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Ultrasound-assisted electrodeposition of nickel: Effect of ultrasonic power on the characteristics of thin coatings

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ABSTRACT

The effect of ultrasonic power on the characteristics of low-frequency ultrasound-assisted electrodeposited Ni coatings from an additive-free Watts bath has been evaluated by different methods. XRD analysis showed that, while mechanical agitation favoured the electrocrystallization of Ni in the [211] direction, ultrasound promoted the electrodeposition of Ni with a [100] preferred orientation. FIB-SEM images of the surface of Ni deposits not only indicated that the surface structure agreed to some extent with the XRD results, but also that ultrasound refined, to a certain extent, some of the grains of the surface of the coatings. FIB-SEM images of the cross-section of the coatings confirmed this effect of ultrasound on the microstructure of the deposits. Such change in the microstructure of Ni, along with work-hardening by ultrasound, resulted in an increase in the hardness of the deposits. The characteristics of the deposits depended on the ultrasonic power employed, and it was found that Ni coatings electrodeposited using an ultrasonic power of 0.124 W/cm^3 presented the higher proportion of crystals with a [100] preferred orientation, the highest degree of grain refinement in the surface and the highest microhardness values. Nevertheless, these deposits also presented visible erosion marks on the surface of the coatings due to the formation of transient bubble structures near the surface of the cathode during the electrodeposition. These erosion marks might be considered the main drawback to the use of ultrasound during the electrodeposition.

1. Introduction

Since Bird first described the formation of 'a crust of metallic nickel on the negative electrode, often of a silvery lustre on the surface immediately applied to the platinum' from a bath consisting of $NiCl_2$ and $NiSO_4$ nearly 180 years ago [1], a wide variety of studies have been focused on the electrodeposition of Ni as it is one of the most common metal plating processes in industry [2]. Its importance in terms of economic and commercial impact in the form of metal and salts annually consumed by the electroplating industry has been roughly estimated around 100,000 tonnes worldwide [3]. Among the different Ni electroplating processes currently employed in industry the Watts bath [4] has grown to become the most widespread Ni electroplating process with little modification. This type of bath not only produces high quality deposits, but it also is a very efficient process as the cathode current efficiency for general Ni Watts bath formulations generally remains around 90–97% [3].

In the last 20 years, the electrodeposition of thin Ni films has received a renewed attention from the research community [5,6]. Recent studies have been focused on the addition of different additives such as saccharin [7,8] and the use of novel plating methods such as pulse plating [9,10] in order to produce novel functional Ni coatings for different applications. The use of ultrasound in electrochemical processes [11] and electroplating in particular [12] has also been reported to improve the electrodeposition process itself and the characteristics of Ni deposits (enhancement of residual stress [13], wear resistance [14], fatigue strength [15] and hardness [16]). In this sense, Kobayasi et al. [17] found that the frequency in the low-frequency range could play a key role on improving charge transfer reaction and modifying crystal orientation (no effect = silent conditions < 100 kHz < 28 kHz < 45 kHz = highest effect) of Ni coatings electrodeposited from a Watts bath. Jensen et al. [18] studied the effect of high-frequency ultrasound (1000 kHz) on Ni deposits produced form a modified Watts bath with some surfactants and other additives (sodium lauryl sulphate, naphthalene trisulphonic acid and butyne diole) and observed that, although high-frequency ultrasound had a beneficial effect in levelling when electrodepositing Ni in deep grooves, it also had an apparently undesired effect in terms of

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pitting over the surface and the appearance of a fringe pattern. This fringe pattern was not only power dependant (it was less severe at high-power, high-frequency ultrasonic irradiation), but it also was affected by the nature of the ultrasonic field (travelling/standing wave). Touyeras et al. [19] also studied the effect of high-frequency ultrasound (300 kHz, 500 kHz and 800 kHz) at different powers (from 0 to 15 W) on the electrodeposition of Ni from a Watts bath (with/without an unspecified brightener). In this case, the authors reported that the grain size of the deposit varied as a function of ultrasonic power for each frequency (the effect being more evident in the presence of a brightener). These researchers also showed how the distribution of pressure nodes/antinodes along the substrate being plated had a strong influence on the surface morphology and hardness of the coating. Sulitanu et al. [20] evaluated the effect of high-frequency ultrasound (2000 kHz) at different powers (1 to 10 kW/m^2) in a sulphate bath with a brightener. In this latter case, increasing ultrasonic power did not only seem to have a grain refinement effect, but also an enhancement of the kinetics of the electrodeposition process in terms of higher limiting currents. Nevertheless, low-power, high-frequency ultrasound was the best way to reduce the roughness of the deposits.

