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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 utilising sonication.

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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.

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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 utilised 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 Fig. 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 (Fig. 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.

### 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

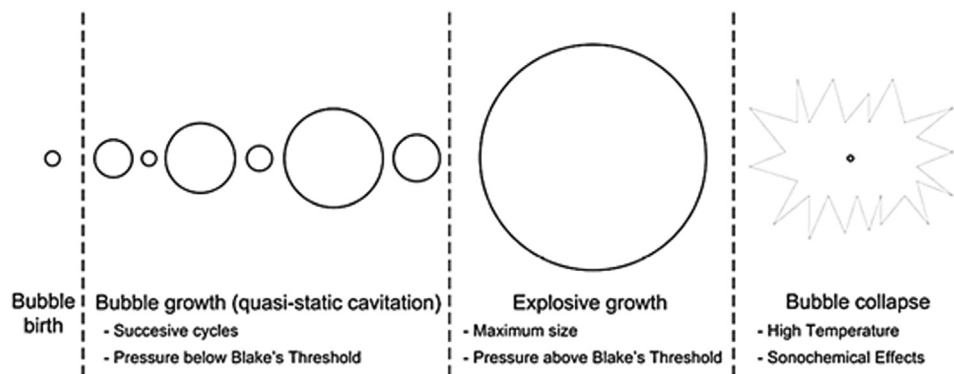


Fig. 1. Bubble growth and implosion in a liquid irradiated with ultrasound. Adapted from Ref. [7], with permission from the Multidisciplinary Digital Publishing Institute.

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