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Magnetic Field Effects on Electrodeposition and The Properties of Electrodeposited Nickel and Nickel-Copper

by

Cora O' Reilly

A thesis submitted to The University of Dublin in application for the degree of Doctor of Philosophy

Department of Physics University of Dublin Trinity College

October 2003
DECLARATION

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O'Kelly
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And thanks to Hugo.
Summary

The association of magnetism and electrodeposition is studied from two separate perspectives. Firstly the effect of an applied magnetic field on the deposition process and secondly the production of magnetic materials by electrodeposition.

The effect of magnetic field, applied parallel to the electrode during electrodeposition, on chronoamperometric current transients was investigated for a range of metals with different valence and different magnetic susceptibilities: Ag/Ag⁺, Zn/Zn⁡²⁺, Bi/Bi³⁺, Cu/Cu²⁺ and Ni/Ni²⁺. A range of potential steps was investigated for all metals. In all cases an enhancement of the steady state limiting current is observed only when the potential step is into the mass transport region. The enhancement ranges from 30%-65 % and reduces significantly when the field is applied perpendicular to the electrode. In all cases, except that of nickel, the diffusion coefficient of the ions is not affected. The enhancement can be explained by induced convection in the system serving to reduce the diffusion layer thickness. The Lorentz force acting on the moving ions and the field gradient force acting on the magnetic properties of the ions in solution are responsible for the induced convection. In addition a damping force in highly conductive solutions and the viscosity of the solution play an important role in determining the degree of enhancement. In the nickel system, the diffusion coefficient was decreased with the application of a magnetic field at high overpotentials. This could be accounted for by the increased effective area due to the repulsion of diamagnetic hydrogen in the high field gradient close to the magnetised nickel electrode surface and the removal of hydroxide from the vicinity of the electrode by magnetically induced convection.

The electrodeposition of bulk nickel foils was carried out from three baths; a simple sulphate bath, a citrate bath and a Watts bath. Fcc crystal structure was obtained from
X-ray diffraction for all deposits. The deposits from the citrate bath showed a change of properties upon a mild heat treatment of 300°C: a reduction in resistivity of 25% and an increase in the saturation magnetisation of 8%. The absence of any outgassing of the samples or any increase in the lattice parameter upon heat treatment ruled out the presence of hydrogen in the deposit. It was found by SIESTA charge density calculations that the most likely source of such instability is the presence of small amounts of carbon taking up interstitial positions in the nickel lattice. This is supported by Auger analysis of the deposits. No effect of heat treatment was observed for deposits from the sulphate or Watts baths.

Ferromagnetic Ni-Cu alloys were potentiostatically deposited from similar baths with the addition of copper sulphate to control the copper composition of the alloy. X-ray diffraction patterns and scanning electron micrographs showed that segregated copper growth occurred with the addition of greater than 0.015 M CuSO\textsubscript{4} in the sulphate bath, immediately from the Watts bath and not at all from the citrate bath. All deposits showed a nickel rich under-layer, a feature of the electrodeposition process. The electrodeposits from the citrate bath showed a copper rich top-layer. Curie temperature measurements of these deposits suggested that the electrodeposits consisted of a range of copper concentrations with pure nickel particles also present. Anisotropic magnetoresistance of the deposits was 2% and the magnetisation values were below those expected in the as-deposited state.
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Chapter 1

The Electrodeposition of Metals
1.1 Introduction

The deposition of a metal onto a substrate by placing it in solution and passing a current is a remarkable process. No elaborate high temperature, vacuum or high voltage power supplies are needed. The appropriate selection of solution and current can give materials of outstanding properties with great versatility. It is a cheap, quick and easy-to-do process that has a fascinating science relating to both solid state physics and physical chemistry.

The electrodeposition of metals has been carried out as an industrial activity for over 150 years. One of the first applications was in the electroforming of printing plates in the mid 19th century. Since the early days electrodeposition has provided a cheap and versatile method for metal finishing for decorative reasons and, more crucially, to enhance the corrosion resistance of materials. These uses still dominate today. However, electrodeposition is now also a vital part of the modern microelectronic fabrication process. It is used to form interconnects between devices via damascene copper plating into vias. It is also one of the main processes involved in producing write heads for magnetic data, being used for the fabrication of the pole pieces and copper coils. Micro electromechanical systems (MEMS) more recently have opened up to electrodeposition as a means of producing high aspect ratio devices with the LIGA (Lithographie, Galvanoformung und Abformung) processes being developed. Future applications lie in the use of electrodeposited multilayers as magnetic sensors and electrodeposited nanostructures in nanotechnology applications.

Needless to say electrodeposition is a well studied phenomena. The fundamental science of the process stems from the more general field of electrochemistry. The science of electrochemistry began with Galvani’s observation in 1791 of a twitching frog’s leg when it was placed between two metal pieces. Volta attributed this to the moist connection between
the metal pieces and in 1799 built a Voltaic pile - the first alkaline battery. In 1834 Faraday
developed the empirical law relating charge passed with deposited mass and Tafel in 1905
empirically related interface potential difference to the current flow. Lewis’s development
of chemical thermodynamics in 1923 led to the idea of standard reduction potentials and
Nernst related these to the chemical parameters of a particular system. Scientists then be­
gan considering the kinetics of electrochemical reactions and reaction mechanisms. This then
lead to theoretical derivations of many of the empirical laws previously established, the most
famous of which is the Butler-Volmer Equation developed in 1920’s. Recently the science
has become an interdisciplinary subject covering topics such as charge transfer processes, in­
terfacial chemistry, solution chemistry, surface science, crystal growth, hydrodynamics and
many more.

The concept of metal electrodeposition is quite straightforward. It is simply the reduc­
tion of the metal ion in solution to a solid.

\[ M^{n+}_{(aq)} + ne^- \rightarrow M(s) \]  \hspace{1cm} (1.1)

The reaction is facilitated by the supply of electrons, from a power supply, to a cathode
onto which the metal atoms adhere. A typical electrochemical cell has a cathode, where
electrons are consumed, an anode, where electrons are donated and a conducting solution,
the electrolyte, which consists of both reacting and other non-reactive ions. The anode and
the cathode are connected via a power source which can apply a potential difference between
them and allows the electrical circuit to be completed. The power supply or potentiostat
can have quite sophisticated electronics allowing precise measurement and control of current,
potential and period for which they are applied. The deposition involves three main steps:
i) the movement of the metal ion to the cathode, ii) the reduction of the ion at the cathode
surface and iii) the addition of the metal atom to the solid lattice. The structure of the interfacial region is first discussed and then each of these processes in turn.
1.2 The Interfacial Region.

If a charged metal electrode is placed in an ionic solution there will be rearrangements of the ions in the solution around the electrode to the most energetically favorable formation such that there is a compensating excess of charge in the solution leading to a neutral interfacial region. A number of models have been developed to explain how the structure of the interfacial region accounts for the electrostatic behaviour of the electrode.

1.2.1 Helmholtz Model

The simplest and earliest model is the Helmholtz compact double layer model which assumes that this excess charge all lies in one plane parallel to the metal surface and at a distance determined by the hydration sphere attached to the ions. This is a simple capacitance model where the capacitance $C_H$ is given by,

$$C_H = \frac{\varepsilon}{4\pi d}$$

$\varepsilon$ being the dielectric constant and $d$ being the distance between the layers. This model is shown in Figure 1.1(a). This simple model does not however explain the dependence of the capacitance on the potential of the electrode or on the concentration of ions in the solution.

1.2.2 The Gouy-Chapman Diffuse Charge Model

The Gouy-Chapman diffuse charge model proposes that the excess charge in the solution is not held strictly within a fixed distance from the metal surface but falls off according to a Boltzmann distribution; therefore the charge density at a distance $x$ from the electrode is given by $\sum_i c_i^\infty n_i e^{-\frac{nee(x)}{k_bT}}$ where $c_i^\infty$ is the number of ions of species $i$ per unit volume in the bulk, $n$ is the valence of the ion, $e$ is the electronic charge, $k_b$ is the Boltzmann con-
stant and $T$ is the absolute temperature. $\psi(x)$ is the local potential at a distance $x$ from the electrode surface, derived from Poisson equation and described by $\psi(x) = \psi(0)e^{-\kappa x}$ where 

$$\kappa = \left( \frac{8\pi e^2 n^2 c^\infty}{\varepsilon k_b T} \right)^{\frac{1}{2}} \kappa^{-1}$$

is taken as the characteristic thickness of the diffuse layer. This theory predicts a parabolic capacitance-potential relationship,

$$C_{GC} = A\sqrt{c^\infty \cosh \left( \frac{e\psi_{Max}}{k_b T} \right)} \quad (1.3)$$

where $A$ is a constant and $\psi_{Max} = \psi(x = 0)$. This is shown in Figure 1.1(b). This theory however only explains the behavior at low potentials and in dilute solutions.

1.2.3 **Stern Model and Triple Layer Model.**

Stern in 1924 introduced a hybrid theory of Helmholtz and Gouy-Chapman where he considered the excess charge being divided into two types: $q_H$, tightly bound charge in a single plane close to the metal, the Helmholtz plane and $q_{GC}$, charge distributed beyond this in a diffuse layer, leading to an effective capacitance $C$ where $\frac{1}{C} = \frac{1}{C_H} + \frac{1}{C_{GC}}$. At low concentrations $C_{GC}$ is small according to Equation (1.3) and thus the capacitance is dominated by this, at high concentrations $C_{GC}$ is large and the capacitance is dominated by $C_H$. This model is further refined by considering that ions in solution can have various degrees of hydration and therefore some ions can move closer then others, leading to an inner and outer Helmholtz layer or the inner and outer planes of closest approach. Due to the dipole nature of water dehydrated adsorbed anions are found at the inner Helmholtz layer. This model is known as the triple layer model and was proposes by D. C. Grahame in 1947. These models are shown in Figure 1.1 (c) and (d).
Figure 1.1. Schematic showing the structure, capacitance models and potential variation with distance of the various models of the interfacial region [1].
1.3 Kinetics of Homogeneous Electron Transfer

If the cathode and anode are placed in a electrolyte solution but no external potential is applied, thermodynamic equilibrium is achieved between the electrodes and the solution, Equation(1.1) is occurring in both directions at the same time. The system is in dynamic equilibrium. This is illustrated in Figure 1.2. In order to determine the current flowing in either direction we consider first one direction only; the reduction process. During the reduction reaction the oxidized species will migrate across the interfacial region at the rate, $v_o$, given by the Arrhenius expression $v_o = A e^{E_a/RT}$ where A is the frequency factor which is related to the concentration of the species at the interface $c_Q^O$. The activation energy, $E_a$, is the standard free energy of this migration process, $\Delta G$. Therefore

$$v_o = \frac{k_b T}{h} e^{\Delta G/kT} = k_R c_Q^O$$  \hspace{1cm} (1.4)$$

where $h$ is Plank’s constant, $R$ is the gas constant and $k_R$ is the rate constant for the reduction process. As was discussed in the previous section there is also a potential which
migrating ions have to overcome. The rate of migration now becomes

\[ \nu_0 = k_R c_0^0 e^{-\frac{\beta \Delta \phi_e}{RT}} nF \]  

(1.5)

where \( \beta \) is the symmetry factor related to the fraction of the potential barrier, \( \Delta \phi_e \), that acts on the migrating ion, \( n \) is the number of electrons involved in the reaction and \( F \) is Faradays constant \((96500 \text{ C Mol}^{-1})\), the amount of charge per mole of electrons. This rate gives the cathodic current, \( j_R \)

\[ j_R = nF k_R c_0^0 e^{-\frac{\beta \Delta \phi_e}{RT}} nF \]  

(1.6)

Similarly for ions migrating in the opposite direction

\[ j_O = nF k_O c_0^0 e^{-\frac{\beta \Delta \phi_e}{RT}} nF \]  

(1.7)

The total current flowing is

\[ j = j_O - j_R = nF k_O c_0^0 e^{-\frac{\beta \Delta \phi_e}{RT}} nF - nF k_R c_0^0 e^{-\frac{\beta \Delta \phi_e}{RT}} nF \]  

(1.8)

At equilibrium there is no net current flowing, therefore \(|j_R| = |j_O| = j_0\) where \( j_0 \) is known as the equilibrium or exchange current density. If an additional potential drop or overpotential, \( \eta \) is applied to the interface, then the total overpotential \( \Delta \phi = \Delta \phi_e + \eta \) and the resulting current is:

\[ j = j_0 (e^{\frac{(1-\beta)\eta F}{RT}} - e^{-\frac{\beta \Delta \phi_e}{RT}}) \]  

(1.9)

This equation is known as the **Butler-Volmer Equation**.

