/dm<sup>3</sup> H<sub>2</sub>SO<sub>4</sub> (aq) than a deposit plated under silent conditions (amorphous structure). In addition to this micro-cracks from stress corrosion cracking were visible in the ultrasound assisted Ni-P deposit (Yang *et al.*, 1997). Other authors report Ni coatings deposited by ultrasound are

likely to exhibit pitting (Bonin *et al.*, 2017) and galvanic corrosion (Zou *et al.*, 2014) when analysed after corrosion tests in NaCl (aq).

There is evidence that Ni-P or Ni-B coatings co-deposited with other metals, and plated using ultrasonic irradiation have greater corrosion resistance in NaCl than a binary Ni-P or Ni-B coating prepared using the same agitation method. Yan *et al.* deposited Ni-P coatings with varying  $[Cu^{2+}]$  in an electroless solution (pH 8.5, 353.15 K and 40 kHz / 150 W), and compared these coatings with a binary Ni-P deposited under the same conditions. Their results show a Cu/Ni ratio of 0.02 increases the time it takes for rust to appear on the coating from ~ 216 to 1843.2 kiloseconds in neutral salt spray compared to binary Ni-P. Polarisation curve results also showed that 0.02 Cu/Ni in Ni-P coating has the highest corrosion resistance than other Cu/Ni ratios and binary Ni-P. The coating containing 0.02 Cu/Ni ratio was less porous than coatings prepared using higher ratios of Cu/Ni, and the 0.02 Cu/Ni ratio gave an amorphous coating. Coatings deposited using Cu/Ni ratios higher than 0.03 were polycrystalline, and phase boundaries weakened the coatings corrosion resistance (Yan *et al.*, 2009).

Recently a coating of Ni-B-Ce (**Table 5.2**, labels 4 - 7) on mild steel has been shown to enhance corrosion resistance compared to Ni-B (Qian *et al.*, 2017); both exhibited an amorphous structure (by XRD) and were deposited by ultrasound (60 kHz, 150 W). However, a Ni-B-Ce deposited from a silent solution was still more corrosion resistant than binary Ni-B deposited by ultrasonication.

#### **5.4 Electroless Ni Composite Plating Enabled by Ultrasonically Dispersed Particles**

Particle reinforced Ni metal matrix coatings (MMC) have enhanced wear and corrosion resistance, and can enable thinner coatings to be deposited in some cases. It has been proposed that particles distributed uniformly throughout the coating thickness (*e.g.* **Figure 5.15**) inhibit growth of

corrosion paths, and dislocation movement in the Ni-P matrix. Generally, the morphology of Ni MMC is rougher than binary Ni-P or Ni-B. Particles in Ni coatings dispersed by ultrasonication are refractory ceramics, oxides (*e.g.* TiO<sub>2</sub>, ZrO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>) or graphene based, and no papers were found where polymer particles, *e.g.* polytetrafluoroethylene (PTFE), were co-deposited in an electroless Ni coating using ultrasonic irradiation.

[insert: Fig 15 MMC coat Ashassi-Sorkhabi 2013]

**Figure 5.15:** SEM image of sectioned sample showing 4 nm sized diamond nanoparticles co-deposited through thickness of Ni-P coating, 35 kHz / 450 W (358.15 K, pH 9) (Ashassi-Sorkhabi & Es'haghi, 2013).

Particles in a electroless Ni MMC are deposited using similar ultrasonic parameters to standard electroless Ni solutions, the main difference is that in some studies surfactants are added to the plating solution to reduce particle agglomeration. The type of surfactant used depends on the particle surface chemistry, and this is balanced with ultrasonication parameters. As stated previously, surfactants can significantly influence the efficacy of sonication but no in depth study has been done on the influence of surfactants on ultrasound when co-depositing particles in electroless Ni composites.

#### **5.4.1 Distribution of Particles in a Ni Matrix**

A study by Song *et. al.* demonstrated that one benefit of ultrasound is that the weight ratio of ZrO<sub>2</sub> particles increases in a Ni-P deposit, see **Figure 5.16a**, (Song, Shan & Han, 2008). As pressure released from cavity collapse in an ultrasonic solution increases particle movement and collisions (Crum & Suslick, 1995). The maximum weight ratio of ZrO<sub>2</sub> (~ 5.25 %) in Ni-P was achieved at 60 % amplitude of 40 kHz frequency (**Figure 5.16b**).

[insert: Fig 16a MMC coat Song 2008]

[insert: Fig 16b MMC coat Song 2008]

**Figure 5.16:** (a) Bar chart of ZrO<sub>2</sub> (wt%) in Ni-P coating with/without ultrasound. (b) Amount of ZrO<sub>2</sub> (wt%) in Ni-P coating when different percentages of most ultrasonic frequency (40 kHz) are applied (Song *et al.*, 2008).

