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ULTRASOUND-ASSISTED ELECTRODEPOSITION OF COMPOSITE COATINGS WITH PARTICLES

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ABSTRACT: The electrodeposition of multifunctional composite coatings has rapidly emerged in the last decade due to the enhanced mechanical properties and corrosion resistance that such composite coatings exhibit compared to electroplated single metal and alloy deposits. Many studies have indicated that the implementation of ultrasound in composite electroplating processes can bring about many benefits, not only as a tool to improve the dispersion and de-agglomeration of particles in the electroplating bath, but also to enhance the incorporation of finely dispersed and uniformly distributed particles into the metal matrix. The present paper summarizes the fundamentals of the use of ultrasound and acoustic cavitation and how it may influence the electrodeposition of composite coatings with particles by commenting on some of the most significant works on this topic presented by the scientific community in the last 10 years. This paper will review these investigations and discuss how the ultrasonic parameters may affect the dispersion of the particles in the electrolyte and its effect on the characteristics of the composite coatings, generally resulting in the enhancement of the mechanical properties and corrosion resistance of the composite coatings. In addition, this paper will review some of the issues that may arise when using ultrasound in such processes and the pros and cons of the different transducer systems available, highlighting the need for detailed information regarding the ultrasonic parameters and equipment used when utilizing sonication.

KEYWORDS: Composite coatings, Electrodeposition, Electroplating, Ultrasound, Particles

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1. INTRODUCTION

Since Fink and Prince first studied the co-deposition of Cu and graphite [1], the electroplating of metal-based composites with inert particles has received a wide attention from the scientific community. Particles, when properly dispersed into an electroplated coating, may substantially improve certain operational properties of the coating such as hardness, wear or the resistance to corrosion, whilst imparting on them new properties (magnetic, catalytic, etc.) [2]. The importance of the development of such multifunctional electrodeposited composite coatings in the last decade can be seen in the fact that there have been several publications on the topic in recent years. Among them is a paper by Low et al. [3] focused on the different operational parameters utilized during the electrodeposition process and the use of different approaches to increase the particle content in the coating: i) high particle concentration in the plating bath, ii) use of particles with small size, iii) low concentration of electroactive species, iv) pulsed-plating techniques and v) employment of ultrasound. The first three approaches just mentioned may seem unsuitable for most of the electroplating industry due to different issues: i) high density, high viscosity and dispersion instability are expected at high particle concentrations, ii) increase in cost related to particles used, health and safety and effluent treatment is expected when using very small particles, and iii) problems related to poor mass transport and hydrogen evolution are predicted when electroplating from electrolytes with lower conductivity. However, the latter two present an enormous potential for industrial purposes. In this sense, pulsed-plating techniques are gaining more attention and there are many recent review papers available for such techniques [4,5] including its use for composite plating. However, no review papers on the use of ultrasound on the electrodeposition of composite coatings are available. This review paper aims to introduce the use of ultrasound in the electrodeposition of composite coatings and how this technology not only enhances the dispersion of particles in the plating bath, but also how it can improve the incorporation of particles into electrodeposited metal coatings and the effect on the coating's properties.

2. USE OF ULTRASOUND IN ELECTROPLATING

When ultrasound is applied to a liquid media the phenomenon of acoustic cavitation [6] occurs. As with any mechanical wave, ultrasound is propagated through a liquid by a series of compression (positive pressure) and rarefaction (negative pressure) cycles induced in the molecules of the medium through which it passes. When the power is high enough, a cavity or 'bubble' may form in the liquid during the cycles of negative pressure as the 'expanding' forces during the rarefaction cycle exceed the 'attraction' forces of the molecules of the liquid. When the bubble grows to a critical size, it becomes unstable and violently collapses, as shown in Figure 1 [7]. At this point, known as a 'hot spot', high temperatures and pressures (around 5000 K and 1000 atm, respectively) can be achieved (depending on the frequency and power applied), involving heating and cooling rates of an order of magnitude above 10^{10} K/s and the formation of liquid jet streams of around 400 km/h [8]. The mechanical and chemical events which result as a consequence of the existence of these cavitating bubbles (Figure 2 [9]) are the basis for the application of ultrasound in several areas of Chemistry [10] in general and Electrochemistry [11] in particular.

Diverse cavitation phenomena such as acoustic streaming and micro-jetting [12], shock waves [13], mass-transfer enhancement from/to the electrode [14] and surface cleaning [15] can be observed as a consequence of establishing an ultrasonic field in a liquid electrolyte, substantially improving many different electrochemical processes [16]. In this sense, the use of ultrasound in the electrodeposition of metals may present many benefits [17], not only in terms of the electrodeposition process itself (mass transfer enhancement in diffusion-controlled electroplating [18]. charge-transfer improvement [19], higher cathode current efficiency [20]), but also in terms of the final characteristics of the deposits such as the grain size [21]. This beneficial effect of ultrasound on refining the grain size was considered by Walker and Walker as the controlling factor in increasing the hardness and decreasing the porosity of electroplated coatings [22]. Regarding this, the increase in hardness of different ultrasonically-assisted

electrodeposited metals such as Cr [23-24], Cu [25-27] and Fe [10] has been extensively reported over the years. Other mechanical properties can also be improved by using ultrasound during the electrodeposition, Ni coatings being the best example, as sonication during electrodeposition increased the hardness [28], decreased the residual stress [29], and enhanced the wear [30] and fatigue strength [31] of the Ni deposits. Other beneficial effects of the use of ultrasound in the electrodeposition of metals are the enhancement of corrosion resistance of Zn [32], increase in cathode current efficiency and reduction of crack formation and surface roughness of Ir [33,34] and the reduction of toxic mist in the electrodeposition of Cr [35].

3. USE OF ULTRASOUND ON THE ELECTRODEPOSITION OF COMPOSITE COATINGS WITH PARTICLES

In the last decade, many different research groups have studied how ultrasound may assist the dispersion of particles in electroplating baths and the effect that sonication during the electrodeposition process may have on the characteristics of the resulting composite coatings. Table 1 gives some details on the effect of ultrasound on the dispersion of particles and/or during the electrodeposition stage and the properties of the subsequent composite coatings. Ni and its alloys are the main metal materials used and the most commonly employed electrolyte is the Watts solution. No surfactants were required in many of the works where particles were dispersed with ultrasound in Ni-based electrolytes demonstrating that the use of surfactants is not as critical when particles are dispersed with ultrasound.

1 **Table 1. Composite coatings prepared with ultrasound assistance. Ultrasound was used during dispersion and/or during**
 2 **electrodeposition.**

Metal matrix	Particle	Electrolyte	Ultrasonic parameters	Effect of ultrasound/particles/plating parameters on final properties of coatings	Ref
Ni	Al ₂ O ₃	Sulphamate bath	<ul style="list-style-type: none"> - System: horn - Frequency: 22.5 kHz - Power: 0.005 W/cm³ 	<ul style="list-style-type: none"> - Ultrasonic irradiation of the electrolyte prior to electrodeposition significantly reduced particle agglomeration. - Both ultrasonic and chemical dispersion with a surfactant presented similar results, although particle content was slightly higher for the latter. - Decrease in Ni²⁺ concentration in electrolyte generally led to higher particle de-agglomeration and particle content in composites. 	[36]
Ni	Al ₂ O ₃	Watts bath	<ul style="list-style-type: none"> - System: horn - Frequency: not available (N/A) - Power: N/A 	<ul style="list-style-type: none"> - Ultrasound during deposition improved the incorporation of particles in both continuous and pulse-plating. - No significant difference in corrosion resistance between composites and pure Ni deposits was reported as particle agglomeration was not completely avoided by ultrasound. 	[37]