If we assume that the rate constants \( k_R \) and \( k_O \) of Equation (1.6) and (1.7) are equal and denote them as \( k_0 \) and also acknowledge that while the system is in equilibrium the concentration of ions in the bulk is equal to the concentration at the interface \((c_R^0 = c_R^\infty)\).
By equating Equations (1.7) and (1.8) we can relate \( j_0 \) to bulk concentrations \( c_R^\infty \) and \( c_O^\infty \):

\[
j_0 = nFk_0 \left( c_R^\infty \right) ^\beta \left( c_O^\infty \right) ^{1-\beta} \tag{1.10}
\]

The Butler-Volmer equation now becomes the more general current density-overpotential equation.

\[
j = j_0 \left[ \left( \frac{c_O}{c_R} \right) e^{\frac{(1-\beta)\eta nF}{RT}} - \left( \frac{c_R}{c_O} \right) e^{\frac{-\beta nF}{RT}} \right] \tag{1.11}
\]

The first term representing the reduced species being oxidized; the anodic current density, and the second representing the oxidized species being reduced; the cathodic current density.

Cathodic: \(|j| = j_0 \left( \frac{c_O}{c_R} \right) e^{-\frac{\beta nF}{RT}} \quad \text{Anodic: } |j| = j_0 \left( \frac{c_R}{c_O} \right) e^{\frac{(1-\beta)\eta nF}{RT}} \tag{1.12}\]

The Butler-Volmer equation has two limiting cases, the first when the overpotential is low, then \( \frac{\beta nF}{RT} \ll 1 \) and the expansion of the exponential term can be limited to the first term in the expansion\(^1\).

\[
j = j_0 \frac{nF}{RT} \eta \tag{1.13}
\]

This corresponds to the linear region of the Butler-Volmer Equation. The second limiting case occurs if the applied overpotential is sufficiently negative (<-0.1V) and the cathodic current density dominates or when it is sufficiently positive and the anodic current density dominates. The anodic and cathodic equations (1.12) can then be written with the overpotential expressed as a function of the current which leads to the Tafel equation in both cases.

\[
\eta = a \pm b \log |j| \quad \text{where } a = \frac{2.303RT}{\beta nF} \log |j_0| \quad \text{and } b = \frac{2.303RT}{\beta nF} \tag{1.14}
\]

A plot of \( \log |j| \) vs \( \eta \), known as a Tafel plot, allows the determination of \( \beta \) from the slope and the exchange current density, \( j_0 \), from the intercept. The Butler-Volmer equation can

\[^1\epsilon^2 = \sum_{n=0}^\infty \frac{x^n}{n!} = 1 + x + \frac{x^2}{2} + \frac{x^3}{6} + \ldots\]
also be used to determine the equilibrium potential of electrochemical system. By equating (1.6) and (1.7) we can arrive at
\[ \Delta \phi_e = \Delta \phi_e^0 + \frac{RT}{nF} \ln \frac{c_0^\infty}{c_R^\infty} \] (1.15)
\[ \Delta \phi_e^0 \] being the potential drop across the interface when the \( c_0^0 \) and \( c_R^0 \) are unity. This equation gives the equilibrium potential across an interface due to the two-way reaction of the metal ions. It is called the Nernst Equation and can also be derived from thermodynamic reasoning.

The standard Gibbs free energy, \( \Delta G^0 \), of this reaction is expressed as the potential across the interface i.e. \( \Delta G^0 = -nF \Delta E^0 \). Using the thermodynamic relation, \( \Delta G = \Delta G^0 + RT \ln Q \) also leads to the Nernst equation:
\[ E = E^0 + \frac{RT}{nF} \ln Q \] (1.16)
where \( Q \) is the reaction quotient - which can be simplified to the ratio of concentration of reactants to products if the concentration is low, at higher concentrations the ion-ion interactions need to be considered and the activities of the ions are used to determine the reaction quotient. \( \Delta G^0 \) and \( E^0 \) refer to the respective values under "standard" conditions, i.e. when the activity of all chemical species is unity and the system is at 1 atm. and 25°C.

The Nernst equation describes the rest potential of the system - it is in equilibrium. Since this work is concerned with electrodeposition, we will primarily be concerned with reduction processes rather than oxidation.

Because an electrochemical system always has two electrode reactions associated with it, the reduction and oxidation processes, the standard reduction potentials of a single process cannot be measured directly - a standard electrode reaction is considered against which the potential of all others can be measured. This standard electrode reaction is \( 2H^+_{(aq)} + 2e^- \rightarrow 2H_2 \).
$H_2(g)$ \uparrow, the standard hydrogen reaction (SHE). Standard reduction potentials tell us the thermodynamic favourability of a reaction i.e. sodium is not easily reduced, silver on the other hand will do so readily.

<table>
<thead>
<tr>
<th>Electrode Reaction</th>
<th>Standard reduction potential / V</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Ag^++e^- \rightarrow Ag$</td>
<td>0.7996</td>
</tr>
<tr>
<td>$Cu^{2+}+e^- \rightarrow Cu^+$</td>
<td>0.3402</td>
</tr>
<tr>
<td>$2H^++2e^- \rightarrow H_2 \uparrow$</td>
<td>0.000</td>
</tr>
<tr>
<td>$Ni^{2+}+2e^- \rightarrow Ni$</td>
<td>-0.257</td>
</tr>
<tr>
<td>$Co^{2+}+2e^- \rightarrow Co$</td>
<td>-0.280</td>
</tr>
<tr>
<td>$Ni(OH)_2+2e^- \rightarrow Ni+2OH^-$</td>
<td>-0.66</td>
</tr>
<tr>
<td>$Zn^{2+}+2e^- \rightarrow Zn$</td>
<td>-0.7628</td>
</tr>
<tr>
<td>$H_2O+2e^- \rightarrow H_2(g)+2OH^-$</td>
<td>-0.8277</td>
</tr>
<tr>
<td>$Na^++e^- \rightarrow Na$</td>
<td>-2.71</td>
</tr>
</tbody>
</table>

Table 1.1. Standard rest potentials of various reactions

The Butler Volmer equation determines the current density from the kinetics of the reaction. It assumes that the reacting ions are in constant supply to the electrode. This, however, is not the case. When the reaction proceeds at large overpotentials the kinetics of the reaction are quick. The rate determining step is no longer the kinetics but the mass transport of these ions to the interface region where they will react. This deviation of the observed current-potential from that predicted by the Butler-Volmer equation is illustrated in Figure 1.3.

Figure 1.3. Regions of the current-potential relation. Deviation of experimental observation from the Butler-Volmer relation is shown at high overpotentials
1.4 Mass Transport

Mass transport in the electrolyte can occur by three main processes, migration under the application of a electric field, diffusion of a species due to concentration gradients and convection within the system.

1.4.1 Migration

When an ion in solution experiences an electric field, $E$, a force, $F_m = neE$, acts on the ion. The ion attains a steady state velocity, $v_s$, rather than an acceleration due to collision with other ions in solution.

\[ v_s = \pm \mu E \]  \hspace{1cm} (1.17)

The flux of material is given by

\[ J = \frac{n c \infty F D}{RT} \nabla V \]  \hspace{1cm} (1.18)

where $\nabla V$ is the potential gradient in the electrolyte, $D$ is the diffusion coefficient of the ion and $\mu$ is the ionic mobility. However, because electrolyte solutions contain large amounts of ions, most of which do not take part in any electrode reaction but form a supporting electrolyte, the conductivity of the solution is often such that there is very little potential drop across it and the ions see little electric field except when they reach the charged double layer.

1.4.2 Diffusion

The electrochemical reaction that occurs at the electrode means that the electroactive species is consumed at the electrode. This generates a concentration gradient down which ions diffuse. This is referred to as the diffusion layer. The force per unit volume acting on these ions is $F_D = RT \nabla c$, $\nabla c$ being the concentration gradient. As the reaction proceeds
more and more of the species are consumed and the concentration gradient reaches further
from the electrode. The flux of a material, $J$, down this concentration gradient is governed
by Fick's first and second laws of diffusion $J = -D \nabla c$ and $-D \nabla^2 c = \frac{\partial c}{\partial t}$ which can be
rearranged to give $\nabla c = \frac{c_0 - c}{\sqrt{\pi Dt}}$. Assuming that the kinetics of the reaction are quick enough
for instant reduction at the electrode surface, i.e. $c^0 = 0$, and since $j = nFJ$

$$j = -nFc\sqrt{\frac{D}{\pi t}}$$

Equation (1.19) is known as the Cottrell equation. If we assume that the concentration
gradient is linear over the distance of the diffusion layer, $\delta$ (the Nernst diffusion layer model)
then since $J = \frac{j}{nF} = \frac{D\Delta c}{\delta}$ and substituting $j$ from (1.19) leads to an expression for $\delta$

$$\delta = \sqrt{\pi tD}; \quad j = -\frac{nFcD}{\delta}$$

(1.20a)

These equations describe how the diffusion layer varies with time and are illustrated in Figure

Figure 1.4. (a) Variation of concentration with distance from the electrode. (b) Evolution
of the concentration gradient with time during electrodeposition.

1.4. Eventually the spread of the concentration gradient is halted by convection within the
solution and a steady state for the limiting current density is achieved. Now Cottrell's
equation is no longer obeyed and the diffusion layer thickness stops growing. This current is
the maximum current that can be achieved at a given concentration and under the particular convection of a system. It is known as the limiting current density and often denoted as \( j_L \). If a larger current than the diffusion limited current is applied to the electrode the double layer becomes more charged until some other process gives rise to a current.

### 1.4.3 Convection

Convection arises either naturally, due to density differences in the solution or it can be forced, due to stirring of the solution for example. The forces causing convection will depend on the source. For natural convection due to gravity \( F_{cN} = \Delta \rho g \), where \( \Delta \rho \) is the change in density and \( g \) is acceleration due to gravity. Viscous drag, arising due to a fluid layers moving relative to one another, gives a convective force \( F_{cV} = \nu \nabla^2 v \) where \( \nu \) is the viscosity of the electrolyte and \( v \) is its velocity. The velocity gradients of the fluid associated with convection and the condition that fluid velocity is zero at the electrode surface will set up a hydrodynamic boundary layer \( \delta_H \) near the electrode surface as seen in Figure 1.5.

![Figure 1.5](image)

**Figure 1.5.** The hydrodynamic boundary layer \( \delta_H \) also showing the Nernst diffusion layer \( \delta \).

The hydrodynamic boundary layer \( \delta_H \) is defined to be the distance from the electrode within which all the velocity gradients occur. Beyond this the velocity of the fluid will be considered to remain constant. This main stream fluid velocity, \( U \), increases the concentra-
tion gradient of the reducing species close to the electrode by narrowing the diffusion layer. The diffusion layer thickness can be related to $U$ by [2]:

$$\delta \simeq D^{\frac{1}{3}} \nu^{\frac{1}{6}} \sqrt{\frac{x}{U}} \simeq 0.1 \delta_H .$$

(1.21)

where $x$ is the distance to the leading edge of the electrode. According to Equation (1.21) it is reasonable to assume that there is no convection within the Nernst diffusion layer. Forced convection can therefore be used to control $\delta$ and therefore $j_L$. 