Effect of solution temperature (323.15 K – 343.15 K) on co-deposition of Al<sub>2</sub>O<sub>3</sub> in Ni-P at 40 kHz / 60 W was researched by Fan *et. al*; surfactants and stabilisers were used in the plating solution (Fan, Ma & Cao, 2011). Findings from this study concluded that Al<sub>2</sub>O<sub>3</sub> particles do not agglomerate in the Ni-P alloy matrix, and that the corrosion resistance (spot test) and hardness of Ni-P-Al<sub>2</sub>O<sub>3</sub> coating are greatest at plating temperature of 333.15 K (3000 seconds at pH 7). Other authors have deposited composite coatings using different reinforcing phases and there seems to be no fixed pH range across the different studies (**Table 5.5**). In a later study, Fan *et. al.* prepared low phosphorus (2.1 wt%) Ni-P-Al<sub>2</sub>O<sub>3</sub> coating on a magnesium alloy from an electroless Ni solution by ultrasonic agitation and measured the rate of plating for different pH (5 – 11) values (Fan, Qiu & Ma, 2014). Their findings show that a Ni-P-Al<sub>2</sub>O<sub>3</sub> coating prepared from a pH 7 solution has the fastest deposition rate, lowest roughness and the thickest coating.

Wang *et. al.* described a method of co-depositing SiC particles (0.5 - 0.7 µm size) in Ni-P with a gradient of SiC through the coating thickness (35 µm). A pre-made electroless Ni plating solution containing SiC (4 g/L) was added dropwise to the main electroless plating solution, at 353.15 K (pH 5.4) over 5400 seconds while applying ultrasound (Wang *et al.*, 2013). SiC concentration added to the electroless plating solution affects SiC and P content in content in Ni-P-SiC deposit (**Figure 5.17a**), and rate of deposition increases with temperature (**Figure 5.17b**). Lowering of P (wt %) in the deposit with increasing SiC (g/dm<sup>3</sup>) in the plating solution was explained by reduction in available H<sup>+</sup> ions, which adsorb to SiC particles instead of reducing H<sub>2</sub>PO<sub>2</sub><sup>-</sup> ions to form P. Adhesion test results indicated the coating does not blister or crack after aging the coating at 493.15 K (3600 seconds) and quenching in water (ambient temperature).



Other tests comparing Ni-P to Ni-P-SiC gradient coating, *i.e.* corrosion in 3.5 wt% NaCl by polarization curves and microhardness, also show an improvement.

[insert: Fig 17a MMC coat Wang 2013]

[insert: Fig 17b MMC coat Wang 2013]

**Figure 5.17:** (a) Plot showing effect of increasing SiC concentration in electroless plating solution on SiC and P content in the coating; (b) plot of deposition rate ( $\mu\text{m/h}$ ) vs. temperature showing experimental values from weight gain data and values calculated from a kinetic model (Wang *et al.*, 2013).

The preferred orientation of the Ni-P grain growth and an increased compactness of the deposit can be achieved using a combined electromagnetic-ultrasonic field (Zhou *et al.*, 2016). SiC particles (20 nm size) were added to an electroless Ni electrolyte to prepare a Ni-P-SiC deposit by ultrasound, and the optimum deposit was formed using 20 kHz / 300 W (magnetic field strength of 0.7 T). The coating was comprised of 200 nm Ni-P/SiC particles distributed evenly. Coatings prepared with a magnetic field and ultrasound had lower nano-indentation hardness (than just ultrasound).

#### 5.4.2 Adhesion of Co-Deposited Particles to the Ni Matrix

Very large diameter (150  $\mu\text{m}$ ) particles of cubic boron nitride (cBN) were co-deposited in Ni-P coating to form an abrasive grinding wheel (Okumiya *et al.*, 2003). The optimal frequency and amplitude for deposition of this composite were found to be 15.5 kHz and 11  $\mu\text{m}$  respectively. The transport of Ni ions to the cBN grains was improved by ultrasonication which resulted in a stronger Ni-cBN bond. In the follow up study, adhesion of the cBN to the Ni-P matrix in the abrasive wheel was characterised (Okumiya *et al.*, 2005) by measuring the Vickers indent load (N) required to push particles out of the Ni matrix. Their results showed that when Ni-P-cBN was deposited with 11  $\mu\text{m}$  ultrasonic amplitude, there is a 20 % increase in the load required for particles to drop out of the matrix compared to a deposit from a silent bath.

Yu and coworkers prepared Ni-P-graphene oxide (GO) coatings; GO flakes had a very high aspect ratio of length to thickness and deposited like a thin film (Yu *et al.*, 2018). A composite coating of Ni-P-GO also had very high surface roughness (2.84  $\mu\text{m}$ ) compared to a standard Ni-P deposit (0.26  $\mu\text{m}$ ) because GO flakes acted as barriers preventing even growth of Ni grains. The rate of deposition with ultrasound was faster and the coating was more compact; without ultrasound the coating had pores on the surface.