Metal matrix	Particle	Electrolyte	Ultrasonic parameters	Effect of ultrasound/particles/plating parameters on final properties of coatings	Ref
Ni	Al ₂ O ₃	Watts bath	<ul style="list-style-type: none"> - System: horn - Frequency: 24 kHz - Power: 38 W/cm² 	<ul style="list-style-type: none"> - Ultrasonic irradiation of the electrolyte prior to electrodeposition minimized particle agglomeration, shifting peaks observed in particle size distribution curves towards smaller diameters. - Increasing particle concentration in bath increased particle incorporation into the metal matrix. Composites electrodeposited under ultrasound always presented higher particle content. - For both pure Ni and composite coatings, ultrasound during plating further enhanced grain refinement. - Ultrasound enhanced particle dispersion in coatings. - Higher hardness and wear resistance were observed when increasing particle content in composites. Composites electrodeposited under ultrasound always presented improved hardness and wear resistance. 	[38]

Metal matrix	Particle	Electrolyte	Ultrasonic parameters	Effect of ultrasound/particles/plating parameters on final properties of coatings	Ref
Ni	Al ₂ O ₃ whiskers	Sulphamate bath	N/A	<ul style="list-style-type: none"> - Ultrasound to prevent particle agglomeration prior to deposition. - Particle incorporation with/without ultrasound increased when decreasing pulse-plating frequency. - Composite coatings produced with ultrasound seemed to have lower particle content than those without ultrasound, although the latter presented larger aggregates. 	[39]
Ni	CeO ₂	Watts bath with sodium dodecyl-sulphate (SDS, surfactant)	<ul style="list-style-type: none"> - System: bath? - Frequency: 28 kHz - Power: 300 W 	<ul style="list-style-type: none"> - Incorporation of particles caused a significant increase in hardness and wear rate of coatings. Further improvement in both properties was observed when ultrasound was used during the electrodeposition. - The orientation of Ni crystals in composite coatings was strongly affected by ultrasound. 	[40]

Metal matrix	Particle	Electrolyte	Ultrasonic parameters	Effect of ultrasound/particles/plating parameters on final properties of coatings	Ref
Ni	Nd ₂ O ₃	Hard Nickel bath with SDS	<ul style="list-style-type: none"> - System: bath, horn and dual (combination of bath and horn) - Frequency: 100 kHz (bath), 20 kHz (horn) - Power: 0-300 W (bath), 0-45 W (horn) 	<ul style="list-style-type: none"> - Introduction of ultrasound during plating resulted in finer grain size and higher particle incorporation, especially under dual ultrasonic conditions (combination of bath and horn). - Composite coatings showed higher corrosion resistance than pure Ni deposits. Ultrasound further enhanced corrosion resistance of composite coatings, especially under dual ultrasonic conditions. - Particle content in the coating increased when increasing bath power in both 'bath only' and dual set-ups. Particle content in the coating increased when increasing horn power in both 'horn only' and dual set-ups up to 30 W of horn power, and then it significantly dropped at higher intensity values. 	[41,42]
Ni	TiO ₂	Watts bath with SDS	<ul style="list-style-type: none"> - System: bath - Frequency: 28 kHz - Power: N/A 	<ul style="list-style-type: none"> - Ultrasound reduced the incorporation of agglomerated particles into the coatings. - Particle content in coating increased by increasing particle concentration in electrolyte. Hardness related to particle content in composites. 	[43]

Metal matrix	Particle	Electrolyte	Ultrasonic parameters	Effect of ultrasound/particles/plating parameters on final properties of coatings	Ref
Ni	TiO ₂	Watts bath with SDS	<ul style="list-style-type: none"> - System: bath/horn - Frequency: 35/30 kHz - Power: N/A 	<ul style="list-style-type: none"> - Nano-size particles well dispersed in the coating when ultrasound was used during the electrodeposition. - Application of ultrasound during plating of pure Ni coatings resulted in grain modification and refinement. The incorporation of TiO₂ nano-size particles into the coating resulted in further refinement of the grain size. - Particle size affected final properties of the composite. 	[44,45]
Ni	ZrO ₂	Sulphamate Hard Nickel bath with SDS	<ul style="list-style-type: none"> - System: bath - Frequency: 28 kHz - Power: 120 W 	<ul style="list-style-type: none"> - Ultrasound during electrodeposition with/without agitation enhanced particle incorporation and grain refining of composite coatings. Combination of ultrasound and mechanical agitation yielded the composite coatings with smallest grain size and smoothest surface. - Composite coatings prepared under ultrasound always showed higher corrosion resistance than coatings prepared in silent (conventional agitation) conditions. Combination of ultrasound and mechanical agitation yielded the composite coatings with highest anti-corrosion properties. 	[46]

Metal matrix	Particle	Electrolyte	Ultrasonic parameters	Effect of ultrasound/particles/plating parameters on final properties of coatings	Ref
Ni	SiC	Watts bath with SDS	<ul style="list-style-type: none"> - System: bath/horn - Frequency: 35/30 kHz - Power: N/A 	<ul style="list-style-type: none"> - Ultrasound used during the dispersion and electrodeposition stages to prevent particle agglomeration and incorporation of large agglomerated into the coatings. - Particle content and size affected final properties of the composite. 	[44,45]
Ni	SiC	Watts bath with sodium dodecyl-glycol (surfactant), 1,4-butynediol (brightener) and p-toluene sulphonamide (carrier)	N/A	<ul style="list-style-type: none"> - Ultrasound employed to obtain a better dispersion of particles in the electrolyte. - Composites deposited under ultrasound presented finer grain size than those produced without ultrasound. - Incorporation of particles into Ni deposits changed the orientation of crystals. - Composites exhibited better corrosion resistance than pure Ni deposits. 	[47]

Metal matrix	Particle	Electrolyte	Ultrasonic parameters	Effect of ultrasound/particles/plating parameters on final properties of coatings	Ref
Ni	SiC	Watts bath	<ul style="list-style-type: none"> - System: bath - Frequency: N/A - Power: N/A 	<ul style="list-style-type: none"> - Ultrasound drastically reduced particle agglomeration, especially at lower pH. - Ultrasound did not affect particle content for continuous plating, but significantly increased particle incorporation into pulse-plated coatings. - Composites plated in all conditions presented enhanced hardness compare to pure Ni deposits. Pure Ni and composite coatings deposited under ultrasound had an improved corrosion resistance by reducing the porosity of the deposits. 	[48]
Ni	SiC	Watts bath	<ul style="list-style-type: none"> - System: horn - Frequency: N/A - Power: N/A 	<ul style="list-style-type: none"> - Ultrasound to prevent particle agglomeration prior to deposition. - Ultrasound during deposition improved the incorporation of particles in both continuous and pulse-plating. - Composites exhibited improved corrosion resistance compared to pure Ni deposits. 	[37]

Metal matrix	Particle	Electrolyte	Ultrasonic parameters	Effect of ultrasound/particles/plating parameters on final properties of coatings	Ref
Ni	SiC	Sulphamate bath with SDS and cetyl-trimethyl-ammonium bromide (CTAB, surfactant)	<ul style="list-style-type: none"> - System: bath - Frequency: 38 kHz - Power: 200 W 	<ul style="list-style-type: none"> - Ultrasound improved the incorporation of finely de-agglomerated particles into the coating, resulting in composite coatings with a homogeneous distribution of particles. - Corrosion resistance was improved, especially in those composites produced under ultrasound. - Synergic effect of ultrasound and particles on the mechanical properties of the coatings. 	[49]
Ni	WC	Watts bath with SDS and CTAB	<ul style="list-style-type: none"> - System: N/A - Frequency: 40 kHz - Power: 350 W 	<ul style="list-style-type: none"> - Ultrasound used to disperse particles in baths where no surfactant was used. - Composites exhibited higher hardness, elastic modulus and corrosion resistance. - Incorporation of particles strongly affected surface morphology of deposits. 	[50]