1.5 Crystallization

The final stage of electrodeposition is the growth of a crystal onto the electrode. How this occurs can vary. If the electrode was an ideal crystal with a smooth surface a new layer would have to nucleate on its surface (2D nucleation) and then grow. However due to the vast array of crystal defects on a real surface, such as kink sites, step edges and dislocations, a monolayer does not have to nucleate but incorporation into the existing layer may occur. At low overvoltages the adjoining atoms will have little energy, slowly losing their hydrated molecules while diffusing along the surface to join the crystal in the easiest possible manner, normally at a kink site. As the overpotential increases, incorporation into the pre-existing crystal is now not the only option; a new monolayer may be formed by 2D nucleation or an entirely new crystal may be formed by 3D nucleation and subsequently grow. The speed at which new crystals form and then grow has a large bearing on the deposit’s properties such as crystalline size, morphology and texture.

Figure 1.6. The stepwise growth: (1) movement of hydrated ion to electrode, (2) partial dehydration and adsorption onto surface (3) Surface diffusion to step and further dehydration, (4) complete dehydration and addition into crystal lattice
1.5.1 Ion Incorporation and Step propagation.

The ion can deposit onto any site on the metal surface and diffuse to a step edge or transfer directly to the step edge. In the latter case if the surface diffusion penetration, $\lambda_s$, is greater than half the step distance, the current is independent of the step density and is given by the Butler-Volmer Equation (1.9) directly. If this is not the case then the current will depend on the step density $L_s$. If we assume that we are in the linear Butler-Volmer region then:

$$j = j_{0,ad} 2\lambda_s L_s \left( \frac{ne}{kT} \right) \eta = \kappa_{SD} L_s \eta \text{ where surface diffusion occurs and}$$

$$j = j_{0,ad}^t L_s \left( \frac{ne}{kT} \right) \eta = \kappa_{DT} L_s \eta \text{ where direct incorporation occurs}$$

where $j_{0,ad}$ is the exchange current density of adions and $j_{0,ad}^t$ is the exchange current density of step edge ions per unit step length, other symbols having their usual meaning. The propagation of steps in such a manner can lead to macroscopic features on the electrode-deposited material. One of these are macrosteps where the numerous microsteps catch-up with each other, their rates differing due to adsorbed impurities or other surface defects blocking growth. The steps bunch together to form macrosteps. Growth along screw dislocations lead to spiraling growth which join resulting in closed loop spirals.

1.5.2 Nucleation

Nucleation on the cathode follows similar physical laws to other systems such as evaporation. The free energy of formation of nuclei onto a substrate, $\Delta G(N)$, is given by

$$\Delta G(N) = -N ne \vert \eta \vert + \phi(N)$$

where $N$ is the no of atoms in the cluster and $\phi(N)$ is the excess free energy of the
cluster surface including the energy associated with the cluster-solution interface and the cluster-substrate interface. The form of $\Delta G(N)$ is shown to have a maximum value, $\Delta G_c$, 
\[
\left( \frac{d\Delta G(N)}{dN} = 0 \right) \quad \text{at } N_c.
\]
This is the critical size needed for a nuclei to be stable and is achieved by statistical fluctuations in the system energy. For the three-dimensional case the critical free energy for nucleation and the critical nuclei size are calculated using the Gibbs-Wulff-Kaischew theorem [3][4][5]. In these calculations consideration is given not only to the cluster-solution interface and the cluster-substrate interface energies but also to the overpotential. The free energy of formation of 2D nuclei considers periphery energies as opposed to surface energies.

The rate of nucleation, $A$, is given by Volmer and Weber as
\[
A = k_1e^{\frac{\Delta G_c}{kT}}.
\]
The nucleation rate is inversely proportional to the square of the overpotential for 3D nucleation or to the overpotential for 2D nucleation. Much of the theory of crystallization and particularly the theory of electrocrystallization is contained in a review by Budveski et al. [7].

At high overpotentials when the critical nuclei are only a few atom in size bulk values are no longer physically meaningful and an atomic approach has to be taken. $\phi(N)$ is taken to be the difference in disassociation energy of $N$ atoms from a kink site $N\varphi_{kink}$ and the dissociation energy of cluster atoms from themselves. The substrate $\psi_i$. $\Delta G(N)$ depends linearly on $\eta$. For high over voltages the frequency of attachments of atoms to the critical cluster, $\varpi$, will also become significant, $\varpi = e^{\left(\frac{N_c(1-\alpha)ne\eta}{kT}\right)}$, and has to be accounted for in the nucleation rate. The free energy of formation is now:

\[
\Delta G(N) = -Nne\left|\eta\right| + N\varphi_{kink} - \sum_{1}^{N} \psi_i \quad (1.25)
\]
leading to (for 3D nucleation) $A = ke^{\left(\frac{N_c(1-\alpha)ne\eta}{kT}\right)}e^{\left(-Nc\varphi_0 - \sum \psi_i\right)} \quad (1.26)$

These rate laws for the formation of nuclei have been confirmed experimentally by the double
pulse technique. A pulse at a given overpotential is applied, nucleation occurs and the time is measured for the current to start flowing, this is estimated to be $A^{-1}$ [8]. These nuclei can be further grown at a lower potential so that they are visible in a microscope, allowing the number of nuclei formed as a function of time to be determined.

1.5.3 Crystal growth

Once the nuclei have formed they must continue to grow, the rate of this growth will depend largely on their shape, and is directly seen in the change in current with time i.e. by the current transients after an applied pulse. The most widely studied system is the 3D nucleation and continued diffusion-limited growth processes of hemispherical growing centers. A large number of models have been developed relating the process to currents measured over time. These include the Scharifker Hill Model [9], the Scharifker Mostany Model [10] and the Heerman Tarallo Model [11]. These are all based on nuclei growth which is limited by the diffusion of atoms towards the nuclei centre and are reviewed by Hyde et al. [12]. The starting point for these models is the first order kinetic model of nucleation

$$N = N_0(1 - e^{-At})$$

(1.27)

where $t$ is the time since the potential was applied, $N$ is the number of nuclei, $N_0$ is the saturation nucleus density, i.e. the number of active sites. The models consider hemispherical diffusion towards nuclei and use Avrami’s theorem to treat the overlap of their diffusion zones. Each model is a refinement of the previous model considering mainly redefined diffusion zones and their degree of overlap. There are two extreme cases of crystal growth, the first known as instantaneous nucleation, where $A \to \infty$ i.e. a large amount of nuclei form immediately and the second, progressive nucleation, where $A \to 0$ i.e. nuclei form at a much slower pace.
According to the Scharifker Hill model these current transients follow the Equations:

\[
I = \frac{nFD^{1/2}c}{\pi^{1/2}t^{1/2}} \left[1 - e^{(-N\pi kDt)}\right] \text{ where } k = \frac{8\pi cM}{\rho} \text{ for instantaneous nucleation} \tag{1.28}
\]
\[
I = \frac{nFD^{1/2}c}{\pi^{1/2}t^{1/2}} \left[1 - e^{(-AN_{\infty} \pi k'Dt^2/2)}\right] \text{ where } k' = \frac{4}{3} \left(\frac{8\pi cM}{\rho}\right)^{1/2} \text{ for progressive nucleation} \tag{1.29}
\]

where M the molar mass and \(\rho\) the density of the depositing species. The first term of these equation is simply the Cottrell equation, Equation (1.19). The second is due to the overlapping diffusion zones of newly formed and growing nuclei and the modifications due to a spherical diffusion layer. It can be seen from these expressions that the current transient goes through a maximum, \(I_m\) at a time \(t_m\). The dimensionless plots of \(I/I_m\) vs \(t/t_m\) are often used to distinguish the two cases. Experimental data has been successfully fitted to such models [14].

\[
\left(\frac{I}{I_m}\right)^2 = \frac{1.9542}{t/t_m} \left\{1 - e^{[-1.2564(t/t_m)^2]}\right\}^2 \text{ for instantaneous nucleation} \tag{1.30}
\]
\[
\left(\frac{I}{I_m}\right)^2 = \frac{1.2254}{t/t_m} \left\{1 - e^{[-2.3367(t/t_m)^2]}\right\}^2 \text{ for progressive nucleation} \tag{1.31}
\]
Figure 1.7. Theoretical non-dimensional plots of $\left(\frac{t}{t_m}\right)^2$ for (a) instantaneous and (b) progressive nucleation[12]

The Scharifker Mostany model refines the above to a single equation describing both nucleation processes by redefining $k$ and considering diffusion layer growth only upon the appearance of nuclei. The Heerman and Tarallo models model the diffusion layer thickness as a function of nucleation rate and time, not a constant as is assumed in the Scharifker Mostany model. The Heerman and Tarallo model also incorporates the idea of Sluyters-Rehbach, Wijenburg, Bosco and Sluyters [13] of planar diffusion zones with uniform thickness.

There has been much development of the models of nucleation and growth where diffusion is the rate limiting step for growth. There is less to read on the modelling of the system when it is the charge transfer that is limiting the growth. One such model is that of Armstrong et al.[15] for the growth of right circular cones and Abyaneh [16] for the growth of hemispheres.
Figure 1.8. The current transients derived for the model of growth of (a) right circular cones and (b) hemispheres [17]

The shapes of each curve in Figure 1.8 above are quite different, showing a monotonic increase for growth of right circular cones and a maximum current for the growth of hemispheres. However it has been shown that both expressions fit equally well to experimental data for nickel and cobalt current transients [17]. This is due to hydrogen evolution which will interfere with the current transients from the metal nucleation. Both cases then can only be fitted to rising transients and provide similar nucleation rates. There is little experimental work to be found in which this model is applied. A model for mixed diffusion and charge transfer control was introduced by D’Ajello et al. where a reaction rate $k$ is considered along with diffusion [18].
1.6 Microstructure, Effect of Additives and Current Distribution

1.6.1 Microstructure

The speed at which new crystals form and then grow has a large bearing on deposit properties such as crystallite size, shape and texture. These properties can have a large effect on the mechanical, electrical and magnetic properties of the material. High current densities lead to mass transfer control of the current and small grain size. Any protrusion on the cathode surface is quickly amplified with time leading to fast and dendritic growth, this effect is illustrated in Figure 1.9 where the cause of the different growth rates on the surface is shown as is the effect on the morphology of the electrodeposit. Many interesting features are formed and in the extreme cases powder is formed. The practically important requirement for smooth planar electrodeposits involves avoiding this dendritic growth. The extent of mass transport control in the plating process can be determined by the plating current density as a fraction of the limiting current density or equivalently by the cation concentration at the surface as a fraction of the cation concentration in solution.

![Diagram](image)

Figure 1.9. (a) Effective thickness of diffusion layer, $\delta$, over micro-features (b) resultant in dendritic growth of electrodeposit.

Low current densities lead to slow near equilibrium growth which can result in near epitaxial film growth and large grain sizes. For intermediate current densities there have been many classifications of the growth structures; columnar, fine grained, fibrous and banded
(these are smaller grained high strength deposits usually plated with additives) is one classification [19]. While columnar, equiaxed (columnar growth with larger grains), dendritic, nodular (or cauliflower type) and fibrous are also used [20]. In general grain size is increased by increasing metal ion concentration, plating temperature and agitation and it is reduced by increasing overpotential, current density and additive concentration.