A monolayer of graphene has a Young's modulus of 1.0 TPa and a breaking strength of 42 N/m (Huang *et al.*, 2012). One of the benefits of using GO in a composite is that the material becomes tougher. The Young's modulus of as plated Ni-P derived from load-displacement curves (164.0 GPa) by Yu *et al.* is not significantly lower than Ni-P-GO MMC (167.1 GPa). Annealing at 673.15 K improved the mechanical properties of both types of coatings, but there was no significant change as seen in polymer-GO composites described by Huang *et al.* The maximum achievable strength of a composite can be realized when GO flakes are covalently bonded to the surrounding matrix (Huang *et al.*, 2012). Therefore, when Yu *et al.* increased the compactness of the Ni-P-GO deposit by ultrasound (40 kHz / W not stated), the strength of the bond between the Ni-P matrix and GO flakes was not considerably improved.

#### **5.4.3 Corrosion of Ni Composite Coatings**

Song *et al.* focused on enhancing corrosion resistance of Ni-P by ZrO<sub>2</sub> composite coatings. A Ni-P-ZrO<sub>2</sub> composite plating on an AZ91D Mg alloy deposited by ultrasound, withstood 720 kiloseconds in 3.5 wt% NaCl (aq) spray. This is two times the duration of a Ni-P plating (360 kiloseconds) from a silent electrolyte. However, they also demonstrated that the corrosion resistance is increased to 3600 kiloseconds by coating the ultrasonically deposited Ni-P-ZrO<sub>2</sub> with an interlayer of electroplated pure Ni (20  $\mu\text{m}$ ) followed by Ni-P (5  $\mu\text{m}$ ). In the multilayer coating

of NiPZrO<sub>2</sub>-Ni-NiP, only the Ni-P-ZrO<sub>2</sub> layer on the electrode was deposited by ultrasound, (40 kHz at 60 % amplitude / W not stated). The multilayer coating corroded more slowly because the Ni-P (the sacrificial layer) was the net anode, and the pure Ni interlayer acted as a net cathode because it had a higher  $E_{\text{corr}}$  (-0.3 V) than Ni-P (-0.4 V). The ultrasonically deposited compact composite layer (Ni-P-ZrO<sub>2</sub>) under areas where the corrosive NaCl eventually pitted the Ni interlayer further delayed the corrosion of the Mg substrate (Song *et al.*, 2008).

Sharifalhoseini and Entezari deposited a compact Ni-P coating by ultrasound, and a second layer of just ZnO was deposited by ultrasound to provide corrosion protection on the Ni-P surface. They found that ZnO particle coated Ni-P surface has a lower corrosion rate compared to a bare Ni-P coating also deposited by ultrasound (Sharifalhoseini & Entezari, 2015). Their method can be improved by reducing/controlling the size of the particles as the ZnO particles they deposited were not capped with functionalizing agents.

A multi-layer coating of Ni-P and 20 nm sized diamond nanoparticles (DNP) was deposited in the following order (Mazaheri & Allahkaram, 2012): (1) two layers of Ni-P on substrate, (2) Ni-P-DNP MMC inner layer, (3) Ni-P interlayer, (4) final Ni-P-DNP MMC outer layer. Only the Ni-P-DNP layers were deposited by ultrasound (kHz / W not stated) whereas the Ni-P layers were deposited from a silent solution. Multi-layer coatings were prepared from three DNP concentrations (0.5 g/dm<sup>3</sup>, 1 g/dm<sup>3</sup>, and 4 g/dm<sup>3</sup>), and the optimum was 1 g/dm<sup>3</sup>. Mazaheri and co-worker concluded that the Ni-P-DNP coating had a higher corrosion resistance and hardness than a binary Ni-P deposit. The corrosion resistance improved because DNP in Ni-P deposit acted as pore fillers, reducing the density of pores on the coating surface.

Ashassi-Sorkhabi and Es'haghi optimized corrosion resistance of Ni-P-diamond nanoparticle (DNP) MMC (**Figure 5.15**) by adjusting the 4 nm sized DNP concentration in

ultrasonically assisted electroless Ni solution. Their data shows that the optimum level of DNP in the Ni-P electroless electrolyte is  $100 \text{ mg/dm}^3$ , but how much of this concentration is co-deposited with Ni-P has not been stated. They also compared binary Ni-P deposited using the same ultrasonic conditions as Ni-P-DNP MMC (35 kHz / 450 W at 358.15 K, pH 9), and both types were amorphous. All coatings prepared with DNP had  $i_{\text{corr}}$  values from Tafel analysis of polarization curves that were lower than binary Ni-P (Ashassi-Sorkhabi & Es'haghi, 2013).