Metal matrix	Particle	Electrolyte	Ultrasonic parameters	Effect of ultrasound/particles/plating parameters on final properties of coatings	Ref
Ni	TiN	Watts bath	<ul style="list-style-type: none"> - System: N/A - Frequency: N/A - Power: 0-300 W 	<ul style="list-style-type: none"> - Composite coatings with dispersed particles were obtained when ultrasound applied during deposition. Slightly less agglomerated particles were noticed at high ultrasonic powers. - Composite coatings electrodeposited with ultrasound exhibited smaller grain size and smoother surface finish, and lower XRD intensities for (111) crystal planes compared with (200) crystal planes. 	[51]

Metal matrix	Particle	Electrolyte	Ultrasonic parameters	Effect of ultrasound/particles/plating parameters on final properties of coatings	Ref
Ni	WS ₂	Watts bath with CTAB	<ul style="list-style-type: none"> - System: horn - Frequency: 24 kHz - Power: 0-40 W/cm² 	<ul style="list-style-type: none"> - Ultrasonic irradiation (20 W/cm²) of the electrolyte was applied 10 minutes prior to electrodeposition to avoid particle agglomeration. - Particle content in the coating increased with ultrasonic power up to 30 W cm⁻², slightly decreased at higher intensity values. - More compact deposits with uniform thickness produced in the presence of ultrasound. - Composite coatings, especially those produced under ultrasound, presented better mechanical properties (i.e. hardness, reduced Young's modulus, elastic strain to failure and elastic recovery). - Composite coatings, especially those produced under ultrasound, presented better tribological performance (i.e. lower coefficient of friction). 	[52]

Metal matrix	Particle	Electrolyte	Ultrasonic parameters	Effect of ultrasound/particles/plating parameters on final properties of coatings	Ref
Ni-Co	Al ₂ O ₃	Sulphamate bath with cobalt sulphamate	<ul style="list-style-type: none"> - System: bath - Frequency: 35 kHz - Power: 240 W 	<ul style="list-style-type: none"> - The presence of ultrasound during deposition increased particle incorporation of finely dispersed particles. - Composites produced with ultrasound exhibited higher particle content, plastic deformation and hardness, and lower elastic modulus. - The plating parameters also affected Co content in composites. 	[53]
Ni-Co	Al ₂ O ₃	Watts bath with cobalt sulphate and surfactant	<ul style="list-style-type: none"> - System: N/A - Frequency: N/A - Power: 0-160 W 	<ul style="list-style-type: none"> - Increasing ultrasonic power led to lower incorporation of particles into the metal matrix, lower Co content in deposits, higher residual macrostress, finer grain size, promotion of (220) crystal planes and attenuation of (200) crystal planes. - Hardness gradually increased with increasing ultrasonic power during electrodeposition up to 90 W and then decreased. 	[54]
Ni-Co	SiC	Watts bath with cobalt sulphate	<ul style="list-style-type: none"> - System: N/A - Frequency: 40 kHz - Power: 350 W 	<ul style="list-style-type: none"> - Ultrasound to prevent particle agglomeration prior to deposition. - Higher particle incorporation by increasing particle concentration in electrolyte and current density. - Incorporation of particles leads to an increase in hardness and improved corrosion resistance (positive shift in corrosion potential and reduction in corrosion). 	[55]

Metal matrix	Particle	Electrolyte	Ultrasonic parameters	Effect of ultrasound/particles/plating parameters on final properties of coatings	Ref
Ni-P	SiC	Sulphamate bath with phosphoric acid	N/A	<ul style="list-style-type: none"> - Ultrasound to effectively disperse particles prior to plating. - Higher particle incorporation and lower P content by increasing particle concentration in electrolyte and current density. - Composites showed lower residual stress compares with pure alloys deposited at different current densities. Hardness affected by both particle and P content. 	[56]
Ni-W	Al ₂ O ₃	Alkaline bath: nickel sulphate, sodium tungstate and sodium citrate	<ul style="list-style-type: none"> - System: N/A - Frequency: 35 and 130 kHz - Power: N/A 	<ul style="list-style-type: none"> - Ultrasound during plating significantly reduced particle agglomeration, resulting in a more uniform dispersion of particles in composites. - Higher ultrasonic frequencies yielded composites with lower and less uniform particle content. - Differences in particle shape and size affected final properties of composites. 	[57,58]
Ni-W	WC	Alkaline bath: nickel sulphate, sodium tungstate, sodium citrate, ammonium chloride and sodium bromide	N/A	<ul style="list-style-type: none"> - Ultrasound used to prevent particle agglomeration in electrolyte prior to plating. - Pulse-plating parameters affected the surface morphology, particle content and hardness of coatings. 	[59]

Metal matrix	Particle	Electrolyte	Ultrasonic parameters	Effect of ultrasound/particles/plating parameters on final properties of coatings	Ref
Cu	Al ₂ O ₃	Sulphate bath	N/A	<ul style="list-style-type: none"> - Ultrasound used to improve dispersion of particles in electrolyte prior to plating. - Composites coatings exhibited improved wear resistance and corrosion resistance than pure Cu deposits. Wear rate, corrosion rate and porosity decreased by increasing particle content in composites. 	[60]
Cu	Carbon nano-fibres	Sulphate bath with polyacrylic acid	N/A	<ul style="list-style-type: none"> - Ultrasound used to improve dispersion of particles in electrolyte prior to plating. - Surface morphology affected by the types of fibres incorporated. 	[61]
Cu-Sn	Graphite	Cyanide bath with potassium stannate and poly-vinyl-pyrrolidone (surfactant)	<ul style="list-style-type: none"> - System: horn - Frequency: 20 kHz - Power: 70 W 	<ul style="list-style-type: none"> - Combination of ultrasound and surfactant improved dispersion of particles in electrolyte prior to deposition, resulting in effective embedding of particles in pulse-plated composites. 	[62]

Metal matrix	Particle	Electrolyte	Ultrasonic parameters	Effect of ultrasound/particles/plating parameters on final properties of coatings	Ref
Zn-Ni	Al ₂ O ₃	Chloride bath (low ammonium) with sodium acetate	<ul style="list-style-type: none"> - System: horn - Frequency: 20 kHz - Power: 0-1.2 W/cm² 	<ul style="list-style-type: none"> - Ultrasound during the deposition process improved the dispersion of particles in the alloy matrix. - Ultrasonic power strongly affected particle content in composites. - Hardness and corrosion potential increase with increasing particle content in coatings. - Corrosion current was related to both particle content and particle dispersion in the alloy matrix. 	[63,64]
Cr	Al ₂ O ₃ + SiC	Modified chromic acid bath with Fs-10 (surfactant)	<ul style="list-style-type: none"> - System: N/A - Frequency: N/A - Power: 2.8 W/cm³ 	<ul style="list-style-type: none"> - Ultrasound used to disperse particles in electrolyte prior to plating. - Incorporation of particles into the metal matrix significantly improved the corrosion resistance of coatings. 	[65]
Au	Diamond	Sulphite electrolyte	<ul style="list-style-type: none"> - System: N/A - Frequency: 20 kHz - Power: N/A 	<ul style="list-style-type: none"> - Ultrasound used to improve dispersion of particles in electrolyte prior to plating. - Composites deposited from electrolytes where particles were dispersed with ultrasound presented a higher particle content and higher hardness values. 	[66]
Au-Ni	PTFE	Commercial bath: <ul style="list-style-type: none"> - Au = 10 g/L - Ni = 1.5 g/L 	<ul style="list-style-type: none"> - System: bath - Frequency: 500 kHz - Power: 0-0.147 W/cm³ 	<ul style="list-style-type: none"> - Ultrasound improves both plating rate and particle incorporation. - Composites deposited with ultrasound generally presented lower coefficients of friction after greater number of cycles. 	[67]

