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Chronoamperometric And Structural Studies Of Potentiostatistically Deposited Nickel In Presence Of Ultrasound

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Abstract:

The influence of ultrasonic irradiation on the electrodeposition of Ni from chloride baths has been analyzed. The relationship between the deposition potential and deposit morphology and habitat at relatively high deposition times has been established.

Keywords: Nickel, Electrodeposition, Ultrasound, Chronoamperometry, AFM

1. Introduction:

Electrodeposited Nickel has been used for various applications, such as transport, decorative coating, service apparatus, and functionally suitable metal coating for its improved surface finishing, corrosion resistance, and wear properties [1, 2]. The nucleation and growth of Nickel depends on the deposition parameters such as P^H, concentration of electrolyte, temperature, types of bath, current density, types of substrate, deposition potential [3-10]. It is generally accepted that the growth of deposits during electrodeposition is influenced first by the substrate and then this influence disappears by the deposition condition [11]. Therefore an understanding and control of the factors governing the morphological, structural and properties of metal deposits is of significant importance.

Moreover, the deposition of metals under the influence of ultrasound has received significant attention, as sonication is thought to confer various benefits over conventional silent electrodeposition [12, 13]. The use ultrasound irradiation during the deposition generates a specific agitation resulting from the cavitation phenomena, which occurs both on the surface and in the liquid [14]. The effect of ultrasound upon an electrochemical system may be predicted, a general improvement of hydrodynamics and movement of species [15]. The high rates of mass transfer are only encountered when an electrode is placed close to (< 5mm) the surface. In this region the pressure field produced dictates the highest likelihood of the generation of inertial cavitation [16]. Sonication leads to a decrease of cathodic overpotential and increasing exchange current density [17-20], and thus are expected to affect the structures and thus properties of nickel electrodeposits.

In this paper, nickel deposition from a chloride bath prepared potentiostatistically at various overpotentials on brass electrodes under ultrasonic irradiation is discussed. The principal advantage of chloride bath is its ability to operate effectively at high cathode overpotentials. Other advantage includes its higher conductivity, its slightly better throwing power, and a reduced tendency to form nodular growth on edges. However the deposits from Chloride bath re highly stressed [21] than the deposits from other conventional baths. Hence, a stress free deposit with superior topography and smoothness are anticipated and thus explored in the present paper. A comparison between the behavior predicted in absence and presence of ultrasound are predicted by X-Ray diffraction (XRD), scanning electron microscope (SEM) and atomic force microscope (AFM).

2. Experimental:

Analytical grade $NiCl_2.6H_2O$ (200 gl^{-1}), NaCl (36.88 gl^{-1}) and Boric acid (8 gl^{-1}) are used for the electrolyte preparation for the Nickel deposition. The solution is prepared with doubly distilled water. Nickel is electrochemically deposited on the Brass substrate of an exposed surface area of 0.0625 cm^2. Prior to each experiment, the plates are polished to mirror finish and then cleaned in an ultrasonic cleaner (20 kHz frequency) for 10 minutes. The Electrochemical experiments were performed with a potentiostat/galvanostat (Eco Chemic Netherland, Autolab PGSTAT 12) system having computer interface of GPES software. A standard three-electrode cell is assembled. A Pt rod of 5 cm long as counter electrode, and an Ag/AgCl reference electrode is used. Morphological studies of prepared samples are performed by means of SEM (JEOL 6480LV) and AFM (Veeco diInnova). The phase analysis is done with XRD (Philips x-pert MPD), and the patterns are recorded from 40-100° at a scanning rate of 1°/Min with CuKα radiation.