Niksefat *et. al.* rotated (300 rpm) the mild steel substrate in an electroless plating solution for Ni-B-TiO<sub>2</sub> composite coating while applying ultrasound, 40 kHz / 150 W. The Ni-B-TiO<sub>2</sub> coating was compared to binary Ni-B deposited from a silent solution with agitation by rotation (300 rpm) of substrate only, and no comparison was done with ultrasonically deposited Ni-B. Binary Ni-B has a cauliflower type surface morphology, and the nodules on the cauliflower type structures were finer in Ni-B-TiO<sub>2</sub>. The structure of as plated Ni-B-TiO<sub>2</sub> was crystalline, because the nanocrystalline size calculated from XRD patterns was 55 nm. Hardness of as plated Ni-B-TiO<sub>2</sub> (1263 Hv) was higher than binary Ni-B (890 Hv), and the friction coefficients of the two coatings increased from 0.41 (Ni-B) to 0.43 (Ni-B-TiO<sub>2</sub>). Corrosion current density, from polarization curves, of binary Ni-B ( $I_{\text{corr}} = 1.2 \text{ } \mu\text{A/cm}^2$ ) was improved in ultrasonically deposited Ni-B-TiO<sub>2</sub> ( $I_{\text{corr}} = 0.2 \text{ } \mu\text{A/cm}^2$ ) suggesting an increase in corrosion resistance (Niksefat & Ghorbani, 2015).

**Table 5.5:** Examples of Ni composite coatings deposited using ultrasonic electroless solution.

Coating Surface (Citation)	#	Sonication parameters	RESPONSE					Particles through thickness	PLATING PARAMETERS			Particle g/dm <sup>3</sup> (Size)	pH (temp, K)	Time (sec)
			Thick (µm)	Hard (Hv)	P % (B %)	i <sub>corr</sub> (µA/cm <sup>2</sup> )	E <sub>corr</sub> (V)		Reduce agent (M) / Ni <sup>2+</sup> (M)	Chelate agent (M)	Other			
<b>Ni-P-SiC</b>	1	Silent	29.2	640	Not stated	Not stated	Not stated	Uniform	0.24 / 0.095	Sodium pyrophosphate decahydrate (0.11)	Not stated	5 (20 nm)	10 (298.15)	3600 - 5400
<b>Ni-P-SiC Steel</b> (Zhou <i>et al.</i> , 2016)	2	40 Hz / 100 W + Magnetic 7.5 T/m	29.6	680	Not stated	Not stated	Not stated	Uniform	0.19 / 0.095	Sodium citrate dehydrate (0.034) + Glycine (0.33)	SDS (10 ppm)	0.1 (4 nm)	9 (358.15)	3600
<b>Ni-P</b>	3	Silent	~ 15	Not stated	Not stated	3.55	-0.655	Uniform	0.22 / 0.036	Sodium citrate (0.046)	KF (0.14 mol/dm <sup>3</sup> )	5 (20 nm)	6 (353.15)	1800 - 3600
<b>Ni-P-diamond Steel</b> (Ashassi-Sorkhabi & Es'haghi, 2013)	4	35 kHz / < 450 W	~ 15	Not stated	Not stated	0.85	-0.380	Uniform	0.23 / 0.10	Lactic acid (0.28)	None	0.04 (5 µm)	4.7 (348.15)	7200
<b>Ni-P</b>	5	Silent	15	Not stated	Not stated	1.412	-0.404	Uniform	0.19 / 0.076	Citric acid (0.013) Glycine (0.016) Alanine (0.011)	40% HF (12 mL/L) MBT (0.25 ppm) SDS (150 ppm) Thiourea (1 ppm)	4 (0.5 – 0.7 µm)	5.4 (353.15)	5400
<b>Ni-P-ZrO<sub>2</sub> AZ91D Mg alloy</b> (Song <i>et al.</i> , 2008)	6	40 kHz (60% amplitude)	15	Not stated	Not stated	0.9674	-0.361	Gradient	0.026 / 0.13	Ethylendiamine (1.5)	CH <sub>3</sub> COOTI (18 ppm)	2 (0.2 – 0.3 µm)	14 (358.15)	3600
<b>Ni-P</b>	7	Silent	14.3	Not stated	Not stated	Not stated	Not stated	Uniform	0.026 / 0.13	Ethylendiamine (1.5)	CH <sub>3</sub> COOTI (18 ppm)	2 (0.2 – 0.3 µm)	14 (358.15)	3600
<b>Ni-P-GO Stainless steel</b> (Yu <i>et al.</i> , 2018)	8	40 kHz <sup>x</sup>	29.9	772.7	Not stated	Not stated	Not stated	Uniform	0.026 / 0.13	Ethylendiamine (1.5)	CH <sub>3</sub> COOTI (18 ppm)	2 (0.2 – 0.3 µm)	14 (358.15)	3600
<b>Ni-P</b>	9	40 kHz <sup>x</sup>	29.9	746.8	Not stated	Not stated	Not stated	Uniform	0.026 / 0.13	Ethylendiamine (1.5)	CH <sub>3</sub> COOTI (18 ppm)	2 (0.2 – 0.3 µm)	14 (358.15)	3600
<b>Ni-P</b>	10	kHz Not stated	35	560	8.75	1.75	-0.383	Gradient	0.026 / 0.13	Ethylendiamine (1.5)	CH <sub>3</sub> COOTI (18 ppm)	2 (0.2 – 0.3 µm)	14 (358.15)	3600
<b>Ni-P-SiC AZ91D Mg</b> (Wang <i>et al.</i> , 2013)	11	kHz Not stated	35	620	7.25	1.36	-0.382	Gradient	0.026 / 0.13	Ethylendiamine (1.5)	CH <sub>3</sub> COOTI (18 ppm)	2 (0.2 – 0.3 µm)	14 (358.15)	3600
<b>Ni-B</b>	12	Silent	30	890	(6.6)	1.2	-0.64	Uniform	0.026 / 0.13	Ethylendiamine (1.5)	CH <sub>3</sub> COOTI (18 ppm)	2 (0.2 – 0.3 µm)	14 (358.15)	3600
<b>Ni-B-TiO<sub>2</sub> Mild steel</b> (Niksefat & Ghorbani, 2015)	13	40 kHz / 150 W + rotation (300 rpm)	15	1263	(6.1)	0.2	-0.59	Uniform	0.026 / 0.13	Ethylendiamine (1.5)	CH <sub>3</sub> COOTI (18 ppm)	2 (0.2 – 0.3 µm)	14 (358.15)	3600