3.1. EFFECT OF ULTRASOUND ON THE DISPERSION OF PARTICLES

The use of ultrasound for the dispersion of particles is widely employed due to the unique features that ultrasonic cavitation presents in order to de-agglomerate large agglomerates and aggregates in aqueous and non-aqueous suspensions. In the electrodeposition of composite coatings ultrasonic irradiation of the electrolyte is, in many cases, an essential step prior to the electrodeposition process itself in order to finely disperse the particles and reduce their agglomeration and in some studies is combined with the addition of a surfactant to further improve particle dispersion. The efficiency of ultrasound for particle de-agglomeration in surfactant-free electroplating baths was clearly demonstrated by García-Lecina et al. [38]. In their study, focused on the electrodeposition of Ni-based composite coatings with embedded Al_2O_3 particles, the authors reported that only ten minutes of ultrasonic irradiation were required to achieve a significantly better particle size distribution with smaller agglomerates in the Watts bath employed (Figure 3). Indeed it has been shown that ultrasound can be so effective in dispersing particles in the electrolyte that composite coatings produced from a plating bath which had been previously sonicated may present higher particle content even if ultrasound was not used during the electrodeposition process [66]. This improved dispersion and de-agglomeration effect of ultrasound is due to different reasons [68]: i) presence of micro-turbulence caused by the oscillating acoustic pressure and cavitation fields, and ii) van der Waals forces broken by high speed particle collisions induced by acoustic streaming, microjetting and shockwaves. Nevertheless, although the presence of ultrasound improves the dispersion of particles in the plating bath, it may not be enough to completely avoid the agglomeration of particles to form large clusters in certain cases [56].

The use of ultrasound during the electrodeposition process also promotes the incorporation of well disperse, uniformly distributed particles into the electroplated coatings [38,41-43,46,47,49,57,58,64]. A more uniform distribution of particles in the deposits was also observed by Dietrich et al. [53] when incorporating Al_2O_3 particles in electrodeposited Ni-Co

coatings under ultrasound. In earlier studies, the same research group had already observed the benefits of implementing ultrasound to achieve a more uniform distribution of particles in metal deposits where they added micro-scale and nano-scale particles of TiO₂ and SiC to Ni coatings [44,45]. They observed that the use of ultrasound during the electrodeposition stage yielded a far more homogeneous coating with no large aggregates (Figure 4).

Ultrasound has also been successful in increasing the amount of particles incorporated into electrodeposited coatings [37,38,41,42,49,53,67]. Zanella et al. [48] observed that, although ultrasound did not have a significant effect on particle content in Ni/SiC composites produced by continuous-current plating, it significantly increased particle incorporation into the coatings deposited by pulsed-plating methods. Nevertheless, the same authors also noted that, in some cases, a reduction in particle content in composite coatings electrodeposited with ultrasound may be expected due to the fact that large agglomerates are not incorporated into the deposits [48].

3.2. EFFECT OF ULTRASOUND ON THE MORPHOLOGY AND STRUCTURE

The morphology and structure of electrodeposited composite coatings is not only affected by the incorporation of particles into the coatings but also by the presence of ultrasound during the electrodeposition process. Many works have reported a beneficial effect of ultrasound in refining the grain size of the composite coatings [38,41,42,44-46,49,53,54] achieving a smoother finish partly due to a much more uniform distribution of well-dispersed particles. For example, Cai et al. [47] found that a combination of mechanical agitation and sonication produced Ni/SiC composite coatings with a finer surface morphology (Figure 5) as the mechanical agitation avoided the sedimentation of the SiC particles while the ultrasound prevented their agglomeration. Xia et al. also [51] observed that when TiN nanoparticles were homogeneously dispersed with ultrasound and incorporated into Ni-based coatings extremely smooth coatings were achieved.

Regarding the crystal orientation of the deposits, although there are some cases where ultrasound does not really make a difference in terms of the preferred orientation of electrodeposited composite coatings [38,52] the growth mode of the crystals in the composite coating may be affected by ultrasound [49,54]. This effect was reported by Xue et al. on Ni/CeO₂ composite coatings [40]. The authors observed a free growth mode (more than 90 % of (200) crystal planes) in their pure Ni coatings while the addition of the 30 nm CeO₂ particles to the Watts bath resulted in a significant modification of the crystal textures in the deposit: not only was the presence of (111) crystal planes increased and a similar proportion of (111) and (200) crystal planes were observed, but also it enhanced the electrocrystallization of Ni crystals showing (220), (311) and (222) planes. However, when ultrasound was used during the electrodeposition, it counteracted the effect of the particles in the dispersion as a high proportion of (200) textures was noticed again, followed by an increase in the number of (220) crystals and a significant decrease in the presence of (111) and (311) crystal planes. A similar effect of ultrasound on the crystal orientation was noticed by Xia et al. on their Ni/TiN composite coatings [51] as a relative decrease in the peak intensity associated with the presence of (111) crystal planes was observed in comparison with the peak intensity related to the presence of (200) crystal planes when ultrasound was used during the electrodeposition.

3.3. EFFECT OF ULTRASOUND ON THE MECHANICAL PROPERTIES

It is well known that the incorporation of hard particles into electrodeposited coatings generally results in an increase in hardness and the improvement of other mechanical properties such as wear resistance and/or the coefficient of friction. The use of ultrasound during the electroplating of composite coatings seems to further enhance this hardening effect [48-50,54,64,66] as would be expected considering the effect of ultrasound on grain size and hardness of electrodeposited metals and alloys [22]. Xue et al. [40] not only observed an improvement in the hardness of their Ni deposits by adding CeO₂ particles but also observed a further increase in hardness and enhancement of wear resistance in those composite coatings

that were electrodeposited under ultrasound. Similar results were obtained by García-Lecina et al. [38] on Ni/Al₂O₃ composite coatings where they found that both ultrasound and the concentration of particles in the electrolyte had an effect on the hardness of the coatings (Figure 6). They proposed that the combination of two phenomena (as previously suggested by Lampke et al. [44]) could explain the increase in hardness of composite coatings plated under ultrasound: i) the presence of fine, well-dispersed Al₂O₃ nanoparticles in the Ni matrix that would act as strong obstacles for dislocation movement and ii) a finer grain size of the Ni crystals due to the grain refining effect of ultrasound. In this case, wear resistance was also enhanced when increasing the particle concentration in the electrolyte and the presence of ultrasound further improved the performance of the coatings. Similar results were observed by the same authors when incorporating WS₂ particles into Ni deposits [52] where the composites produced under ultrasound exhibited a further enhancement in both hardness and tribological performance when compared with Ni/WS₂ composite coatings produced in the absence of ultrasound. In the case of Ni-Co deposits with Al₂O₃ [53] the presence of ultrasound during deposition not only increased the hardness but also the plastic deformation of the coatings.

3.4. EFFECT OF ULTRASOUND ON THE CORROSION RESISTANCE

The incorporation of particles into electrodeposited metal coatings generally results in the improvement of the corrosion resistance of the coatings [3]. This effect is reported in many of the papers where ultrasound is used prior to the electrodeposition stage in order to achieve a better dispersion of particles in the plating electrolyte [50,55,60,65]. However few researchers have studied the effect that the use of ultrasound during the electrodeposition stage may have on the corrosion resistance of the resulting composite coatings as most studies are only focused on those composite coatings produced under the presence of ultrasound that exhibited the best surface finish and quality [45,47].