1.6.2 Additives

The major factors which affect electrodeposition have been discussed up to now. An additional factor, however, which is not necessarily related directly to electrochemical processes is the effect of foreign or non electro-active species on the current densities. These are known as additives and the vast majority of these act as inhibitors to the crystal growth. Inhibition will increase the exchange current density and their importance during deposition can be assigned to the ratio of the plating current density to the exchange current density. The effect of inhibition and mass transport on the crystal growth is illustrated in Winand's diagram shown in Figure 1.10 [21] using Fischer classifications of growth types [23]. Inhibitors act by being adsorbed onto a fraction of the cathode surface, normally at active sites such as kinks; these sites are then blocked as nucleation sites and also reduce the surface diffusion of adions. The sensitivities of metals to inhibitors will depend on their stability and are classed in Table 1.2 according to information from [21] and [22]. The inhibition effect of

<table>
<thead>
<tr>
<th>Metals</th>
<th>Class I Normal</th>
<th>Class II Intermediate</th>
<th>Class III Inert</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb, Sn, Cd, Zn</td>
<td>low</td>
<td>medium</td>
<td>high</td>
</tr>
<tr>
<td>Bi, Cu, Ag</td>
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<td>high</td>
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<td>medium</td>
<td>yes</td>
<td>10^{-12} &lt;j_o&lt;10^{-2}</td>
</tr>
<tr>
<td>no</td>
<td>no</td>
<td>10^{-2} &lt;j_o&lt;1</td>
<td>small</td>
</tr>
<tr>
<td>j_o&gt;1</td>
<td>large</td>
<td>medium</td>
<td></td>
</tr>
</tbody>
</table>

Table 1.2.Classification of metals according to behaviour in aqueous solutions.
**Figure 1.10. Different possible types of polycrystalline electrodeposits as a function of $J/C_{M^{++}}$ and inhibition intensity.**[21]

An adsorbed metal hydroxide layer is known as secondary inhibition and can be related to the pH of the electrolyte, other than this H⁺ ions are not considered to act as inhibitors. Inhibitors can be of many different forms varying from single inorganic anions and cations to large complex organic molecules. Inorganic cations such as Na⁺ and K⁺ have limited effect. Some anions can change the activation energy of electron transfer by influencing the double layer structure; ions known to do this are Cl⁻, Br⁻, and I⁻, which may have the opposite effect to inhibition. NO₃⁻ and SO₄²⁻ are weak inhibitors while NH₂SO₄⁻ and ClO₄⁻ are strongly inhibiting.

The effect of these inhibitors can have implication beyond that of crystal structure: they can be used to produce levelling and brightening of the deposit. Levelling is either (a) the progressive reduction of surface roughness (geometric levelling) or (b) a planar deposition.
between micro-features and surface (electrochemical levelling). Geometric levelling can be achieved without the use of additives when the deposition thickness of the deposit is equal or greater than the size of the surface features. Additives are necessary for electrochemical levelling where they are preferentially adsorbed onto areas where there would ordinarily be a high current density and inhibit deposition, allowing the slower growing areas to catch up. The quantity of additives in plating baths which perform these tasks is surprisingly small and each system has very specific additives that will work. Much of the information relating to inhibition is of an empirical nature. The brightening effect also arises from the use of additives, here the reduction of grain size to less than 0.4 \( \mu \text{m} \) and the orientation of crystals towards a light-reflecting plane are responsible for such an effect.

To achieve the effect of levelling and brightening, rather complex large, generally organic, molecules are used. They affect the bath in a number of ways. All levellers and brighteners are found to reduce the grain size of the deposit as the adsorbed molecules prevent surface diffusion of adions and also create disorder during incorporation of adions. This also means that a greater current density can be applied to the cathode while acceptable deposit morphologies are still obtained. The inhibiting effect of additives means that there is an increase in the polarization of the cathode at a given current density. It is also possible that additives can be incorporated into the deposit. There are two reasons for this to occur: 1) additives are adsorbed onto the surface in a dynamic equilibrium so if the rate of growth of the deposit is greater than the rate of adsorption/desorption they can be incorporated into the growing deposit and 2) if the additive chemically reacts on the cathode then the product can be incorporated into the deposit. This incorporation into the matrix of the deposit may affect the crystal structure of the deposit. Texturing of the crystal structure may
also be possible due to the preferential adsorption of the additive on a particular crystal face. The mechanism of these effects is described in more detail by Oniciu et al.[24]. Much work has been done to develop a system where copper can be plated in microvias where there is no void in the centre, this is known as the superfilling by the use of additives. The process of Damascene plating was developed [25] allowing for the copper metallization of interconnects for integrated circuits.

Much of the effect of additives on crystal structure by the blocking of sites where nucleation can occur is effectively a modification of the current distribution on the cathode. The current distribution can also be affected by many other parameters. In fact it could be said that the defect sites on the cathode surface such as kinks and dislocations are areas of high current density on a microscopic scale.

1.6.3 Current Distribution

In order to achieve a homogeneous deposit, a uniform distribution of current is needed on the cathode. Current distribution is a direct consequence of the potential distribution in the electrolyte. There are three significant components to the potential distribution; the polarization or potential (i) at the electrode, (ii) in the diffusion layer and (iii) in the bulk electrolyte. If the overpotential of the system was zero, then the current distribution would rely on the geometry of the cell. In such a case the area of the cathode nearest the anode would have a higher current density as would edges. This is known as the primary distribution. If a potential is applied to the cathode and the reduction takes place under kinetic control i.e. mass transport considerations are neglected, then the secondary current distribution prevails. This is always more uniform than the primary current distribution. The Wagner number, Wa, characterises the equalising influence of overpotential on the current
distribution and is defined as the ratio of the polarization resistance, \( \frac{\partial n}{\partial t} \), over the ohmic resistance of the electrolyte.

\[
Wa = \frac{\frac{\partial n}{\partial t}}{\rho_e L}
\]

(1.32)

\( \rho_e \) is the electrolyte resistance per unit length and \( L \) is the characteristic length of the system, normally the cell width. If the Wagner number is large (\( \gg 1 \)) and the reactions are kinetically controlled then the current distribution tends to be uniform. In the presence of significant mass transport the tertiary current distribution is in effect. This is determined by geometrical factors, electrode kinetics and mass transport. At the limiting current density the distribution of current is entirely governed by mass transport. On this macro scale, if the current efficiency of deposition decreases with increasing current density, due to the onset of a side reaction such as hydrogen evolution, as is often the case, an increase in the current density will not have too large an impact on the non-uniformity of the deposit. The geometry required to give a good primary distribution of current is normally very different to that which gives a good tertiary distribution. Many interesting cell designs have been developed in order to achieve predetermined current distributions, an interesting example of which is described by Landolt [26]. Much work has been done on the computational modeling of current distribution in specific cells [27].

Deposition onto patterned electrodes is of particular interest [27] [28] and current distribution is normally looked at on a number of different scales, the workpiece scale, the pattern scale, the feature scale and the roughness scale. The workpiece scale deals with current distributions over the entire electrode and is concerned with the same issues as current distribution on an unpatterened electrode discussed in the previous paragraph. The pattern scale considers the active area density effect where zones which have different densities of in-
sulating patterns yield different current distributions. The feature scale, in the micron region considers nonuniformities in mass transport due to geometric effects on the diffusion layer thickness. These considerations are also of foremost concern on the slightly smaller scale of roughness. Any protrusions are quickly amplified under tertiary current distribution. Creating a smaller diffusion layer which will follow the topography of the surface will avoid this. This can be achieved by plating below the limiting current density and with increased convention within the electrolyte. In such cases the use of additives to electrochemically level is the most common solution to this problem in obtaining uniform deposits. More detailed explanation of the theory involved is given by Barkey et al. [29].
Figure 1.11. Electrodeposition of binary and ternary alloys. The dark grey area denotes alloys of particular importance. The added elements indicate a third element for ternary alloys [32].

1.7 Alloy Electrodeposition

An important use and intriguing aspect of electrodeposition is the possibility of codepositing metals from a single bath leading to alloys which have superior properties when compared to the pure metal and even allowing for properties exclusive to electrodeposited alloys. This is particularly true for the tertiary alloys of NiCoFe [31]. However, there are only particular alloy combinations possible to electrodeposit due to the need for a stable bath and mutually soluble salts.

If the equilibrium potentials of each metal are considered, as by Brenner [32], then at a given potential we would expect the less noble metal to have lower partial current. If this is indeed the case this is known as ‘normal’ codeposition. This can be further refined to consider where mass transport controls the rate as regular codeposition and where kinetics control the rate as irregular codeposition. When the partial current of the less noble metal
exceeds the partial current of the more noble metal it is considered *anomalous codeposition*. It is also possible to deposit an alloy, one component of which would not deposit alone. This is known as *induced codeposition*. Such an example is Ni-Mo, where Mo does not deposit on its own. It is thought that a stable Ni-Mo oxide acts as an intermediate allowing the reaction [26].

Following the Mixed Potential Theory, as introduced by Wagner and Traud for corrosion theory, the net current is a sum of currents for each reaction proceeding. The partial currents are considered independent and can be under kinetic or mass transport control, which would explain such features as anomalous codeposition. Such a non-interacting systems is considered to be the case for nickel and copper [26].

Unfortunately the partial currents during deposition are not always non-interacting. They can be coupled. The partial current of one may be reduced in the presence of other reactions. This inhibition is likely to be caused by competitive adsorption of reaction inter-
mediates where one becomes more dominant. The rate of codeposition can also be affected by the mass transport of another species being either consumed or reduced at the cathode. The most common example of this is the effect of hydrogen evolution, which increases the pH near the cathode. This changes the deposition kinetics of other reactions taking place often by the formation of a metal hydroxide at the cathode. If the hydrogen formation is mass transport controlled, as is often the case when proton reduction is the mechanism, then the alloy deposition properties will also be mass transport controlled. Complexing agents can also have a substantial effect on codeposition. They can shift the rest potential of the metal ions nearer to each other and thereby increase the composition range that can be deposited. They can change the charge transfer kinetics and they can also prevent metal hydroxide formation thereby reducing the effect hydrogen evolution has on the codeposition process. If both metals compete for complexing agents the rate of deposition of one will affect the other. When metals are codeposited at low overpotentials the rate of growth is slow and a solid solution is formed often supersaturated. If the rate of growth is quicker, as it is at larger overpotentials often two distinct alloy phases are seen and composition uniformity can become an issue of current distribution.

The complex issues of not only interacting electrochemical properties but also interacting chemical properties make predication of the effect of plating parameters on the alloy very difficult. It becomes necessary to consider each system individually. This has been done in a number of reviews by Brenner [32], Loweheim [33] and Safranek [34].
1.8 Thesis Outline

This chapter presented an overview of the main concerns in electrodeposition of metals. This thesis will look in detail at two topics. Firstly the effect of an applied magnetic field on the electrodeposition process is studied. The effect of a magnetic field on electrodeposition is considered to be due to the Lorentz force acting on the moving charges in the electrolyte and increasing the convection in the system. There have been suggestions that the magnetic properties of the ion will experience a magnetic force that affects the deposition process. These forces will be comprehensively introduced in Chapter 2. The magnetic field effect on many different metal systems Cu$^{2+}$/Cu, Ni$^{2+}$/Ni, Bi$^{3+}$/Bi, Zn$^{2+}$/Zn and Ag$^{+}$/Ag are investigated and it is hoped to clarify whether the magnetic properties of the reduced species have any bearing on the magnetic field effects observed in the different systems. It is therefore possible to elucidate the dominant forces present.