\* = 60 wt % suspension. GO = graphene oxide flakes. <sup>x</sup> = Intermittent repeats = 60 second sonication and 600 second silent. SDS = Sodium dodecyl sulphate. MBT = 2-Mercaptobenzothiazole. M = mol/dm<sup>3</sup>.

### 5.5 Electroless Ni Deposition onto Micro and Nanoparticles in the Presence of Ultrasound

Sonication can be employed to disperse micron and nanometre sized particles in an electroless Ni electrolyte enabling them to be coated to form core-shell particles. Electroless Ni plating of particles is done using a similar bath composition to plating used for standard substrates except the temperature of plating solution has been varied between ambient and 323.15 K, and this is lower than the temperatures used for plating engineering components (see **Table 5.2**). Consequently, the thickness of the deposit on micro or nano-structures is much thinner ( $< 1 \mu\text{m}$ ).

An example of the benefits of coating particles in Ni is the study by Wu *et al.* where  $\text{CaF}_2$  ( $5 \mu\text{m}$ ) solid lubricant powders at 318.15 – 323.15 K (900 – 1200 sec) were coated in a Ni-P electroless solution (pH 9.5 – 10.0) agitated using ultrasound (40 kHz / 150 W). The Ni- $\text{CaF}_2$  particles (10 vol%) were hot pressed with alumina and carbide particles to form a self-lubricating high wear cutting tool (Wu *et al.*, 2016). A comparison of cutting tools containing bare  $\text{CaF}_2$  or Ni- $\text{CaF}_2$  particles shows that the cutting tool containing Ni- $\text{CaF}_2$  had higher: flexural strength, Vickers hardness, fracture toughness, and friction coefficient at cutting speeds (80 m/min and 170 m/min).

Luo *et al.* investigated the effect of  $\text{Cr}_3\text{C}_2$  particle (150-200  $\mu\text{m}$ ) concentration, in an electroless Ni-P plating electrolyte, on the morphology of the deposited Ni coating by ultrasound (CCW-50W generator). Particles were ultrasonically roughened, and Ni-P (7.32 wt%) was deposited by ultrasonication at room temperature followed by drying in vacuum (453.15 K – 473.15 K). The optimal weight of  $\text{Cr}_3\text{C}_2$  was 40 g/L based on uniformity and compactness of the Ni-P deposit, and concentrations higher than 40 g/L in the Ni-P plating solution yielded incomplete and uneven coatings. A plot of the plating rate vs.  $\text{Cr}_3\text{C}_2$  powder concentration demonstrated a trend where Ni-P rate of deposition (g/minute) increased linearly with  $\text{Cr}_3\text{C}_2$  powder ( $\text{g}/\text{dm}^3$ ) concentration in

the electroless plating solution, thereby reducing reaction time (Luo *et al.*, 2010).

Xu *et al.* compared electroless Ni-P coated graphite microparticles by ultrasound (25 KHz / 250 W) and mechanical stirring (200 rpm) from an alkaline solution (pH 12) at 313.15 K. Their results show a significant improvement in uniformity, surface roughness and compactness of deposit when ultrasound is applied. The main difference was that the Ni-P coating prepared by mechanical stirring had spherical grains on the surface with areas of exposed graphite (**Figure 5.18a**); Ni deposited by ultrasound was an amorphous thin continuous film (**Figure 5.18b**). Samples of the powders were weighed at different plating stages to obtain a sigmoidal curve of weight gain vs. time; from this curve Xu *et al.* deduced four stages of the plating process: (1) incubation, (2) initial deposition, (3) uniform deposition, and (4) retarded deposition. In the incubation stage nuclei of Ni seeds are deposited at the graphite surface, in the mechanically stirred Ni deposition method graphite has less seeding of Ni nuclei on the graphite surface than ultrasonically deposited Ni. Therefore, in the mechanically stirred Ni deposition method, when Ni seeds grow over time the grains do not merge leaving gaps in the coating (Xu *et al.*, 2014). Other research articles have also described an incubation period before Ni plating proceeds, a similar mechanism of Ni film growth.