Gyawali et al. [49] studied the effect of ultrasound on the corrosion behaviour of Ni/SiC composite coatings. In their work, the measured corrosion currents, corrosion potentials,

anodic/cathodic Tafel slopes, corrosion resistance and corrosion rates indicated that, while Ni/SiC composite coatings electrodeposited under silent conditions showed better behaviour than pure Ni deposits, the introduction of ultrasound during the plating process resulted in a further enhancement of the corrosion resistance of the coatings. These measurements were in agreement with other results obtained by electrochemical impedance spectroscopy studies in the same investigation confirming the improvement in the corrosion resistance of the Ni/SiC composite coatings electrodeposited with ultrasound. Zanella et al. [48] also evaluated the influence of sonication during the electrodeposition of Ni/SiC composite coatings finding that pure Ni and Ni/SiC deposits were prone to pitting corrosion, whereas pure Ni and Ni/SiC deposits produced with ultrasound showed more stable behaviour. This improvement, observed in both Ni and Ni/SiC deposits electrodeposited in an ultrasonic field, was attributed to the lower porosity and higher compactness of the deposits produced under such conditions, and is in agreement with the idea that grain refinement by ultrasound results in lower porosity of electroplated coatings [22]. The enhancement of the corrosion resistance of composite coatings electrodeposited when ultrasound is implemented in the electrodeposition stage has also been reported for other composite coatings [41,42,46,64], where again a strong link between grain refinement, particle incorporation and corrosion behaviour was observed. However, the application of ultrasound during deposition will not always result in the improvement of the corrosion resistance. Zanella et al. [37] did not report any significant effect of ultrasound on the corrosion resistance of electrodeposited Ni/Al₂O₃, as the ultrasonic irradiation employed in this study was not enough to completely avoid the agglomeration of the particles.

4. INFLUENCE OF THE ULTRASONIC PARAMETERS ON THE ELECTRODEPOSITION OF COMPOSITE COATINGS WITH PARTICLES

The previous section has shown how the introduction of ultrasound into composite plating processes may result in a better dispersion of particles in the electroplating bath, higher incorporation of well-dispersed and uniformly distributed particles, and hence, better mechanical properties and enhanced corrosion resistance. However, most of the studies found in the literature have only focused on the general use of ultrasound and extracting information from these papers on the exact ultrasonic conditions employed is difficult (e.g. the ultrasonic frequency and power employed, the ultrasonic equipment utilised and how the transducers are placed in the overall system, etc.). All this information, which may not be seem important in the first instance, is critical in order to optimize the beneficial effects of ultrasound in general sonochemistry and sonoelectrochemistry [69] and to understand how ultrasound may affect the electrodeposition of composite coatings.

4.1. EFFECT OF ULTRASONIC FREQUENCY

There are few studies on the effect of the ultrasonic frequency on the electrodeposition of composite coatings with particles. An exception is the work conducted by Indyka et al. focused on the electrodeposition of Ni-W alloys with Al_2O_3 particles under ultrasound [57,58]. In these papers the authors investigated the effect of two different frequencies (35 and 130 kHz) of ultrasound on the characteristics of the electroplated composites. Their results not only illustrated that the presence of ultrasound during plating significantly reduced particle agglomeration resulting in a more uniform dispersion of particles in composites, but also that composites produced at 130 kHz exhibited a lower particle content (and worse particle distribution) than those electrodeposited at 35 kHz. This finding is illustrated in Figure 7 for Ni-W/ Al_2O_3 composite coatings produced from baths with different particle concentrations. Similar results were obtained by Li et al. on their Ni composite coatings containing Nd_2O_3

particles [41,42], as they found that Ni/Nd₂O₃ coatings produced at a lower frequency (20 kHz) presented higher particle content and finer grain size than those electrodeposited at a higher frequency (100 kHz). This resulted in Ni/Nd₂O₃ composite coatings with higher corrosion resistance. Generally speaking, the formation and intensity of cavitation phenomena progressively decreases as the ultrasonic frequency is increased as rarefaction and compression cycles are shorter, resulting in bubbles with a smaller resonant size [10]. Larger bubbles undergo a more violent collapse, and therefore, mechanical effects caused by the presence of cavitation phenomena are predominant at lower frequencies, whereas chemical effects are more significant at higher frequencies [70-72]. Chemical effects, such as radical formation, are of great interest in many chemical reactions [7] and processes where mechanical effects have little influence [73]. However, mechanical effects are of great importance in the electrodeposition of composite coatings with embedded particles as mechanical events such as acoustic streaming, formation of microjetting and shockwaves significantly enhance the dispersion and de-agglomeration of particles in the electrolyte and the incorporation of well-dispersed and uniformly distributed particles into the electrodeposited coating.

4.2. EFFECT OF ULTRASONIC POWER

Among the first works evaluating the effect of ultrasonic power is the study by Rezrazi et al. which focused on the ultrasound-assisted electrodeposition of Au-based composite coatings with PTFE particles [67] at high frequencies (500 kHz). In this investigation it was found that enhanced deposition and higher incorporation rates were obtained when ultrasound was applied. The authors also noticed that a higher ultrasonic power yielded a higher incorporation of particles to the coatings. Zheng et al. investigated the effect of ultrasonic power at low frequencies (a 20 kHz ultrasonic horn) [64] and they showed that using higher ultrasonic powers yielded an increase in the content of Al₂O₃ nanoparticles in Zn-Ni alloy coatings (Figure 8 A). However, they also observed that there was a maximum value for the particle content versus ultrasonic power such that a further increase in the power would lead to a decrease in

the particle content in the coating. According to the authors, a possible explanation for this could be that the Al_2O_3 particles under high power sonication collide with the cathode and then break away from it which would result in a decrease in the content of Al_2O_3 in the coating. They observed the same trends when evaluating the corrosion and mechanical properties of the coatings: an increase in both the electropositive corrosion potential and the hardness was obtained when the particle content was increased by working at a certain ultrasonic power (Figures 8 B and C, respectively). Nevertheless, the authors also noticed that when particle content in the deposit was 'too much', the large number of particles within the alloy matrix could result in a porous composite coating which exhibited reduced corrosion resistance than other deposits with lower particle content. The same effect of the ultrasonic power on the particle content was observed by García-Lecina et al. who studied the incorporation of WS_2 particles into Ni deposits [52] and observed that the particle content in the coating increased when increasing the ultrasonic power up to 30 W cm^{-2} , and then slightly decreased at 40 W cm^{-2} (a 24 kHz horn was used in this case). Again, different properties of the composite coatings were strongly linked to the particle content in the coating (reduced Young modulus, elastic recovery), although other properties were both linked to particle content and the applied ultrasonic power. For example, the same hardness was observed in coatings produced at either 30 or 40 W cm^{-2} whilst the highest elastic strain to failure and lowest coefficient of friction were achieved in composite coatings produced at 40 W cm^{-2} . Li et al. [41,42] observed the same effect of ultrasonic 'horn' power on the Nd_2O_3 particle content in their Ni-based composite coatings when working with either 'horn only' and dual (combination of 20 kHz horn and 100 kHz bath) set-ups. However, no maximum in particle content was achieved if the authors progressively increased the ultrasonic power on an ultrasonic bath system when working with both 'bath only' and dual set-ups.