The second section looks at the properties of electrodeposited nickel and nickel copper. Inherent in the electrodeposition process is the formation of a material at room or near room temperatures yet far beyond equilibrium. This has the potential to lead to materials with high energy defects and hence stabilize a crystal structure which would be otherwise unobtainable. The properties could be interesting and useful. This has already been shown to be the case for Ni-Fe-Co alloys, where high saturation magnetisation is observed due to a stabilised fcc/bcc mixed crystal structure. This stabilisation is considered to be due to a small amount of sulfur incorporated within the deposit [35]. In the case of nickel and nickel copper, the morphology, crystal structure and electrical properties and magnetic properties such as saturation magnetisation and magnetic susceptibility are studied. The aim was to determine properties of these materials that are particular to the electrodeposition
preparation technique and also to address the problem of the lack of literature on the effect of electrodeposition parameters on the magnetic properties of nickel.
Appendix A

List of Symbols

\( C \) Capacitance (F)
\( \varepsilon \) Dielectric constant or relative permittivity
\( n \) Valence of the ion
\( e \) Electronic charge \((1.60217733 \times 10^{-19} \text{ C})\)
\( k_b \) Boltzmann Constant \((1.3806568 \times 10^{-23} \text{ JK}^{-1})\)
\( \psi(x) \) Potential at a distance \( x \) from charged electrode surface (V)
\( T \) Temperature (K)
\( \kappa \) Inverse of the effective thickness of diffuse layer (m\(^{-1}\))
\( v_o \) Rate of migration of oxidised species across electrified interface (mol m\(^{-3}\) s\(^{-1}\))
\( E_a \) Activation energy of process (J mol\(^{-1}\))
\( h \) Plank’s constant \((6.6260755 \times 10^{-34} \text{ Js})\)
\( R \) Gas constant \((8.314510 \text{ J mol}^{-1} \text{ K}^{-1})\)
\( c^o \) Concentration of species at the interface (mol m\(^{-3}\))
\( c^\infty \) Concentration of species in the bulk solution (mol m\(^{-3}\))
\( \Delta G \) Gibbs Free Energy (J mol\(^{-1}\))
\( \Delta G^0 \) Standard Gibbs Free energy (J mol\(^{-1}\))
\( F \) Faraday’s constant \((96485.309 \text{ C mol}^{-1})\)
\( k_O \) Rate constant for oxidation reaction (s\(^{-1}\))
\( k_R \) Rate constant for reduction reaction (s\(^{-1}\))
\( k_0 \) Rate constant \( k_0 = k_O = k_R \) (s\(^{-1}\))
\( \beta \) Symmetry factor fraction of the potential overcome for reduction reaction
\( \Delta \phi_e \) Potential barrier that acts on the migrating ion (V)
\( \Delta \phi \) Total potential drop at the interface (V)
\( \Delta \phi^0_e \) Potential drop across the interface when the \( c^O \) and \( c^R \) are unity (V)
\( \eta \) Potential applied to the interface, the overpotential (V)
\( j_R \) Cathodic current density (A m\(^{-2}\))
\( j_O \) Anodic current density (A m\(^{-2}\))
\( j_0 \) Exchange current density (A m\(^{-2}\))
\( j \) Current density (A m\(^{-2}\))
\( j_L \) Mass transport limited current density (A m\(^{-2}\))
\( Q \) Reaction quotient \( \approx \frac{\text{Product}}{\text{Reactant}} \)
\( E \) Rest potential at interface or Electric field (see context) (V)
\( E^0 \) Standard rest potential (V)
\( v_a \) Velocity of ion (m s\(^{-1}\))
\( \mu \) Ion mobility (m\(^2\) V\(^{-1}\) s\(^{-1}\))
\( \nabla V \) Potential gradient at the electrode (V m\(^{-1}\))
\( \nabla c \) Concentration gradient (mol m\(^{-3}\))
\( J \) Flux of material (m\(^{-2}\)s\(^{-2}\))
\( D \) Diffusion coefficient (m\(^{-2}\)s\(^{-2}\))
\( \delta \) Diffusion layer thickness (m)
\( \nu \) Viscosity (kg m\(^{-1}\) s\(^{-1}\))
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Delta \rho )</td>
<td>Change in density within solution (kg m(^{-3}))</td>
</tr>
<tr>
<td>( S )</td>
<td>Hydrodynamic boundary layer (m)</td>
</tr>
<tr>
<td>( \lambda_s )</td>
<td>Penetration depth of concentration depletion due to surface diffusion (m)</td>
</tr>
<tr>
<td>( \rho_{,a,d} )</td>
<td>Exchange current density of adions (A m(^{-2}))</td>
</tr>
<tr>
<td>( \rho_{,a,d}^{\lambda_s} )</td>
<td>Exchange current density of step edge ions per unit step length (A m(^{-1}))</td>
</tr>
<tr>
<td>( AG(N) )</td>
<td>Free energy of formation of nuclei onto a substrate</td>
</tr>
<tr>
<td>( N_0 )</td>
<td>Saturation nucleus density (m(^{-3}))</td>
</tr>
<tr>
<td>( \phi(N) )</td>
<td>Excess free energy of the cluster surface</td>
</tr>
<tr>
<td>( \psi_i )</td>
<td>Critical no. of atoms needed for a nucleus to be stable</td>
</tr>
<tr>
<td>( N_c )</td>
<td>Critical no. of atoms needed for a nuclei to be stable</td>
</tr>
<tr>
<td>( \Delta E_{\text{kink}} )</td>
<td>Binding energy of an atom in the kink position</td>
</tr>
<tr>
<td>( E_{\text{atom}}(i) )</td>
<td>Binding energy of an atom in position ( i ) to a cluster (includes substrate interaction)</td>
</tr>
<tr>
<td>( \nu )</td>
<td>Frequency factor (s(^{-1})) or rate of nucleation (nuclei m(^{-3}) s(^{-1}))</td>
</tr>
<tr>
<td>( M )</td>
<td>Molar mass (g mol(^{-1}))</td>
</tr>
<tr>
<td>( \rho )</td>
<td>Density of the depositing species (kg m(^{-3}))</td>
</tr>
<tr>
<td>( W_a )</td>
<td>Wagner number</td>
</tr>
<tr>
<td>( \rho_e )</td>
<td>Electrolyte resistivity (( \Omega ) m(^{-1}))</td>
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References


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Chapter 2

Effect of Magnetic Field on Electrodeposition: Chronoamperometry Technique
2.1 Introduction

The effect of a magnetic field on the electrodeposition process was first reported by Faraday in his early work [1]. It is well established that a static uniform magnetic field will increase the electrochemical plating current of a metal in the mass transport limited region [2] [3] [4]. Typically the plating current in a concentrated acidified electrolyte can be doubled in a field of 1 Tesla. The fundamental Lorentz force is generally accepted to have a large part to play in the effects observed but is by no means the only source to be considered. Significant reviews on the effect of a magnetic field on all electrochemical processes are those by Tacken and Janssen [5] and Fahidy [6]. These along with works reported below and recently completed work by G. Hinds [8] on the field effects in the copper electrochemical system has lead to a clarification of the forces that need to considered. These forces are now described.

2.1.1 Lorentz Force

It has been established that the principal magnetic field effect on the plating current is due to the Lorentz force:

$$\vec{F}_L = \vec{j} \times \vec{B}$$

where $\vec{j}$ is the current density in A m$^{-2}$, $\vec{B}$ is the applied field in Tesla and $\vec{F}_L$ is the Lorentz force per unit volume in Nm$^{-3}$. $\vec{F}_L$ is considered to be a uniform magnetic body force acting on a solution volume element and it is known in literature as the magnetohydrodynamic force [6]. This force acts on the moving ions in the solution resulting from the electrolytic current and by momentum transfer leads to convective flow with velocity, $U$, of the whole electrolyte. When the ions are moving towards the electrode, if the field is applied parallel to the electrode then the convective flow arises parallel to the electrode. This increases the
rate of transport of ions through the diffusion layer, the diffusion layer thickness, $\delta$, reduces in size and the current increases. This in turn increases the convective flow setting up a positive feedback mechanism as shown in Figure 2.13. Eventually a steady state is achieved due to viscous forces in the hydrodynamic boundary layer.

![Figure 2.13. Effect of the magnetic field of the diffusion layer. $\delta_H$ is the hydrodynamic boundary layer.](image)

For $j \approx 50 \, \text{A m}^{-2}$, $F_L$ is of order $25 \, \text{N m}^{-3}$ in a field of $0.5 \, \text{T}$. This effect of the Lorentz force was first studied by Aogaki [3] [4] who also modelled the results for a particular cell using fundamental magnetohydrodynamic equations. The effect of the field is equivalent to gentle stirring and can be suppressed by increasing the electrolyte kinematic viscosity [6], for example by the addition of glycerol.

### 2.1.2 Electrokinetic Magnetohydrodynamic Force

It is well established [9] that when an electric field is applied parallel to the electrode surface, it acts on charges in the diffuse layer and induces a flow of these charges known as electro-osmotic motion. The flow velocity is zero at the electrode surface due to the no-slip condition and increases with distance from the electrode - a hydrodynamic boundary layer is set up. Viscous forces oppose the flow allowing a steady state velocity to be obtained. This
phenomenon due to relative motion of the two phases, the electrode and the electrolyte, is known as an electrokinetic effect. Motion of this nature will give rise to a hydrodynamic boundary layer with dimensions equal to that of the diffuse charge layer. Because the electrokinetic force arises due to the charge in the diffuse layer, any process which modifies the structure and charge distribution will modify this force, i.e. contact adsorption of ions or the concentration of the electrolyte will cause modifications to this force.

\[
\text{E- Field} \quad \text{At steady state: } \frac{\eta \nu}{\kappa^{-1}} = \sigma_d E
\]

\[
F_{\text{Ek}} = \sigma_d E
\]

\[
\psi_0 = \frac{4\pi \sigma_d \kappa^{-1}}{\varepsilon}
\]

\[
\Rightarrow \nu = \frac{\psi_0 \varepsilon}{4\pi \eta} E
\]

Figure 2.14. Simple computation of the electro-osmotic velocity showing the forces involved. \( \eta \) is the viscosity of the fluid, \( \sigma_d \) is the charge density of the diffuse layer per unit area assumed to be situated at distance \( \kappa^{-1} \) from the electrode, \( \nu \) is the fluid velocity, \( \nu \) is fluid velocity at distance \( \kappa^{-1} \), \( \psi_0 \) is the potential at \( \kappa^{-1} \) known as the zeta potential, \( E \) is applied electric field and \( \varepsilon \) is the dielectric constant of the solution.

It was proposed by Olivier et al. [10] that if a magnetic field is applied parallel to the electrode and perpendicular to the diffuse charge layer an electric field will be created in a third direction. They suggest that this electric field will then induce electroosmotic motion giving rise to convection in the diffuse layer and thereby increasing the current. This they called the electrokinetic magnetohydrodynamic effect [11].

\[
F_{\text{EK}} = \sigma_d \overline{E}_{\parallel}
\]

(2.2)

or as a body force acting within the hydrodynamic boundary layer

\[
F_{\text{EK}} = \frac{\sigma_d \overline{E}_{\parallel}}{\delta_H}
\]

(2.3)
where \( \sigma_d \) is the charge density of the diffuse layer, \( E_\parallel \) is the induced nonelectrostatic field and \( \delta_H \) is the boundary layer thickness, which for these conditions will also be the diffuse layer thickness. According to Chopart et al.\[12\] this magnetically induced tangential electric field is approximately \( E_\parallel \sim 10 \text{ V m}^{-1} \) at the shear plane within the diffuse layer. The charge density, \( \sigma_d = \frac{\varepsilon \psi}{d} \sim 10^{-1} \text{ C m}^{-2} \) where \( \varepsilon \) is the permittivity of water \( 6.9 \times 10^{-10} \text{ F m}^{-1} \), \( \psi \) is the potential drop between electrode and diffuse layer, \( \approx 40 \text{ mV} \), and \( d \) is the distance to the diffuse layer (\( \kappa^{-1} \)) \( \approx 3\text{Å} \)[9]. A typical hydrodynamic boundary layer thickness of \( \delta_H \approx 10^{-2} \text{ m} \) would lead to a magnitude of \( F_{EK} \) of \( 10^2 \text{ N m}^{-3} \).