It can be seen that none of the studies on the use of low-frequency ultrasound ($\leq$100 kHz) systematically studied the effect that the ultrasonic power could have on the characteristics (visual appearance, crystal orientation of the deposits, surface morphology, grain structure and hardness) of electrodeposited Ni coatings [13–17]. In this sense, the effect of ultrasonic power on the characteristics of the Ni coatings electrodeposited under low-frequency ultrasound may be completely different than the same under high-frequency ultrasound, especially if one takes into account how different ultrasonic cavitation is (both mechanical and chemical effects) depending on the operating frequency [21,22]. Therefore, due to the lack of studies of how ultrasonic power may affect the characteristics of Ni coatings electrodeposited under low-frequency ultrasound, we here present a study focused on the effect of low-frequency ultrasound on the characteristics of thin Ni coatings electrodeposited from a Watts bath currently used in industry. The effect of the ultrasonic power on the visual appearance, crystal orientation, surface morphology, grain structure and hardness of the Ni deposits was evaluated, showing that ultrasonic power had an effect on all these properties. This paper discusses all these responses in detail and defines how low-frequency ultrasound (and the occurrence and nature of ultrasonic cavitation near the surface being plated) influences the characteristics of ultrasound-assisted electrodeposited thin Ni coatings.

2. Materials and methods

2.1. Experimental set-up

For this study, an additive-free Watts bath was chosen as the plating solution (Table 1). This Watts bath, which is currently used in industry for preparing thin Ni coatings analogous to the ones here presented, is a kinetics-controlled process with a cathode current efficiency higher than 90% when operated at a current density of 4 A/dm^2. This means that current plating rate is not affected by any enhancement in mass transport from the bulk solution to the cathode/electrolyte interface by mechanical or ultrasonic agitation, as demonstrated by Hyde and Compton [23] for different electrodeposition processes carried out in highly concentrated and highly conductive plating baths.

Table 1
Ni Watts process 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
Plating conditions	
pH	3.2
Temperature	50 °C
Current density	4 A/dm^2

C106 Cu substrates (5 × 2 × 0.12 cm, 99.9% of Cu) were used as cathodes with an approximate active area of around 4 cm^2 (2 × 2 cm with the back side masked), while Ni anodes (7 × 1.4 × 0.05 cm) with an approximate active area of 20 cm^2 were fabricated from 201 Ni sheets (99.0% of Ni). The plating time was 14 min in order to produce Ni coatings with a thickness of around 5–6 μm in the central area of the active surface after considering edge build-up near the edges of the active area of the cathode. In order to achieve a good adhesion between the substrate and the electrodeposited coating, the substrates were vapour-degreased for 15 min in a Dürr Ecoclean degreaser and the cathode surface was activated with an anodic acid etching process (Cu substrate acting as an anode in a solution of 30% by volume of HCl at 3 A/dm^2 for 90 s) right before the electrodeposition process.

All the electrodeposition experiments were conducted in a 600 mL beaker containing 500 mL of the plating solution immersed in an ultrasonic bath as shown in Fig. 1. The beaker was always placed in the centre of the bath at a controlled depth (around 11 cm between the bottom of the beaker and the surface of the water) with a constant water level (around 2 cm between the edge of the ultrasonic bath and the surface of the water) in the ultrasonic bath to ensure the reproducibility of the experiments. The distance between the cathode and the anode was around 8 cm. The bath was a QS12 ultrasonic bath operating at a frequency of around 32–38 kHz (ultrasonic transducer power: 200 W, heating power: 300 W, working capacity: 12.5 L) provided by Ultrawave. This ultrasonic bath had a built-in thermostat, enabling the control of temperature up to 70 °C. The QS12 ultrasonic bath was calibrated by the calorimetric method [24–26]: for ultrasonic output powers of 60%, 80% and 100%, the estimated ultrasonic power inside the 600 mL beaker, once immersed in the ultrasonic bath and placed in the designated area, was 0.011, 0.124 and 0.180 W/cm^3, respectively. This set-up (ultrasonic bath) was chosen instead of a different one based on an ultrasonic horn due to different reasons [27]:

- Ultrasonic baths are widely available at a much lower cost than horns (Langevin transducers such as those used in submersible transducer units widely used in industry for different purposes share the same basic design than those used in ultrasonic baths).
- Cavitation phenomena are less violent and more uniformly distributed within an ultrasonic bath due to lower attenuation of ultrasound by cavitation than in horn-like systems.

An IPS2010 power supply unit (0 to 20 V, 1 to 10 A) from ISO-TECH was used as the rectifier, while a CAT R18 85 W overhead stirrer (110 to 2000 rpm) equipped with a 3-point propeller shaft (50 mm wide) was used in the electroplating experiments conducted under mechanical agitation. Ni deposits were produced under five different agitation conditions: silent/still (absence of agitation/ultrasound), mechanical agitation at 300 rpm, and ultrasonic irradiation at 0.011, 0.124 and 0.180 W/cm^3.

2.2. Characterisation of the coatings

Different methods were used to characterise the electroplated Ni coatings. X-ray diffraction (XRD) analysis was performed on the coatings with a Bruker D8 ADVANCE equipment to determine the effect of ultrasound on the growth direction of the crystals during the electrocrystallization, while detailed characterisation of the surface morphology and coating structure of the Ni deposits was carried