4.3. EFFECT OF ULTRASONIC SYSTEM

The latter results commented on in the previous section regarding the effect of the ultrasonic power on the incorporation of Ni/Nd₂O₃ particles into electrodeposited Ni coatings produced by Li et al. [41,42] may seem contradictory and might be misinterpreted as a consequence of the variety of set-ups used: ultrasonic source and configuration, electrolyte volume, etc. As noted by Mason et al. [71], a generally accepted method to account for all these differences in the experimental set-up is the calibration of the ultrasonic power by calorimetry [74,75] in watts (W), which is then converted into specific acoustic power by dividing the measured power by either the sonicated volume (W/cm³) or by the emitter surface area of the ultrasonic source (W/cm²). However, such calibration method, which is extensively used in sonochemistry in general and sonoelectrochemistry in particular, has not been used at all in the existing literature dealing with the implementation of ultrasound on the electrodeposition of composite coatings with particles, making the comparison of the results observed in different studies a lot more complicated. In this sense, the work from Li et al. [41,42] represents a good example of how results can appear contradictory when issues such as ultrasonic source and configuration, and the 'real' ultrasonic power introduced into the electrolyte, are not properly accounted for. As previously mentioned, the authors observed that, when increasing the ultrasonic power of the horn up to 40 W, the highest particle incorporation was observed at 30 W (maximum), whereas when increasing the ultrasonic power of the ultrasonic bath up to 300 W, particle content increased as the power was increased. One would find it hard to explain these results if it was not for the following facts [**Error! Bookmark not defined.**]:

- Ultrasonic horns are high power systems where massive ultrasonic cavitation is achieved due to the very large vibration amplitudes that can be achieved at the emitter surface of such electromechanical systems, whereas in ultrasonic baths much lower vibration amplitudes are achieved by the transducers (see Figure 9 which roughly describes the main differences in terms of design between a horn and a ultrasonic bath

[16]). Therefore, the cavitation intensity that could be achieved with a horn operating at a certain electrical power will always be significantly higher than the cavitation intensity achieved in an ultrasonic bath.

- Horns are used to directly irradiate the working electrolyte, whereas vessels containing the electrolyte are usually immersed into ultrasonic baths (no direct contact between emitter surface and working electrolyte). Sound attenuation due to the vessel walls is expected in the latter resulting in a less effective transmission of sound into the electrolyte.
- Whereas the horn used by Li et al. operated at 20 kHz, the ultrasonic bath employed by the same authors operated at 100 kHz [41,42]. As previously mentioned, the higher the ultrasonic frequency, the lower the resonance bubble size will be and this will generally result in less violent cavitation phenomena and lower cavitation activity.
- The position of the vessel containing the electrolyte in the bath strongly affects the intensity of sonication. Very low cavitation activity will be measured in the electrolyte when the vessel is positioned a low-intensity ultrasound area within the bath even if the bath is operating at its highest power.

Taking these comments into consideration, along with the results found in this review of studies dealing with the incorporation of ultrasound on the electrodeposition of composites currently available in the literature, it might be assumed that a horn system operating at an ultrasonic frequency as low as possible (around 20 kHz) would be the best method of achieving a high particle content in an electroplated composite. Nevertheless, these systems present some drawbacks as well:

- Whereas ultrasonic cleaning baths are widely available and are a very cheap option, ultrasonic horns present a more complex design at a much higher cost.
- Ultrasonic horns produce very violent cavitation phenomena that may have a negative effect on particle content in electrodeposited composite coatings as particles may collide

with the surface of the electrode under strong cavitation and then break away from it. Alternatively particles may even be removed from the surface of the cathode due to aggressive cavitation near the surface resulting in lower particle incorporation than expected, even though the particles would be uniformly distributed within the coating [41,42,52,54,64]. Violent cavitation could also result in the erosion of the electrodeposited coatings [76] which would not only affect the surface finish but also the performance of the deposits.

- Very high ultrasonic pressures can be achieved with a horn which would obviously result in violent cavitation phenomena in the fluid. Nevertheless, most of the cavitation actually occurs near the emitter surface of the horn (the well-known cone-like shaped cavitation 'cloud' formed near the emitter surface [77]) as the highest pressures are achieved in this region. This massive formation of bubbles can have a rather negative effect, i.e. a strong attenuation of the ultrasonic field in the region near the emitter surface due to the presence of the cone-like shaped bubble 'cloud' [78,79]. This effect is much less significant in an ultrasonic bath where a fairly even distribution of energy through the bath walls results in a more homogeneous ultrasonic field where cavitation phenomena is not only observed near the emitter surface of the transducers but also further away.

In order to truly understand the effect of ultrasound on electroplating in general and on the electrodeposition of composite coatings with particles in particular, it is critical to clearly know how ultrasound is introduced into the electrolyte and this has been poorly reported in the existing literature. In addition, without this information the scale-up of such processes to a production line would be challenging. In this case, where large plating tanks are usually involved, the introduction of ultrasound would be even more complex, as the nature and location of the ultrasonic source, their operating frequency and power, and the geometry of the tank and its building materials would have a strong influence on the resulting ultrasonic field and its final effect on the electrodeposited coatings. A similar issue is also faced in the design of

sonochemical reactors and processes, and if the methodologies employed by 'sonochemists' in order to characterise sonochemical reactors [80,81] were followed when recording the ultrasonic parameters utilized in the electrodeposition of composite coatings a better comparison of the various studies, and there suitability for scale-up could be made.

5. CONCLUSIONS

The introduction of ultrasound on the electrodeposition of composite coatings with embedded particles has been reviewed. Ultrasonic cavitation not only enhances the dispersion and de-agglomeration of particles in the electrolyte, but also the incorporation of finely-dispersed and uniformly distributed particles into the electrodeposited coating. Composite coatings electrodeposited under ultrasound show a further enhancement of the mechanical properties (hardness, wear resistance, coefficient of friction, etc.) and the corrosion resistance. The experimental results observed by different authors indicate that the introduction of low-frequency, high-power ultrasound into the plating bath promotes mechanical events such as acoustic streaming, microjetting and shockwaves caused by the presence of ultrasonic cavitation in the electrolyte and these phenomenon can bring many benefits in the electrodeposition of composite coatings with particles. This review has illustrated that there is a general lack of information regarding the ultrasonic parameters and equipment used in the various studies and this suggests that the advantages and disadvantages of the different ultrasonic systems commercially available have not been adequately considered. This information is not only essential if the studies are to be properly compared but it is also crucial for the understanding of sonochemical effects and to enable the optimisation of ultrasound in electroplating in general and in the electrodeposition of composite coatings in particular.

FIGURES

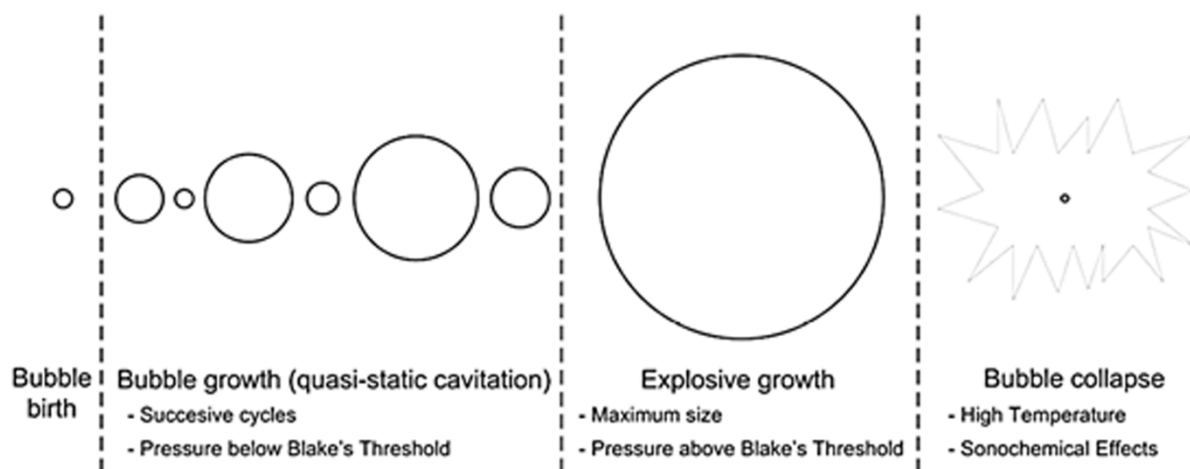


Figure 1. Bubble growth and implosion in a liquid irradiated with ultrasound. Adapted from Ref. and [7], with permission from the Multidisciplinary Digital Publishing Institute.