3. Results And Discussion:

3.1. Chronoamperometry

The Chronoamperometric diagrams of Ni electrodeposition on the Brass electrode prepaired in silent and sonication conditions are given in figure 1. The silent transients exhibit initial sharp decay due to nucleation and growth. However, the nucleation times are short. At more negative potentials, there is pronounce current decay that is typical of planar diffusion-controlled growth. However, the current does not decrease as fast as predicted by the Cottrell equation, indicating mixed diffusion/kinetic control. Now discussing the cavitational transients, they differ significantly. The curve of −0.6 V resembles the silent transients. A morphological study may support the plateaus, as discussed in the next section. For the potentials −1 and −1.4 V, the shape of the curves is highly irregular consisting of batches of nucleation and growth couples. This may be due to crystal fragmentation as observed by Mallik et. al.[]. In order to determine whether these changes are reflected in the deposit morphology, SEM and AFM were performed and mentioned in the next sections.

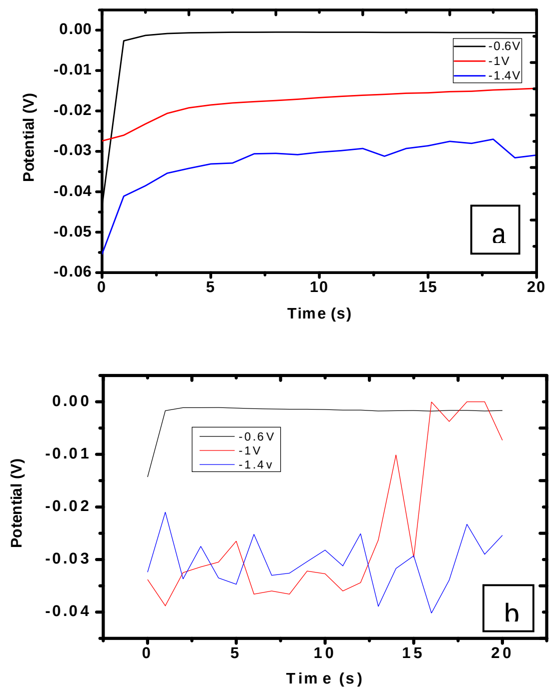


Figure 1: Current transients for Ni electrodeposits in (a) silent and (b) ultrasonic conditions

3.2. Characterization

XRD analysis:

The XRD patterns of the samples synthesized at different deposition potentials are as shown in figure 2. Decrease in either domain size or lattice strain will cause effective broadening of diffracted peaks. The peak pattern shows high crystallinity of nickel along with peaks from the substrate material. Average crystallite size of nickel deposit varies from 97 to 27 nm. Whereas the strain level varies from 0.03 to 0.07.

Microscopic Analysis:

Figure 3 shows the SEM topographies of nickel deposits both in presence and absence of ultrasound at different potentials. It is found that deposition potential strongly affects the density of Ni nuclei, their size, habit and the surface coverage. Indeed, an increase in both the number of nuclei and surface coverage is observed upon shifting the potential to more negative values in silent condition. The crystal habit changes from the fine rice like morphologies to spheroids and finally to well agglomerated Ni covered fully on the brass surface. The crystalline rice shaped particles are aligned in various directions. The increase in Ni loading and in nuclei population, observed when E_{dep} is made more negative, results in