2.1.3 Paramagnetic Gradient Force

A completely different effect of the field has recently been considered by O’Brien et al.\[13\] and Waskaas\[14\]. A uniform magnetic field acts on the susceptibility of the magnetic ions to create a local energy density

\[
E = -c \chi_m B^2 / 2\mu_o
\]

where \( c \) is the concentration in mol m\(^{-3} \), \( \chi_m \) is the molar susceptibility of the ions in m\(^3\)mol\(^{-1} \) and \( \mu_o \) the permeability of free space, \( 4\pi \times 10^{-7} \text{ H m}^{-1} \). The application of a magnetic field to solution in which a gradient of magnetic ion concentration exists due to an electrochemical reaction will result in the appearance of additional driving force, \( F = \nabla E \). This force might induce velocity redistribution in the diffusion layer and the additional convective transfer of all components of the solution could be generated in the vicinity of the electrode surface. Non-uniform concentrations arise during electrodeposition in the diffusion layer near the electrode, this leads to a force \[15\]

\[
\vec{F}_p = \chi_m \frac{B^2}{2\mu_o} \rightarrow \nabla c
\]
This force acts in opposite directions for diamagnetic and paramagnetic ions in an applied magnetic field. This should result in field effects on the deposition rates that depend on the magnetic properties of the ions. A typical value of $F_p$ for paramagnetic ions with $\chi_m \simeq 10^{-8}$ m$^3$/mol$^{-1}$ in 0.1 M $(10^2$ mol m$^{-3}$) solution and a diffusion layer thickness $\delta \simeq 1 \times 10^{-4}$ m is 4000 N m$^{-3}$ when $B = 1$ T. The force on diamagnetic ions will be an order of magnitude smaller and of opposite sign. If the concentration gradient of diffusion is considered then according to this force, the flux towards the cathode of paramagnetic ions will be reduced while that due to diamagnetic ions will be increased.

### 2.1.4 Magnetic Gradient Force

If the applied magnetic field is non-uniform and therefore has a gradient yet another force comes into play on differentiating Equation (2.4). The field gradient has a force associated with it that acts on the magnetic moments of ions in the solution. This force acts on paramagnetic ions and diamagnetic ions in opposite directions; paramagnetic ions being attracted to regions of high magnetic field and diamagnetic ions being repelled from such regions. This force is studied in detail by White [16] [17] [18] where it is suggested as an alternative driving force for convection. An important point to note about this force is that it does not depend on the orientation of the applied field but on the direction of the field gradient.

$$F_{vB} = \frac{\chi_m c B \cdot \nabla B}{\mu_o}$$

(2.6)

With a field of 1 T and a field gradient of 1 T m$^{-1}$, for example, $F_{vB}$ would be expected to be of magnitude $\sim 1$ N m$^{-3}$ for paramagnetic ions with $\chi_m \simeq 10^{-8}$ m$^3$/mol$^{-1}$ in 0.1 M solution.
2.1.5 Hydrodynamic damping force

Yet another force comes into effect when the electrolyte solutions are very conductive. The motion of an electrolyte in a magnetic field will induce an electric field, \( \vec{v} \times \vec{B} \). If the electrolyte is conductive a current, \( \sigma (\vec{v} \times \vec{B}) \), where \( \sigma \) is the conductivity of the solution in \((\Omega m)^{-1}\), is generated. A current moving in a magnetic field will induce motion according to the Lorentz equation, Equation (2.1), [19]

\[
\vec{F}_d = \sigma \vec{v} \times \vec{B} \times \vec{B}
\]  

(2.7)

This acts to impede or dampen the velocity \(\approx 10^{-1}\) ms\(^{-1}\) in the transverse direction while velocity in the longitudinal direction is unimpeded. This force is negligible in aqueous solutions where the conductivity is low \(\sigma \approx 10^2\) \((\Omega m)^{-1}\) but becomes significant as the conductivity reaches higher values. The use of static magnetic fields to control the convection during the growth of crystals from conducting melts relies on this damping force [20].

The work presented in this chapter aims to determine the relevance of each of these forces during the electrodeposition process. To this end many different parameters are investigated. Firstly the effect of the metal ionic species that is reduced is studied - both the ions' charge and magnetic properties are considered. The metals studied are Ag, Cu, Ni, Zn and Bi. They have different magnetic properties. Ag\(^+\), Zn\(^2+\) and Bi\(^3+\) are diamagnetic ions having electronic configurations [Kr] 4d\(^{10}\), [Ar] 3d\(^{10}\) and [Xe] 4f\(^{14}\) 5d\(^{10}\) 6s\(^2\) respectively, whereas
Cu²⁺ is paramagnetic with electronic configurations [Ar] 3d⁹. Their electrolytes also have different conductivities and pH values. The orientation of the electrode relative to the applied magnetic field and the effect of pH is studied for the copper system. The key technique used to investigate the magnetic field effects is the transient response of a cathodic current to a voltage step - Chronoamperometry.
2.2 Experimental Method

2.2.1 Electrochemical Techniques

Linear sweep Voltammogram

This simple technique entails ramping the potential of the working electrode, relative to a fixed reference electrode, from an initial to a final potential at a fixed rate. The current response of the electrode is monitored and is known as a voltammogram. From the shape of the voltammogram we are given valuable information about the electrochemical system: thermodynamic, kinetic and mass transport parameters may all be determined from the relevant portions of the curve as shown in Figure 2.15. Kinetic parameters such as exchange current density and transfer coefficients can be deduced from the slope of the Tafel region of the voltammogram when plotted on a log scale. Mass transport parameters such as diffusion coefficients may be determined from the limiting current in the plateau region. The onset of other reactions, such as hydrogen evolution, can also be detected. When studying the electrodeposition of metal, we are interested in a negative overpotential of the working electrode which results in a negative current response.

Chronoamperometry

Chronoamperometry is carried out by stepping the voltage from the rest potential to a potential at which reduction of the metal ion occurs. The transient current response is then monitored. As has been mentioned in Section 1.4.2 if the potential step applied means that the current is in the mass transport region then we expect the current transients to follow the Cottrell Equation:

\[ j = -nFc \sqrt{\frac{D}{\pi t}} \quad (2.8) \]
Figure 2.15. Linear sweep voltammogram showing, on the left, the current vs potential. On the right the log of the magnitude of the current is shown. The relevant features are highlighted.

From this the diffusion coefficient of the reducing species can be determined. Cottrell behaviour is seen only at intermediate times before a steady state current is achieved by diffusion layer stabilization due to convection. This allows a determination for the time for convection within the system to be set up. If the potential is stepped to a region where mass transport does not govern the reaction rate or only partially governs it the slope cannot be related to the Cottrell equation.
It should also be pointed out that Cottrell behaviour is considered to occur when there is planar diffusion to the electrode surface, and this happens when the entire electrode surface is available for deposition. If this is not the case then the nucleation of clusters and their subsequent growth by spherical diffusion occurs as discussed in Section 1.5.3.

2.2.2 Experimental Details

The electrochemical cell used in this study was a standard three electrode cell. The reference electrode, which provides a constant potential against which the potential of the working electrode can be measured, was a 3 M Ag/AgCl with reference potential 0.22 V rel. SHE. The counter electrode is used to pass current through the cell in order to avoid any polarization of the reference electrode which might affect the stability of it’s potential. The surface area of the counter electrode should be greater than that of the working electrode to ensure that the potential distribution is uniform at the working electrode. The counter
The electrode used in this work was a carbon rod. The working electrode was made of the same material as the metal ion being reduced i.e. Cu, Zn, Ag or Bi. The electrode was made by spot welding a copper wire to the back of a rectangular piece of metal plate. The back and sides of the electrode and the wire were then encased in epoxy, leaving the working area of the electrode exposed (0.5 -1 cm$^2$). Before each experiment the working electrode was polished with 0.3 $\mu$m alumina before being rinsed by deionized and 0.2 $\mu$m filtered water. During most of the experiments the working electrode was placed face horizontally down in the cell in order to reduce the effect of natural convection on the mass transport. A vertical electrode was used during the investigation of magnetic field orientation on the current enhancement.

The composition of the electrolytes that were used to investigate each system are shown in the Table 2.4. All solutions were made with UV deionized and 0.2 $\mu$m filtered water. The magnetic field was applied by placing the entire cell in the centre of the 54 mm bore of a permanent magnet with $B = 0.5$ T in the plane. The field inhomogeneity is 1%
in 1 cm along the bore axis and the maximum field gradient over the entire volume of the cell is 4 T m⁻¹. This is shown in Figure 2.18. The experiments were performed using an

<table>
<thead>
<tr>
<th>Salt acid pH</th>
<th>Cu²⁺/Cu</th>
<th>Zn²⁺/Zn</th>
<th>Bi³⁺/Bi</th>
<th>Ag⁺/Ag⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuSO₄ 50 mM</td>
<td>ZnSO₄ 50 mM</td>
<td>Bi(NO₃)₃ 50 mM</td>
<td>AgNO₃ 50 mM</td>
<td></td>
</tr>
<tr>
<td>H₂SO₄ 0.04 M</td>
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<td>0.02 M HNO₃</td>
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<td>4.5</td>
<td>-0.76</td>
<td>1.2</td>
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</tr>
</tbody>
</table>

Table 2.4. Electrolytes used for each system investigated.

Figure 2.18. 3-Dimensional representation of the magnetic field in the bore of the permanent magnet used during chronoamperometry [21].

EG&G Potentiostat Model 263A which was interfaced to a PC using EG&G Model 270/250 research electrochemistry software to apply, control and measure the current and potential of the electrochemical cell.

Three investigations were carried out.

(1.) Effect of magnetic field on chronoamperometric response

This was the most comprehensive study. Linear sweep voltammograms were collected for all systems both with and without an applied field. The rate of change of the potential was 20mV/sec. This allowed the identification of the rest potential, the kinetic and the mass transport regions. Chronoamperometry was then carried out by stepping the potential from the previously measured rest potential to an appropriate reduction potential. An entire range of potential steps was investigated from the kinetic to the mass transport region. Each
potential step of the chronoamperometry experiment was carried out without a magnetic field and then in a magnetic field. This was repeated three times giving three steady-state limiting currents with and without a field. These were then averaged giving $j_s$ and $j_{sB}$ respectively and a resultant current enhancement was calculated:

$$\frac{j_{sB} - j_s}{j_s} \times 100\%$$

(2.9)

Using the current transients from potential steps into the mass transport regions the diffusion coefficients were also determined from data collected both with and without a field.

(2.) Effect of Field Orientation

The effect of the field orientation was investigated for the Cu$^{2+}$/Cu system. The experimental set up and procedure was unchanged from that described in the previous paragraphs except that the electrode were not horizontal but vertical and were placed either parallel or perpendicular to the magnetic field. The same electrolyte compositions were used.

