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Ultrasound-assisted electrodeposition of thin nickel-based composite coatings with lubricant particles

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ABSTRACT

Thin Ni composite coatings with hBN and WS_2 particles were ultrasonically-electrodeposited on Cu with no need of a surfactant. Although the combination of mechanical agitation and ultrasound yielded the best dispersions, ultrasound on its own during plating yielded coatings with a more uniform distribution of particles. Ni/hBN and Ni/WS_2 composite coatings electrodeposited under ultrasound were characterised by different methods: GD-OES to estimate particle content, XRD to analyse the preferred orientation, FIB-SEM to analyse the surface morphology and microstructure, and microhardness tests to measure the hardness. Whereas Ni/hBN composite coatings showed little difference compared to pure Ni deposits, the incorporation of WS_2 into Ni had a significant effect on the preferred orientation, the surface morphology and the grain size of the coatings, refining the Ni crystal down to the nano-scale. The latter had a significant effect in the hardness of the coatings, despite the 'soft' nature of the WS_2 particles.

1. Introduction

The electrodeposition of Ni-based composites has received a wide attention in recent years due to the improved characteristics that these coatings may present [1]. Many of the studies available in the literature have been focused on the electrodeposition of composites with embedded 'hard' particles from Watts and sulphamate baths [2–5]. However, the incorporation of soft particles has received far less attention from the research community [6,7], despite of the improvement in the tribological performance that could be expected when soft particles are incorporated into Ni coatings due the high lubricity inherent to these particles. This high lubricity would be caused by the characteristic layered structure that these particles have: whereas atoms on same layer are closely packed and strongly bonded to each other, layers are relatively far apart and weakly bonded to each other [8].

The electrodeposition of Ni composite coatings such as those reported in the studies previously referenced strongly relies on the addition of surfactants to the plating bath in order to achieve a good dispersion and prevent particle agglomeration in both the electrolyte and the coating. Nevertheless, the use of surfactants may affect process-control, waste effluent treatment, long-time stability and life-span of the electrolytes in industry. For these reasons, other options are being evaluated for the electrodeposition of Ni-based composites with embedded particles, including the use of ultrasound in electrodeposition processes.

The use of ultrasound has already been proved successful in the electrodeposition of Ni composite coatings with embedded particles, not just in terms of improving the dispersion of particles in electroplating baths, but also to enhance the incorporation of well-disperse particles into the coating [9]. Hard particles such as Al_2O_3 [10], SiC [11] and TiN [12] have been successfully incorporated into Ni coatings electrodeposited from additive-free Watts formulations with the aid of ultrasound, generally resulting in Ni composite coatings with higher incorporation and more uniform distribution of particles. Regarding the use of ultrasound on the electrodeposition of Ni composite coatings with soft particles, very little research has been done so far. However, the work of García-Lecina et al. [13] on the electrodeposition of Ni composite coatings with inorganic fullerene-like WS_2 (IF-WS_2) nanoparticles is the best example of how ultrasound can significantly improve particle content, coating compactness and uniformity, resulting in better mechanical properties and enhanced tribological performance. In this latter case though, the addition of a surfactant (cetyl-trimethyl-ammonium bromide, CTAB) to the Watts bath formulated by the authors was still necessary to produce the Ni/IF-WS_2 composite coatings.

In this study the main goal was to produce thin Ni composite coatings with embedded WS_2 and hBN particles from an additive-free Watts bath. In this sense, the main objectives were: (i) to better understand how different agitation conditions may influence the dispersion of particles and their incorporation into electrodeposited Ni coatings from an additive-free Watts bath, (ii) to produce Ni composite coatings with

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WS_2 and hBN particles uniformly distributed within the Ni matrix, and (iii) to evaluate the characteristics of the novel Ni composites coatings that exhibited the best deposit quality. For this purpose, this study was structured in three main parts:

1. A first stage where WS_2 and hBN particles were dispersed in the Watts bath under different dispersing conditions: (i) ultrasound on its own, (ii) mechanical agitation on its own, and (iii) combined ultrasound/mechanical agitation.
2. A second stage focused on the production and qualitative evaluation of Ni/WS_2 and Ni/hBN composite coatings electrodeposited under different conditions: (i) ultrasound on its own, (ii) mechanical agitation on its own, and (iii) combined ultrasound/mechanical agitation.
3. A third stage focused on the detailed characterisation of those Ni/WS_2 and Ni/hBN composite coatings produced during the second stage of the study that qualitatively presented a more uniform distribution of particles, higher particle content and less large agglomerates in the cross-section.

2. Materials and methods

2.1. Experimental set-up

The same Watts bath employed in a previous study focused on the electrodeposition of Ni deposits under ultrasound [14] was used in this study (Table 1). This Watts bath is currently used in industry for the manufacture of thin Ni coatings, and the electrodeposition from this bath is a kinetics-controlled process with a cathode current efficiency higher than 90% when operated at a current density of 4 A/dm^2. WS_2 and hBN particles (Fig. 1) supplied by M K Impex Corp were employed in this study due to their lubricious nature, their commercial availability and their cost for a future scaling-up of the process. The concentration of particles in the Watts bath was always 15 g/L.