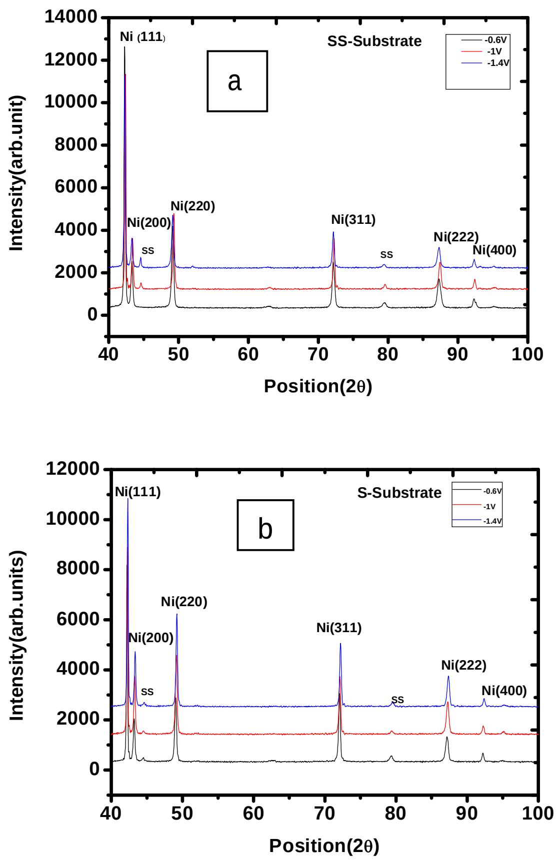
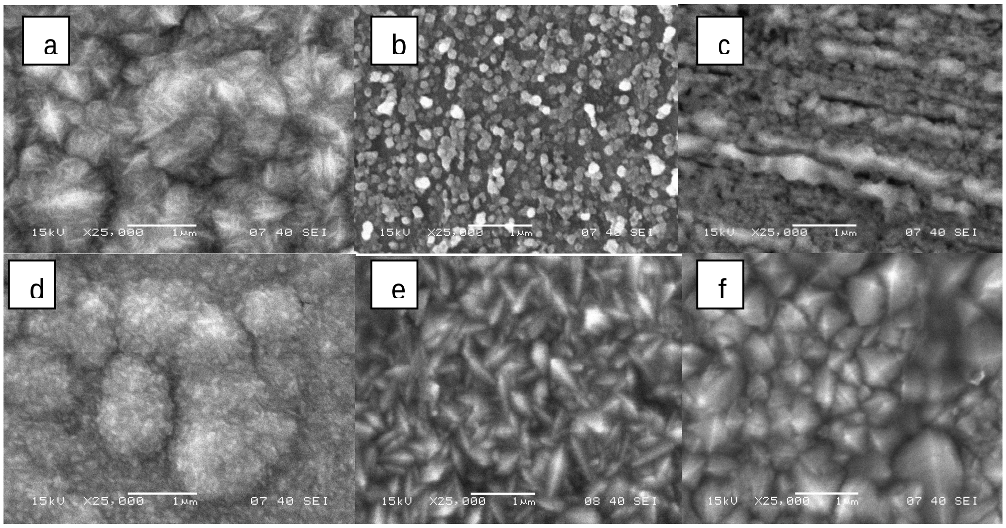


Figure 2: XRD plots of Ni deposition for (a) Silent and (b) Sonication conditions