(3.) The effect of pH and viscosity was investigated for the Cu$^{2+}$/Cu. A horizontal electrode was again used. Firstly, an entire range of potential steps was investigated for a copper sulphate solution of pH -0.8 (3.8 M H$_2$SO$_4$). Secondly, the pH of the solution was varied from pH=2.5 to pH=-0.8 by addition of H$_2$SO$_4$. The magnetic field-induced current enhancement was determined for each solution, using chronoamperometry, after applying a step of -500 mV. Viscosity of the solution was also varied by adding glycerol to the electrolyte.
2.3 Results

2.3.1 Effect of magnetic field on electrodeposition of metals

Copper

The results obtained for the Cu\(^{2+}\)/Cu system are shown in Figure 2.19. Figure 2.19(a) shows the voltammogram for a copper working electrode in 50 mM CuSO\(_4\) from 200 mV to -1 V vs Ag/AgCl. The rest potential is +200 mV both with and without an applied magnetic field. In the current plateau, where mass transport limits the current, the effect of the magnetic field is to increase the cathodic current. Beyond this the current increases with potential due to hydrogen evolution. Typical chronoamperometric data is shown in Figure 2.19(b) and (c). The magnetic field enhancement of the steady state current is shown in Figure 2.19(b). The effect is only seen at potentials steps larger than -200 mV, i.e. in the mass transport region; it saturates at 64%. It can be seen in Figure 2.19(c) that linear Cottrell behaviour occurs at intermediate times. The diffusion coefficient calculated from the slope of this data and using \( n = 2 \) for Cu\(^{2+}\), \( F = 96,500 \) C mol\(^{-1}\), \( c = 50 \) mol m\(^{-3}\) is \( D = (8 \pm 1) \times 10^{-10} \) m\(^2\)s\(^{-1}\) for data collected with and without a field. There is no difference between the diffusion coefficients, which are close to literature values as explained in table 2.5. Deviations from linearity in the Cottrell plot are due to initial double layer charging at short times and the onset of natural convection of the electrolyte at long times. The currents measured in the field show earlier deviation from linearity (Figure 2.19(c)). However when the experiments were carried out at potentials closer to the rest potential where mass transport is not rate-determining (\( \leq -200 \) mV relative to rest potential) the linear variation of current with \( t^{-\frac{1}{2}} \) time was naturally lost. A steady state current is still
reached but there was no appreciable dependence of this current on the field.

Figure 2.19. Electrochemical data for 50 mM CuSO₄ at pH 1.1. (a) Voltammogram both with and without a field. (b) Current time response to -500 mV potential step (c) Cottrell plot of the same data. The diffusion coefficient is given by the slope of the dashed line. (d) Current enhancement in 0.5 T field over the range of potentials investigated.

Bismuth

The voltammogram for a bismuth working electrode in 50 mM Bi(NO₃)₃ in 5.8 M HNO₃ indicated a rest potential of 46 mV rel Ag/AgCl both with and without an applied magnetic field. A narrow Tafel region is also evident in Figure 2.20(a). The diffusion coefficients calculated from the linear section of the Cottrell plots, using \( n = 3 \) for Bi³⁺ are \( D = (5 \pm 1) \times 10^{-10} \text{ m}^2\text{s}^{-1} \) for data collected with a field and \( D = (4 \pm 1) \times 10^{-10} \text{ m}^2\text{s}^{-1} \).
for data collected without a field. Current enhancement, which saturates at \( \approx 30\% \), is first seen at steps of -100 mV corresponding to the narrow kinetically-controlled region. Typical chronoamperometric data are shown in Figure 2.20.

![Figure 2.20](image-url)

**Figure 2.20.** Electrochemical data for 50mM Bi(NO$_3$)$_3$ in 5.8M HNO$_3$.(a) Voltammogram both with and without a field. Sweep rate 20mV/sec. (b) Current time response to -288 mV potential step. (c) Cottrell plot of the same data. The diffusion coefficient is given by the slope of the line. (d) Current enhancement in 0.5T field over the range of potential steps.

**Silver**

The voltammogram for a silver working electrode in 50 mM AgNO$_3$ in 0.02 M HNO$_3$ indicated a rest potential of +500 mV rel. Ag/AgCl both with and without an applied magnetic field. Cottrell behaviour is observed for potential steps beyond -200 mV. The diffusion coefficient calculated for Ag$^+$ with \( n = 1 \), is \( D = (8 \pm 1) \times 10^{-9} \text{ m}^2\text{s}^{-1} \) for
data collected without a field and $(6 \pm 1) \times 10^{-9}$ m$^2$s$^{-1}$ with a field. The dependence of current enhancement on the magnitude of the potential step is shown in Figure 2.21(d). The maximum current enhancement is $\approx 40\%$.

![Graphs](image)

Figure 2.21. Electrochemical data for 50 mM AgNO$_3$ in 0.02 M HNO$_3$. (a) Voltammogram both with and without a field. Sweep rate 20mV/sec. (b) Current time response to -288 mV potential step. (c) Cottrell plot of the same data. The diffusion coefficient is given by the slope of the line. (d) Current enhancement in 0.5T field over the range of potential steps.

**Zinc**

The voltammogram for a zinc working electrode in unacidified ZnSO$_4$ shows a rest potential of -1.003 V rel. Ag/AgCl. The effect of the field is first observed for potential steps greater than -600 mV and reaches a maximum at 36% as shown in Figure 2.22. The calculated diffusion coefficient for Zn$^{2+}$ with $n=2$ is $D = (1 \pm 1) \times 10^{-10}$ m$^2$s$^{-1}$ for data
collected both without a field and \((2 \pm 1) \times 10^{-9} \text{ m}^2\text{s}^{-1}\) with a field.

Figure 2.22. Electrochemical data for 50 mM ZnSO₄. (a) Voltammogram both with and without a field. Sweep rate 20mV/sec. (b) Current time response to -600 mV potential step. (c) Cottrell plot of the same data. The diffusion coefficient is given by the slope of the line shown. (d) Current enhancement in 0.5 T field over the range of potential steps.

2.3.2 Effect of Field Orientation

When a vertical electrode was used as cathode, it can be seen in Figure 2.23 that the current enhancement clearly depends on the field orientation relative to the electrode face. The current enhancement is much reduced when the field is applied perpendicular to the working electrode. When the field is parallel to the working electrode the field effects are comparable to those seen with a horizontal electrode, where the field is also parallel to the electrode.
Figure 2.23. Current enhancement as a function of potential step for 50mM CuSO\(_4\) with vertical electrodes parallel and perpendicular to a 0.5 T field (pH 1.1)

### 2.3.3 Effects of Acid Concentration / Viscosity

The effect of the magnetic field on the steady state current of the chronoamperometric experiment carried out in very acidic solutions of 50 mM CuSO\(_4\) (3.8 M H\(_2\)SO\(_4\)) is shown in Figure 2.24.

Figure 2.24. Current enhancements in 0.5 T for 50 mM CuSO\(_4\) in 3.8M (pH -0.88) and 0.039 M H\(_2\)SO\(_4\) (pH 1.1)

The main difference noted is the much reduced current enhancement at very low pH. At a potential step of -600 mV, it falls from (64 ± 2)% to (24 ± 3)% on changing from 0.04
M H₂SO₄ to 3.8 M H₂SO₄ in copper sulphate solutions. Moreover when the data is collected over a range of acid concentrations it is found that the very high concentrations show little enhancement (8±3%, -500 mV step, 3.8 M), intermediate concentrations show a very large effect (74±6%, -500 mV step, 1 M) and low concentrations again show a low current enhancement (12 ±5%, -500 mV, 0.005 M). This is illustrated in Figure 2.25.

![Figure 2.25](image)

Figure 2.25. Current enhancement in 0.5 T field for 50mM CuSO₄ with different molarity of H₂SO₄ solutions. Circular data point corresponds to glycerol in solution at pH 1.1.

The reduction in magnitude of the field effects at high concentrations may be related to the increase in the kinematic viscosity of the solution. The highly acidic solutions are of high kinematic viscosity \(\nu = 1.64 \times 10^{-6} \text{ m}^2\text{s}^{-1}\) for 3.8 M H₂SO₄ while intermediate and low concentrations have lower kinematic viscosity. The high kinematic viscosity would be expected to damp out any induced convection and reduce the steady state current enhancement due to the magnetic field. Very slightly acidic solutions will have fewer charge carriers leading to a reduction current which is no longer under strict diffusion control and therefore the Lorentz force will not be seen to have as substantial and effect.
This hypothesis was tested by performing chronoamperometry on a solution of comparable kinematic viscosity to 3.8 M H₂SO₄ but of lower acidity. This was achieved by using 2.2 M glycerol (ν =1.661x10⁻⁶ m²s⁻¹). Acidity was maintained by the addition of 0.04 M H₂SO₄ (pH=1.1). A potential step of -500 mV was again applied. The result is included in Figure 2.25. A summary of all the results are presented in Table 2.5.

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<th>Cu²⁺</th>
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<th>Ag⁺</th>
<th>Zn²⁺</th>
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<td>25±5%</td>
<td>28±4%</td>
<td>42±4%</td>
<td>38±4%</td>
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<td>-0.88</td>
<td>-0.76</td>
<td>1.1</td>
<td>5.6</td>
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<td>-600</td>
<td>-600</td>
<td>-1,500</td>
<td>-1,000</td>
</tr>
<tr>
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<td>-400</td>
<td>-560</td>
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<tr>
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<td>+200</td>
<td>+46</td>
<td>+500</td>
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<table>
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</tr>
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<td>Diffusion Coefficients m²s⁻¹</td>
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<td>2×10⁻⁹</td>
<td>5×10⁻¹⁰</td>
<td>8×10⁻⁹</td>
<td>1×10⁻¹⁰</td>
</tr>
<tr>
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<td>-</td>
<td>unavailable</td>
<td>2×10⁻⁹</td>
<td>7×10⁻¹⁰</td>
</tr>
<tr>
<td>Conductivity of soln. σ(Ωm⁻¹)</td>
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<td>1,000</td>
<td>1,000</td>
<td>100</td>
<td>10</td>
</tr>
</tbody>
</table>

Table 2.5. Summary of Chronoamperometric data for 50mM solutions of different ions in a field of 0.5 T when the maximum potential step is applied. Other relevant parameters of each system are included.

² Literature Diffusion coefficients calculated from D=μRT/πF where μ is the ionic mobility in water taken from [22].
2.4 Discussion

From the data gathered it is clear that the effect of the applied magnetic field is present only when the current is controlled by mass transport. The current increases for all systems investigated under such conditions. The Cottrell plots also show that for Cu\(^{2+}\), Zn\(^{2+}\), Ag\(^{+}\) and Bi\(^{3+}\) the diffusion coefficient remains the same both with and without an applied field. It is also observed that the deviation from Cottrell behaviour is achieved at an earlier time when a magnetic field is applied. For the most cathodic potentials investigated for each system the steady state limiting current is used to calculate the diffusion layer thickness from Equation (1.20a). The results from data obtained both with and without a magnetic field are shown in Table 2.6. It can be seen that there is a marked reduction in the diffusion layer thickness with the application of a magnetic field. It can be concluded that the magnetic field for all reduction systems acts so as to induce convection within the electrolyte, reducing the thickness of the diffusion layer and thereby increasing the current.

But what are the forces responsible for this convection and can they be related to the various current enhancements seen in Table 2.5 for each metal?

The paramagnetic gradient force \( \vec{F}_p \), Equation(2.5), might be expected to decrease the flux of paramagnetic ions and increase the flux of a diamagnetic ion since the force acts along the concentration gradient like the driving force, \( \vec{F}_D \), for diffusion within the diffusion layer, where \( \vec{F}_D = RT \nabla c \). \( \vec{F}_p \) is the largest of the four magnetic forces identified.
in the introduction. However, the ratio of the two forces, \( \frac{\vec{F}_p}{\vec{F}_D} = \frac{\chi_m B^2}{2\mu_0 RT} \), taking \( \chi_m \simeq 2 \times 10^{-8} \text{ m}^3\text{mol}^{-1} \), as it is for paramagnetic copper and \( B = 0.5 \text{ T} \) is \( \simeq 8 \times 10^{-7} \). This shows that the paramagnetic gradient force has a completely negligible influence on the mass transport when compared with diffusion and strongly suggests that the driving force for the magnetic enhancement cannot be a susceptibility gradient as proposed by O’Brien and others [13] [14]. This force is therefore not considered to affect the systems investigated.

The magnetic gradient force \( F_{VB} \), Equation (2.6), which acts on the bulk solution may have an effect on the convection in the system. Under consideration in our experimental conditions there is a field gradient of \( \nabla B = 0.5 \text{ T m}^{-1} \) between the electrodes and \( \nabla B = 4 \text{ T m}^{-1} \) between the extremities of the cell leading to \( F_{VB} = 0.4 - 3 \text{ N m}^{-3} \). This is of sufficient magnitude to influence the convection induced by the Lorentz force (25 N m\(^{-3}\)) and acts in opposite directions for diamagnetic and paramagnetic ions. The molar susceptibilities of the solutions used are shown in Table 2.5.