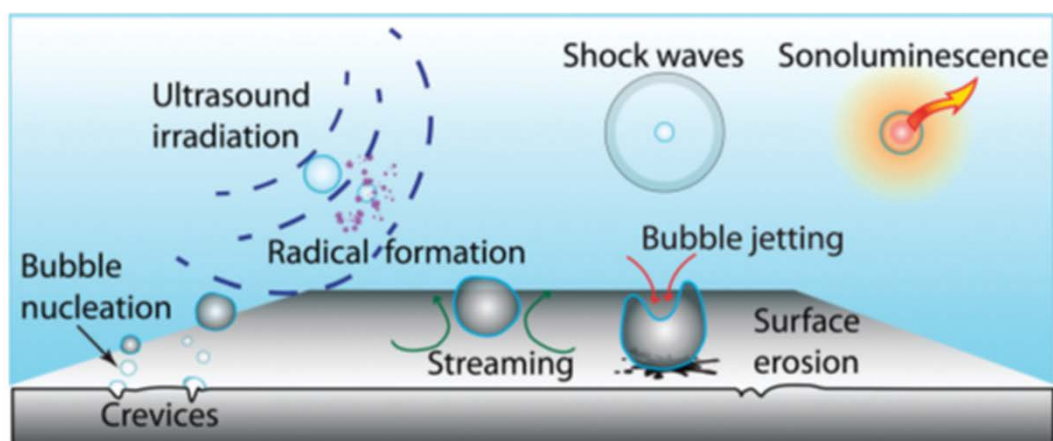


Figure 2. Schematic representation of the main effects of cavitation induced by ultrasound irradiation. Adapted from Ref. [9], with permission of The Royal Society of Chemistry.

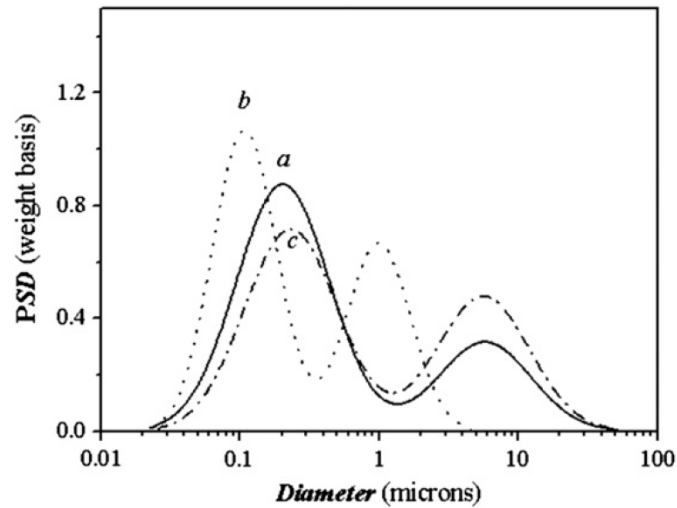


Figure 3. Particle size distribution of Al_2O_3 particles (50 g L^{-1}) dispersed in a Ni Watts bath. The experiments were carried out (a) after 24 h of magnetic stirring; (b) after 24 h of magnetic stirring+10 min of US treatment; (c) same as b after one hour. Adapted from Ref. [38], with permission from Elsevier.



Figure 4. Well-dispersed TiO_2 particles under ultrasound conditions (lower part from substrate up to the markers $><$) and nano-particle agglomeration under silent conditions (upper part) in a Ni coating. Adapted from Ref. [44], with permission from Elsevier.

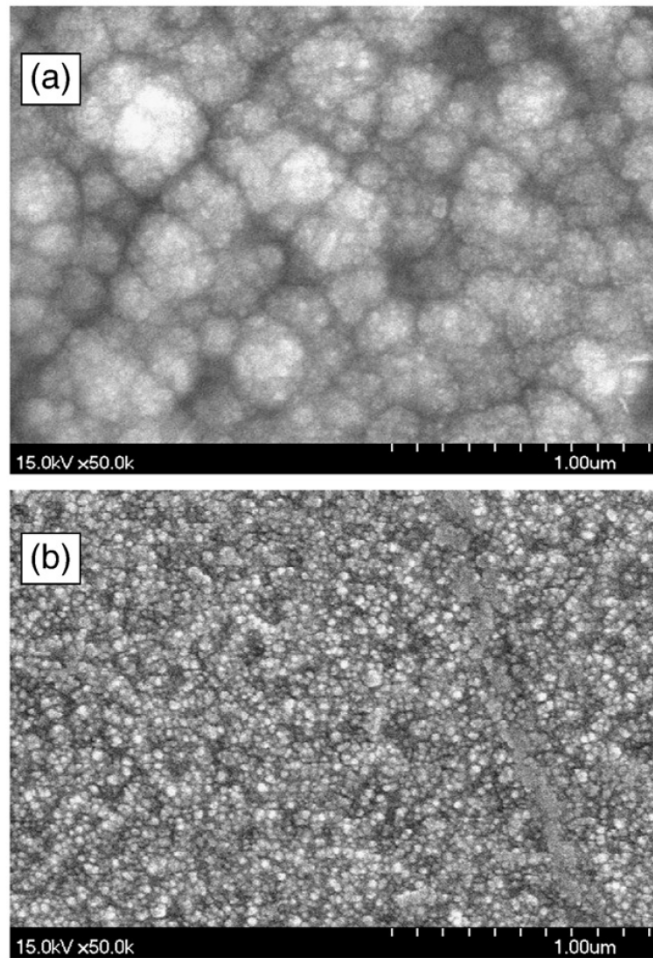


Figure 5. Surface morphologies of Ni/SiC composite films prepared under different conditions: (a) mechanical dispersion and (b) mechanical and ultrasonic dispersion. Adapted from Ref. [47], with permission from Elsevier.

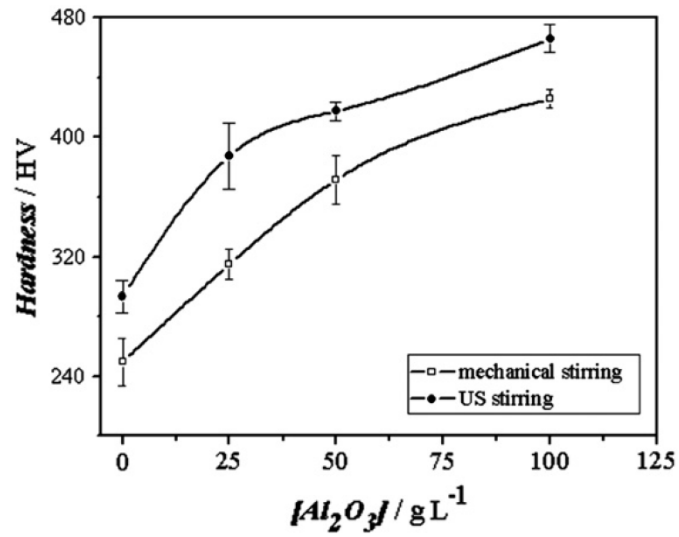


Figure 6. Effect of Al_2O_3 concentration in the electrolyte on the hardness of Ni/ Al_2O_3 composite coating obtained under mechanical stirring and ultrasound. Adapted from Ref. [38], with permission from Elsevier.