[insert: Fig 18a Ni on particles Xu 2014]

[insert: Fig 18b Ni on particles Xu 2014]

**Figure 5.18:** SEM images of Ni-P coated graphite prepared at 313.15 K (pH 12) under (a) mechanical agitation (200 rpm for 900 seconds), (b) ultrasonic agitation (25 KHz / 250 W for 1200 seconds) (Xu *et al.*, 2014).

The mechanism by which Ni is deposited also depends on particle roughness and/or sub-micrometre defects on the surface. Luo *et al.* deposited Ni-P (4.59 wt %) at ambient temperature (pH 10 - 11) on WC particles (2-5  $\mu\text{m}$ ) that have a step like surface morphology on some areas of

the particle. In the early stages of plating Ni particles seed preferentially on the step like features (**Figure 5.19a**), and a continuous Ni-P film (**Figure 5.19b**) is eventually formed by further depositions on Ni seed particles (Luo *et al.*, 2011).

[insert: Fig 19a Ni on particles Luo 2011]

[insert: Fig 19b Ni on particles Luo 2011]

**Figure 5.19:** SEM image of (a) Ni particles deposited preferentially on step like features, and (b) Ni-P coated WC powder with ultrasound (frequency/power not stated) at room temperature (pH 10-11) (Luo *et al.*, 2011).

Zheng *et. al* coated Ni-P on nano-Al<sub>2</sub>O<sub>3</sub> particles (60 nm sized) that were ultrasonically coarsened in HF, and activated by SnCl<sub>2</sub>/PdCl<sub>2</sub> catalyst solution. The electroless Ni plating solution (pH 9) was agitated using intermittent mechanical stirring and ultrasonication (KQ-600DE generator) at 318.15 K. The particles were characterised by TEM and HRTEM. The nano-Al<sub>2</sub>O<sub>3</sub> particles that were Ni-P coated without ultrasound were agglomerated and the coating thickness varied (3 – 12 nm); some nano-Al<sub>2</sub>O<sub>3</sub> particles had Ni nanoparticles on the Ni-P layer. Ni-P film deposited on nano-Al<sub>2</sub>O<sub>3</sub> particles under ultrasonic irradiation and stirring was amorphous, and had a uniform thickness of 5 nm (Zheng, Mo & Liu, 2012).

Gui *et. al.* prepared Ni-P plating on soft Nylon 12 (50-70 µm size) polymer particles. Nylon 12 was functionalised with amine (NH<sub>2</sub>) groups and activated by deposition of SnCl<sub>2</sub>/PdCl<sub>2</sub>. The Ni-P was deposited by applying ultrasound (40 kHz / 120 W) continuously at 333 K (1800 sec) and pH 9. Particles or shells of Ni-P formed on the surface rather than a continuous film when depositing Ni-P from an mechanically stirred or ultrasonic bath. Analysis of XPS results demonstrated that Pd adsorption to Nylon 12 was not hindered unlike the deposition of Ni<sup>0</sup>. The loading of Pd catalyst on Nylon 12 was sufficient to enable Ni-P deposition on the surface. But the method of plating was unsuccessful with/without ultrasound, and there was no explanation on



how Ni-P adhesion to Nylon 12 was weakened (Gui *et al.*, 2018).

Jiang *et al.* synthesised hollow Ni microspheres (170 nm or 3  $\mu\text{m}$ ) by deposition of Ni on polystyrene (PS) beads with low frequency ultrasonic agitation (40 Hz / 100 W) followed by removal of the polystyrene template. The PS beads were activated using a  $\text{SnCl}_2/\text{PdCl}_2$  catalyst and the ultrasonic agitation was applied intermittently to the electroless plating solution (pH 8.5) for 10 seconds every 30 seconds at 313.15 K. PS particles Ni-P coated by stirring only were agglomerated and particles of Ni-P deposited on the Ni-P coating. Ni on the PS beads coated by ultrasound consisted of a compact layer of Ni nanoparticles (**Figure 5.20**), and the XRD phase of as plated Ni-P on PS was amorphous (Jiang *et al.*, 2007).

[insert: Fig 20 Ni on particles Jiang 2007]

**Figure 5.20:** SEM image of an as plated polystyrene bead in electroless Ni-P solution agitated by ultrasound (40 Hz / 100 W) (Jiang *et al.*, 2007).