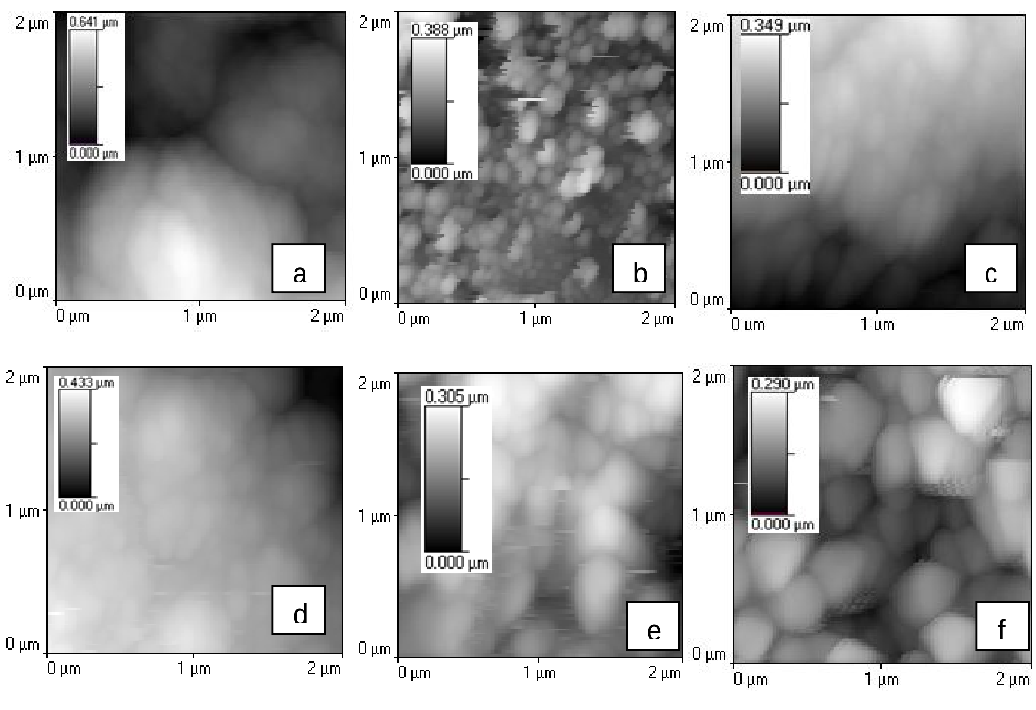
a decrease in the distance between two neighbouring nuclei which favors the planar diffusion and the growth is then diffusion controlled. In the case of a complete coverage of the surface, the electrodeposition of Ni follows two different mechanisms. Firstly, the deposition occurs on the bare brass surface and the first Ni nuclei are formed. In the initial stage Ni is deposited preferentially on the surface steps and on the defects. Afterwards the nuclei population density increases and the deposit expands on the totality of the surface. Secondly a continuous deposition of Ni occurs on the freshly deposited grains. On the other hand, insonicated Ni deposits have an opposite trend in terms of grain size and shape. The deposits are found to have bigger grains with increasing negative potential. The surface morphology has been markedly affected by the presence of ultrasound. The SEM image at −1 V shows spindle like morphologies with well visible facets. The spindles are agglomerated together; however with increase in deposition overpotential they tend to resolve into well defined shape and attain larger sizes. Indication of the transfotmation of the spherical nanocrystallites into the visible faceted grains was witnessed and expected to be the consequence of the sonication environment. This leads us to advocate and argue that the nucleation dominating effect of acoustic cavitation may not have taken place here. One possible explanation is that the fast diffusion along with the potential driven supersaturation has permitted the growth of the nuclei. Further, the shock wave generated during the cavitation sequence might have caused the fragmented secondary particles (if any) to collide into one another with great force, producing crystal clustering. Such characteristics results have not yet been obtained in the traditional nickel plating without any additives.

The average size and roughness of the synthesized Ni films are investigated here in detail by AFM (Figure 4). Though the grain size exploration from SEM studies is further complimented by AFM analysis, the roughness of deposition has decreased in presence of ultrasound for all the deposition potential. Detail analyses of the deposits are given in table 1.



−0.6 V **−1 V** **1.4 V−**

Figure 3: SEM images of Ni deposits for (a-c) Silent and (d-f) Sonication conditions



−0.6 V **−1 V** **−1.4 V**

Figure 4: AFM images of Ni deposits for (a-c) Silent and (b-d) sonication conditions

Table 1 Measured population density, grain size and roughness factor of Ni deposits

E_{dep}(V)	Av. Roughness (nm)		Critical diameter (nm)		Population density (cm^{-2})	
	Silent	Sonication	Silent	Sonication	Silent	Sonication
−0.6	132	63	70	99	6.525×10^{7}	2.5×10^{7}
−1	98	46	59	112	6×10^{8}	1.4×10^{8}
−1.4	60	45	27	127	8.5×10^{8}	3.5×10^{8}

4. Conclusion

Chronoamperometry, SEM and AFM studies have been carried out for Ni electrodeposition from $NiCl_2.6H_2O$ (200 gl^{-1}), NaCl (36.88 gl^{-1}) and Boric acid (8 gl^{-1}) chloride bath onto brass under ultrasonic irradiation at 55 °C. Depositions under silent conditions have the conventional tendency of decreased nuclei size and hence increased population density with elevated deposition potentials. However, we observed an opposite tendency but smoother depositions for Ni topography under ultrasonic irradiation. This could be the clustering tendency aspect of the cavitation mechanism by the generated shock waves.

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