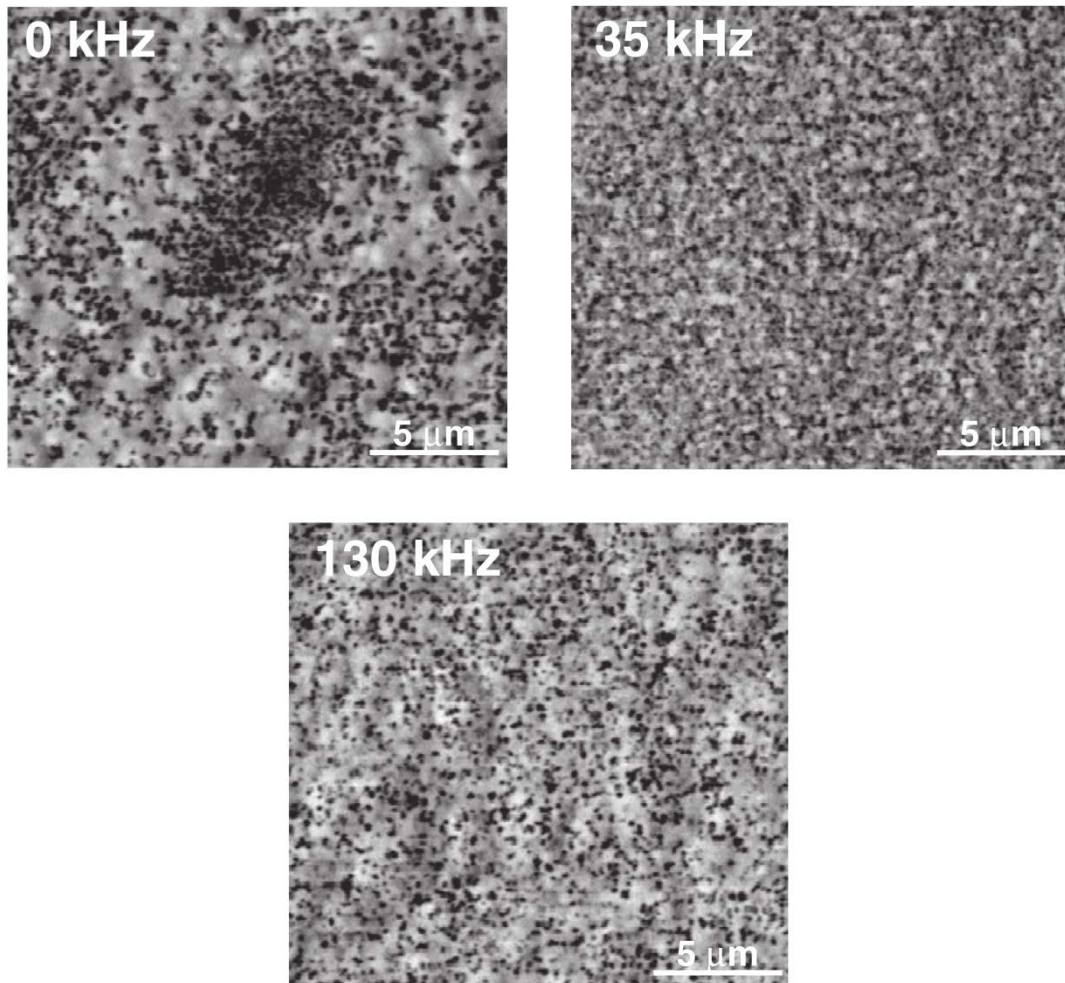


Figure 7. SEM (BSE) images of surface morphology of Ni-W/Al₂O₃ composite coatings electrodeposited at a rotating speed of 340 rpm under different ultrasonic frequencies. Adapted from Ref. [58], with permission from Elsevier.

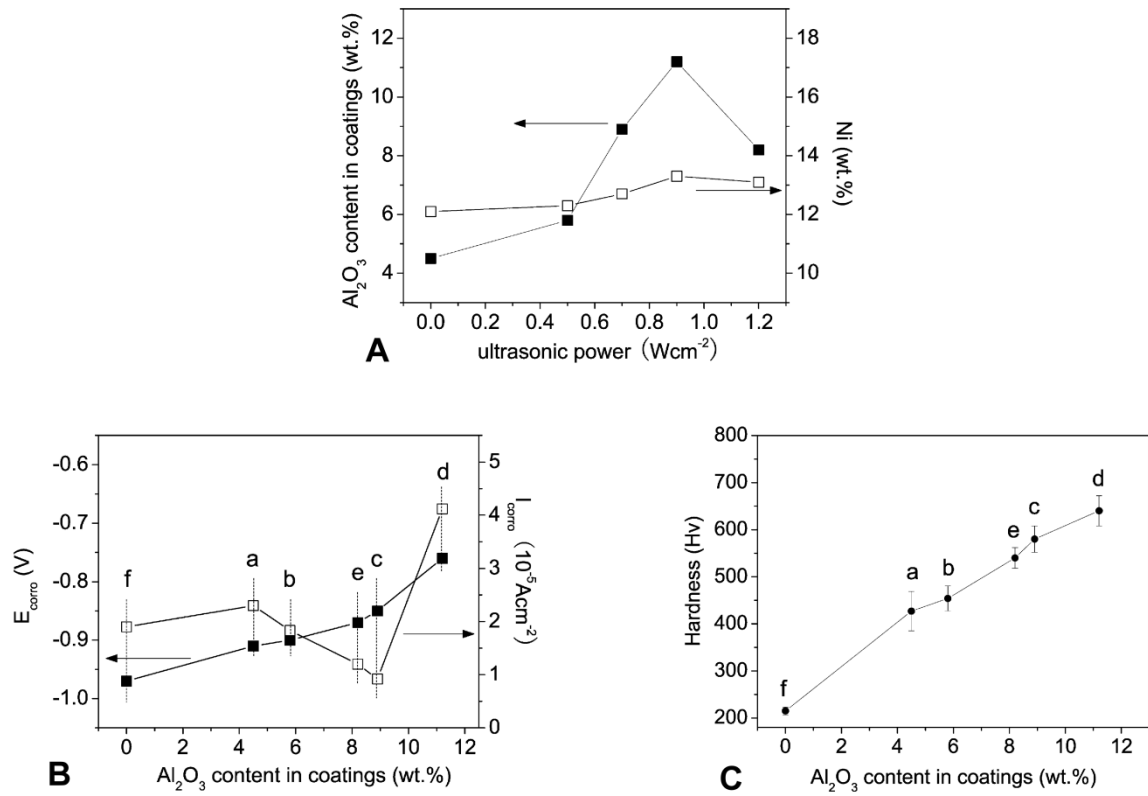


Figure 8. (A) Influence of ultrasonic power on the Al₂O₃ and Ni content in Zn-Ni/Al₂O₃ composite coatings. (B and C) Effect of Al₂O₃ content on (A) the corrosion potential and current and (B) hardness of Zn-Ni/Al₂O₃ composite coatings produced under different ultrasonic power: (a) 0 W/cm², (b) 0.5 W/cm², (c) 0.7 W/cm², (d) 0.9 W/cm², (e) 1.2 W/cm² and on (f) Zn-Ni alloy coating. Adapted from Ref. [64], with permission from Elsevier.

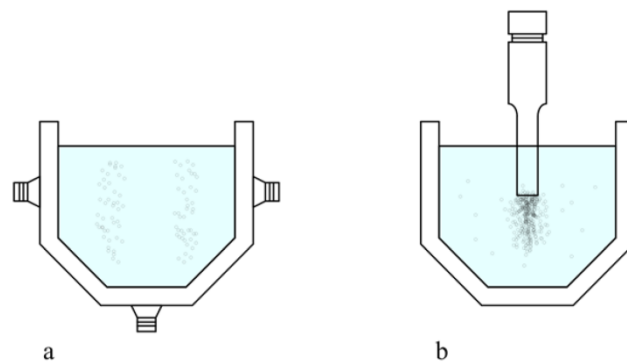


Figure 9. Different ultrasonic transducer set-ups: (a) ultrasonic bath, and (b) ultrasonic horn. Adapted from Ref. [7], with permission from the Multidisciplinary Digital Publishing Institute.

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