## 5.6 The Use of Ultrasound to Improve Coverage of Electroless Ni Deposits on Complex Structures

Electroless deposition is advantageous when plating complex structures because generally a more uniform thickness can be achieved when compared to using an electrolytic approach. However, ultrasound can be used to enhance this uniformity still further, and assist when coating complex shapes.

Ni-P coating (Saito *et al.*, 2006) has been deposited on needle shaped AFM/STM probes using 1 MHz frequency and power densities of 0, 1.6, and 2.2  $\text{Wcm}^{-2}$  (**Figure 5.21**). It was established that 1.6  $\text{W/cm}^2$  enables fabrication of a probe with a tip radius curvature of 25 nm (**Figure 5.21c**), and this radius size could not be achieved without ultrasonication. Starting from the base of the tip the radial thickness of the Ni coating on the probe decreased gradually towards the tip. **Figure**

**5.21d** shows that Ni deposited at 1 MHz frequency and  $1.6 \text{ Wcm}^{-2}$  power density (B1) has a profile closest to the bare probe (labelled A1) at the tip.

[insert: Fig 21a - c complex structure Saito 2006]

[insert: Fig 21d complex structure Saito 2006]

**Figure 5.21:** SEM of (a) Fabricated probe labelled as A1, and its (b) conical taper (dashed line A0 is the profile of a Ni coating deposited from a silent solution). (c) Magnified tip plated in electroless Ni solution at 1 MHz and  $1.6 \text{ Wcm}^{-2}$ . (d) Plot of radial thickness vs. fibre diameter, electroless Ni plating solution with a temperature of 333.15 K (900 seconds) was agitated by ultrasound using power densities of 0, 1.6, and  $2.2 \text{ W/cm}^2$  (B0–B2 respectively). (Saito *et al.*, 2006).

Membrane structures for purifying gases can be difficult to coat because of the surface tension of the plating solution that, for this reason, cannot penetrate pores or flow out easily, and this slows the rate of deposition. Bulasara *et. al.* conducted a detailed study of how rate of deposition of electroless Ni is affected by ultrasonic deposition in a ceramic membrane (Bulasara, Uppaluri & Purkait, 2013). Four different (1:2) molar ratios of  $\text{Ni}^{2+}$  and  $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$  were deposited on ceramic membranes (pore size 275 nm), at 243.15 K (3600 seconds) by ultrasound (37 kHz) or stirring (100 – 200 rpm). From this study an optimal electroless  $\text{Ni}^{2+}$  solution concentration and loading ratio were derived: 0.08 M  $\text{Ni}^{2+}$  and  $393 \text{ cm}^2/\text{L}$ , which increased plating efficiency. Bulasara *et. al.* concluded that sonication instead of stirring improves transport through membrane pores enabling improved: plating efficiency, deposition rate, film thickness, and pore densification.

Chiba *et. al.* ultrasonically deposited Ni-B ( $\sim 65 \mu\text{m}$ ) on a phosphor bronze net (440 mesh) substrate from an acid solution (Chiba *et al.*, 2003). It was found that the coating was harder than when deposited from a silent solution, but a higher density of micro-cracks were present (**Figure 5.22**). Plating deposited from a silent solution had  $I_{\text{corr}} = 5.2 \times 10^{-6}$  and  $E_{\text{corr}} = -0.502 \text{ V}$ ; whereas ultrasonic plating had reduced corrosion resistance ( $I_{\text{corr}} = 8.6 \times 10^{-6}$  and  $E_{\text{corr}} = -0.647 \text{ V}$ ). Consequently the corrosion rate was accelerated in the ultrasonic deposit because the cracks

allowed penetration of 3 % NaCl (aq). This was borne out by the Tafel analysis where Ni-B deposited from a silent solution had  $I_{\text{corr}} = 5.2 \times 10^{-6}$  and  $E_{\text{corr}} = -0.502$  V; whereas the ultrasonic plating had reduced corrosion resistance ( $I_{\text{corr}} = 8.6 \times 10^{-6}$  and  $E_{\text{corr}} = -0.647$  V).

[insert: Fig 22 complex structure Chiba 2003]

**Figure 5.22:** SEM image showing microcracks in Ni-B coating deposited from:  $\text{Ni}^{2+}$  ion:  $0.020 \text{ mol/dm}^3$ ; reducing agent:  $0.034 \text{ mol/dm}^3$ ; pH= 4; deposition time: 1800 seconds, solution temperature: 341.15 K (45 kHz/100 W). (Chiba *et al.*, 2003).

Lu *et al.* coated bamboo fabric (BF) fibres with Ni-B to make the fabric conductive. The electroless plating process was catalysed by reducing  $\text{Ag}^+$ ,  $\text{Cu}^{2+}$  or  $\text{Ni}^{2+}$  onto 3-aminopropyltrimethoxysilane functionalised BF. Electroless Ni-B deposition on BF was accomplished at room temperature (3600 seconds, pH 7) with ultrasound, and all Ni deposits had excellent interfacial adhesion. Of the three catalysts,  $\text{Ag}^+$  resulted in the smoothest Ni deposit on BF that was not cracked (**Figure 5.23**); but the rate of deposition was slowest. XRD patterns of the Ni coated fabric show three crystalline peaks of face centred cubic Ni (Lu, Liang & Xue, 2012).