All the dispersion and electrodeposition experiments were conducted in the same set-up (Fig. 2) used in the electrodeposition of Ni deposits under ultrasound [14] where a 600 mL beaker containing 500 mL of the Watts bath containing either WS_2 or hBN particles was immersed in an QS12 ultrasonic bath (Ultrawave Ltd). The QS12 ultrasonic bath, which was equipped with a built-in thermostat enabling the control of temperature up to 70 °C, operated at a frequency of around 32–38 kHz with an ultrasonic power of 0.180 W/cm^3 estimated by the calorimetric method [15–17]. In those experiments where mechanical agitation was required, a CAT R18 85W overhead stirrer (110 to 2000 rpm) equipped with a 3-point propeller shaft (50 mm wide) was used. An IPS2010 power supply unit (ISO-TECH) was used as the rectifier in all the electrodeposition experiments.

In relation to the ultrasonic conditions chosen, the effect of ultrasonic frequency and power indeed have a strong influence on the dispersion of particles in the bath and their incorporation into the

Table 1
Ni Watts process and particles used in the present study.

Bath composition	
$NiSO_4 \cdot 6H_2O$	290 g/L
$NiCl_2 \cdot 6H_2O$	50 g/L
H_3BO_3	30 g/L
Particles	
Types	WS_2 (D50[a] ≈ 0.6 μm, D90[b] ≈ 5 μm)
	hBN (D50 ≈ 0.5 μm, D90 ≈ 1.1 μm)
Concentration	15 g/L
Plating conditions	
pH	3.2
Temperature	50 °C
Current density	4 A/dm^2

[a] D50 is the median particle size provided by the supplier, meaning that 50% of the particles are smaller than the said size.
[b] D90 is the 90th percentile of the particle size provided by the supplier, meaning that 90% of the particles are smaller than said size.

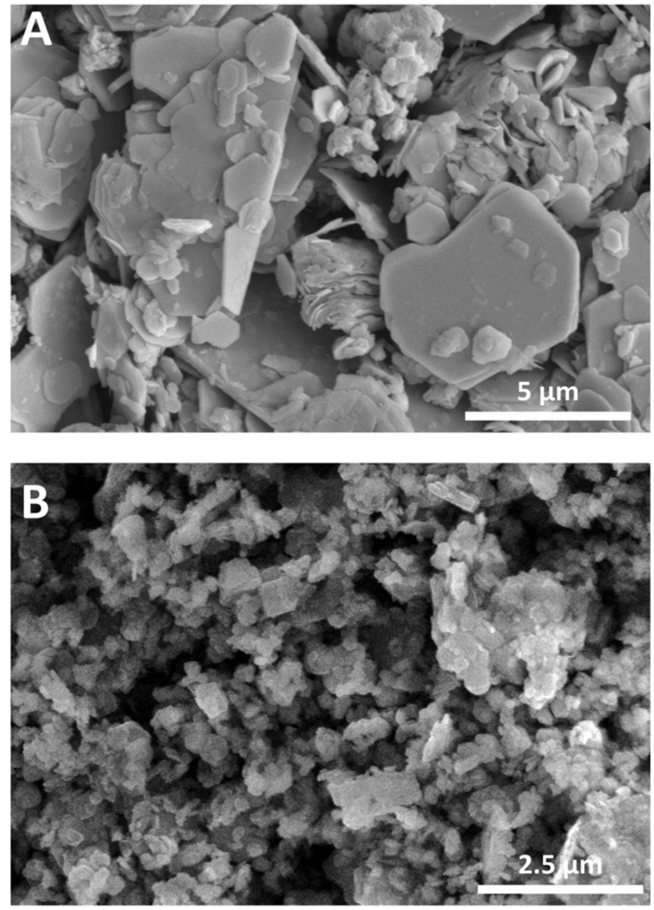

Fig. 1. SEM images of the different lubricant particles used in the present research project: A) WS_2, B) hBN.

Ni coatings during the electrodeposition, as discussed in a previous review paper by the authors [9]. Related to the ultrasonic frequency, although both mechanical and chemical effects of the introduction of ultrasound and the presence of acoustic cavitation in a liquid are observed at both low and high frequencies, mechanical effects (e.g., acoustic streaming, micro-jetting, release of shockwaves) are predominant at lower frequencies, whereas chemical effects (e.g., radical formation, sonoluminescence) are more significant at higher frequencies. These mechanical effects are the ones of special interest in composite electroplating due to (i) its ability to de-agglomerate large agglomerates and aggregates that otherwise would form and grow in the electrolyte and (ii) incorporate particles into the coatings [18,19]. In terms of power, the highest the power, the more effect ultrasound would have. Nevertheless, very high powers such as those achieved with an ultrasonic horn could have a detrimental effect on the incorporation of particles. In previous studies carried out by other researchers, an ultrasonic horn system was used to set the ultrasonic field during the electrodeposition of Ni [13] and Co [20] composite coatings containing IF-WS_2 particles. In this present study though, an ultrasonic bath set-up was chosen mainly due to the next reasons [9]:

1. Cavitation erosion. High-power ultrasonic horns, although very effective in order to disperse particles in short periods of time, produce very violent cavitation phenomena that may erode the surface of the deposits if they are placed near the transducer. Violent cavitation near the electrode can also have a negative effect in particle content in electrodeposited composite coatings, as particles may collide with the surface of the electrode under strong cavitation and then break away from there [13,21] or might be removed from the surface of the cathode by the 'scrubbing action' of cavitating bubbles.