[insert: Fig 23 complex structure Lu 2012]

**Figure 5.23:** SEM image of Ni plated bamboo fabric (BF) fibre coated from ultrasonic electroless Ni solution using Ag catalyst instead of  $\text{PdCl}_2/\text{SnCl}_2$  (Lu *et al.*, 2012).

Afshari and Montazer deposited pure Ni nanoparticle clusters with hedgehog type morphology on polyester from a Ni sulfate and hydrazine electroless solution by ultrasound (50 kHz / 50 W) at 348.15 K (7200 seconds). A central composite design method was employed to identify the optimum electroless Ni solution concentrations of hydrazine hydrate : sodium hydroxide : nickel sulfate based on the weight gain of the fabric and the fastest response to a powerful magnet. XRD of the fabrics shows that the Ni nanostructures are crystalline and SEM shows the average size of nanoparticles in the hedgehog cluster was 40 nm ([insert: Fig 24a complex structures Afshari

2018]

[insert: Fig 24b complex structures Afshari 2018]

[insert: Fig 24c complex structures Afshari 2018]

**Figure 5.24c).** The Ni-hedgehog polyester fabric samples were washed in nonionic detergent at 323.15 K for 2700 seconds with stirring (3000 rpm) and the change in weight and magnetic properties of the Ni-hedgehog fabric was not significant (Afshari & Montazer, 2018).

[insert: Fig 24a complex structures Afshari 2018]

[insert: Fig 24b complex structures Afshari 2018]

[insert: Fig 24c complex structures Afshari 2018]

**Figure 5.24:** SEM images of Ni-hedgehog nanoparticles on fibers of polyester (polyethylene terephthalate) fabric deposited using optimum solution concentration at different magnifications scale bars: (a) 10  $\mu\text{m}$ , (b) 2  $\mu\text{m}$  and (c) 500 nm (Afshari & Montazer, 2018).

## 5.7 Summary of Benefits of Ultrasound Assisted Electroless Ni Deposition

It can be seen from this Chapter that many researchers have studied the effects of ultrasound on electroless Ni deposition. The sheer volume of work does throw up some contradictory results but there are some clear trends. Most research agrees that Ni can be deposited at a higher rate from an electroless bath agitated by ultrasound compared to a silent bath, because:

- Ultrasound reduces the diffusion boundary layer of ions on the electrode surface, and increases mass transport of ionic species to the electrode *via* acoustic streaming.
- After cavities collapse microjetting occurs at speeds  $> 100$  m/s, and this enhances mass transport of active species to the electrode surface.
- Heat released from cavity implosion helps to destabilise ligands on  $\text{Ni}^{2+}$  complex to free  $\text{Ni}^{2+}$  that are reduced on the electrode.

There is no set optimised method of ultrasonic deposition of Ni coatings from electroless solutions.

Nevertheless, there is some agreement across all the studies that, apart from increased deposition rate, the effects of using ultrasound in electroless Ni deposition of a binary alloy are:

- Increase in thickness and compactness of deposit.
- Reduction of pores and voids in the deposit.
- Decreased P content in Ni-P coatings at higher plating temperatures,
- Decrease in hardness of Ni-P coatings with increase in P (%) content.
- Changes in phases *e.g.* amorphous to crystalline.
- Enhanced corrosion resistance and hardness.

The corrosion resistance and hardness of coatings has been shown to further increase by depositing Ni coatings alloyed with other metals, *e.g.* Cu, Ce, Co, as well as P or B.

Areas where very less research has been done in this field include: adhesion of coating, understanding wear mechanisms, and mechanisms of Ni growth.

In recent years, more articles have been published on Ni metal matrix composite (MMC) coatings. The benefit of applying ultrasound is that it enables excellent dispersion of particles, resulting in higher co-deposition of reinforcing micro- or nanoparticles in a Ni MMC coating. Adhesion of the reinforcing phase to the Ni matrix, and corrosion resistance of the coating have been shown to improve when using ultrasound. In addition, ultrasonic dispersion generally leads to a more uniform distribution of particles throughout the coating thickness. Sonication is also useful in the formation of core-shell particles enabling particles to be efficiently dispersed in an electroless Ni electrolyte so that they can be uniformly coated. In addition, ultrasound can enable more uniform plating distribution on complex structures.

The use of ultrasound in electroless Ni deposition clearly has many benefits and has been, and still is an active area of research. However, the vast majority of this work has been small-scale

laboratory studies. The question of whether these benefits of using ultrasound can be scaled-up to an industrial scale is still open.

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