The magnetohydrodynamic damping force \( \vec{F}_d \), Equation (2.7), will also need to be considered particularly for the more highly acidic solutions investigated. Likewise the kinematic viscosity, \( \eta \), of each solution will reduce the effectiveness of all these forces introducing convection to the solution.

The Lorentz force \( \vec{F}_L \), Equation (2.1), acts on the moving charges in the bulk solution and would need to be considered for all metal reactions. The dominance of the Lorentz force is seen where in Figure 2.25 low concentrations of acid produce reduced current enhancement due to the reduction of charge carriers in the bulk solution leading to reduction reaction which is no longer strictly controlled by mass transport but where migration effects will need to be considered. The dominance of the effect of induced convection is seen clearly in Figure 2.23.
When the electrode face is perpendicular to the field, the current is flowing mostly parallel to the field and the Lorentz force will not act on the moving charges - current enhancement is only 10%. This jumps to 55% when the field is parallel to the working electrode face where we would expect a maximum Lorentz force to act. However, a field perpendicular to the electrode would also suppress the induced non-electrostatic field responsible for the electrokinetic magnetohydrodynamic force. The question remains as to whether the field acts directly on the bulk solution via the influence of $\vec{F}_L$ and $\vec{F}_\nabla B$ or on a nanometer scale via $\vec{F}_{EK}$. For this work we consider the magnetic forces due to the Lorentz force and the magnetic field gradient force acting on the solution and relate them to the findings. The electrokinetic force is not considered on the grounds that it relies on a thick diffuse layer. According to the Gouy-Chappman model the diffuse layer for a concentration 50 mM is $\approx 7\text{Å}$ which is too thin for a substantial electrokinetic effect [9]. An estimate of all forces for each system from the data in Table 2.5 is shown in Table 2.7. Included, for convenience, is the current enhancement.

\[
\begin{array}{|c|c|c|c|c|c|}
\hline
\text{Force} & \text{Cu}^{2+} (\text{pH } 1.1) & \text{Cu}^{2+} (\text{pH } 0.88) & \text{Bi}^{3+} & \text{Ag}^+ & \text{Zn}^{2+} \\
\hline
\vec{F}_L \text{ N m}^{-3} & 25 & 27 & 129 & 68 & 68 \\
\vec{F}_\nabla B \text{ N m}^{-3} & 1.49 & 1.49 & -0.087 & -0.047 & -0.047 \\
\vec{F}_\eta \text{ N m}^{-3} & -2.5 & -25 & -25 & -2.5 & -0.25 \\
\eta (\text{m}^2\text{s}^{-1} \times 10^{-6}) & 1.0 & 1.64 & 1.13 & 1 & 1.03 \\
\text{Enhancement at max. step} & \textbf{64±5%} & \textbf{25±5%} & \textbf{28±4%} & \textbf{42±4%} & \textbf{38±4%} \\
\hline
\end{array}
\]

Table 2.7: Estimation of the forces acting in 50mM aqueous solution of various ions.

Copper electrodeposition at pH 1.1 sees the largest effect because $\vec{F}_L$ and $\vec{F}_\nabla B$ are significant when the viscosity and damping force are not large. The effect of increasing viscosity and the damping (i.e. Cu$^{2+}$ at pH -0.88) is to reduce the current enhancement observed. The relative importance of each of these forces is illustrated in Figure 2.25 where increasing the viscosity of solution reduces significantly the current enhancement seen. However the
viscosity effect alone only allows for 50% of the reduced current enhancement - the damping therefore has a significant effect.

The effect of both viscosity and the damping force is again illustrated in the enhancement seen for the bismuth ion. Despite the large Lorentz force, both the viscosity and the damping force act to reduce the current enhancement. The viscosities of the bismuth solutions are substantially lower than that of Cu at pH -0.88 and it might therefore be expected that a larger enhancement than 28% would be observed. However $\overline{F}_{vB}$ will not be operating in the bismuth system as although bismuth is the most diamagnetic ion this force is still negligible when compared to paramagnetic copper.

Comparing the enhancement seen for silver (pH 1.1) to that for copper (pH 1.1) allows the direct effect of the magnetic field gradient force to be seen. All other conditions are of the comparable magnitude except the susceptibility of the ions. Extra convection induced due to $\overline{F}_{vB}$ seems to have a large effect on the enhancement for copper (pH 1.1) whereas this effect is not present for silver and hence there is a reduced enhancement.

The zinc enhancement is directly comparable to that of silver since there is no difference in the magnitude of the forces involved. The difference in pH has no effect due to the large steady state limiting current for zinc.
2.5 Conclusions

Chronoamperometry is an effective way of evaluating magnetic field effects on electrochemical cells. Results on current enhancement are obtained in electrochemical systems with low current densities and low concentrations of ions with different charge and magnetic properties. They show that the Lorentz force in bulk solution, or within the diffuse layer, is driving the effect. Magnetically-induced convection enhances the limiting current by stirring the diffusion layer and reducing its thickness $\delta$. The diffusion of ions themselves is not affected by the application of the magnetic field. The paramagnetic force is not a significant contributing factor. However magnetic field gradients can influence the forced convection and hence the current enhancement.
Appendix A
List of Symbols

\[ \vec{F}_L \] Lorentz force (N m\(^{-3}\))
\[ \vec{j} \] Current density (A m\(^{-2}\))
\[ \vec{B} \] Applied magnetic field (T)
\[ \delta \] Diffusion layer thickness (m)
\[ \delta_H \] Hydrodynamic boundary layer (m)
\[ \vec{F}_{EK} \] Electrokinetic magnetohydrodynamic force (N m\(^{-3}\))
\[ \sigma_d \] Charge density of the diffuse layer (C m\(^{-1}\))
\[ \vec{E}_\parallel \] Induced nonelectrostatic field (V m\(^{-1}\))
\[ E \] Local energy density (J m\(^{-3}\))
\[ c \] Concentration (mol m\(^{-3}\))
\[ \chi_m \] Molar susceptibility of the ions (m\(^3\)mol\(^{-1}\))
\[ \mu_0 \] Permeability of free space, \(4\pi \times 10^{-7}\) H m\(^{-1}\)
\[ \vec{F}_p \] Paramagnetic gradient force (N m\(^{-3}\))
\[ \vec{F}_{\nabla B} \] Magnetic gradient force (N m\(^{-3}\))
\[ \sigma \] Conductivity (\(\Omega\) m\(^{-1}\))
\[ \vec{v} \] Electrolyte flow (m s\(^{-1}\))
\[ \vec{F}_d \] Hydrodynamic damping force (N m\(^{-3}\))
\[ n \] Valence of ion
\[ F \] Faraday's constant (96485.309 C mol\(^{-1}\))
\[ D \] Diffusion coefficient m\(^2\)s\(^{-1}\)
\[ j_{sB} \] Steady state limiting current with applied magnetic field (A m\(^{-2}\))
\[ j_s \] Steady state limiting current (A m\(^{-2}\))
\[ \eta \] Kinematic viscosity (m\(^2\) s\(^{-1}\))
\[ u \] Ionic mobility in water (m\(^2\) s\(^{-1}\) V\(^{-1}\))
References


Chapter 3

Nickel Electrodeposition
3.1 Introduction

Nickel electrodeposition has been carried out on an industrial scale for over a hundred and fifty years due to its high corrosion resistance and bright finish. Initially, nickel was deposited from a double salt solution, acidified nickel ammonium sulphate, with the addition of boric acid to improve quality. This was a slow and inefficient bath leading to the introduction of the Watts bath in 1916 by Prof Oliver P Watts of the University of Wisconsin. This was a high speed formulation which performed successfully over a range of pH values and allowed extremely high current densities to be used. However, nickel deposits were often dull and needed to be buffed or polished after deposition to produce a shiny end-product. Also after time the deposit would tarnish. It was realized that a thin chromium deposition over the nickel would eliminate tarnishing, creating a highly protective and decorative finish that was widely used. The production of smooth mirror-bright deposits became possible in the 1930's with the introduction of alkyl napthalene sulphonates into the plating baths as additives. The use of selenium, tellurium and cadmium compounds with these organic brighteners allowed control of the process. Other organic additives such as aromatic polysulfonates, sulfonamides and saccharin were also found to produce bright nickel. These baths produced bright, smooth and highly levelled deposits. However, the corrosion resistance of these deposits was reduced significantly due to sulfur incorporation. This led to double-layer nickel plating consisting of a sulfur free thick semi-bright underlayer followed by a thin bright nickel layer which gave much better corrosion resistance. Triple layer coatings were also developed with an even more active, sulfur-rich layer of nickel between the bright and semi-bright layers. Until the 1970's the automotive industry was the largest consumer of decorative nickel plates being used on bumpers, mirrors and other trims. In recent
years, it has also been used on styled wheels and other decorative parts. Nickel finishings are also being used in plumbing fixtures, bicycle parts and other consumer goods. In total 100,000 metric tonnes of nickel are consumed each year [1] [2]. In recent years there has been renewed interest in the electrodeposition of nickel due to applications in the field of micro-electromechanical devices and systems [3] and also as a component in multilayer stacks exhibiting Giant Magnetoresistance (GMR) for sensors [4] [5].

Much of the progress in the nickel plating industry was of an empirical nature where plating baths followed a strict recipe for successful production of nickel. However there is a science behind this art. The standard electrode potential of Ni^{2+}/Ni is -0.23V rel. SHE. Therefore the reduction of protons resulting in the co-evolution of hydrogen is a necessary consideration during nickel electrodeposition. Hydrogen evolution arises not only from the reduction of the hydronium ion

\[
2H_3O^+ + 2e^- \rightarrow H_2 + H_2O \text{ or alternatively} \\
H_3O^+ + e^- \rightarrow H_{ads} + H_2O \\
2H_{ads} \rightarrow H_2
\]  

but also, at high pH values, from the reaction

\[
NiOH^+H_2O + e^- \rightarrow Ni(OH)_2 + \frac{1}{2}H_2
\]

If the concentration of hydrogen ions is not large (i.e. at intermediate and high pH), it would be expected that the hydrogen ion reduction would be mass transport limited. This indeed has been confirmed by Dorsch [7]. However at higher pH values, hydrogen evolution depends less on pH than would be expected as the presence of NiOH^{+} is controlled by its solubility product. It has been found for high concentrations of nickel ion in solution that the limiting
current for hydrogen evolution is reached even before nickel deposition begins to take place [6]. The nickel reduction process itself is considered to take place by the following reaction model [8].

\[
Ni^{2+} + H_2O \rightarrow Ni(OH)^+ + H^+ \tag{3.5}
\]

\[
Ni(OH)^+ + e^- \rightleftharpoons Ni(OH)_{ads} \tag{3.6}
\]

\[
Ni(OH)_{ads} + Ni(OH)^+ + 3e^- \rightarrow 2Ni + 2OH^- \tag{3.7}
\]

Reaction (3.7) is considered to occur in several steps which cannot be distinguished. At high overpotentials the reduction of water will occur according to Reaction (3.8) also resulting in hydrogen evolution. This will result in an increase in alkalinity within the electrolyte with implications that will be described shortly.

\[
2H_2O + 2e^- \rightarrow 2OH^- + H_2 \tag{3.8}
\]

![Schematic voltammogram showing the partial currents of hydrogen and nickel.](image)

Figure 3.26. Schematic voltammogram showing the partial currents of hydrogen and nickel.

The high surface energy of nickel means that it has a great ability to adsorb chemical species onto its surface. This has a number of implications for the electrodeposition process.
The presence of adsorbed hydrogen on the cathode leads to the formation of hydrogenated forms of nickel electrodeposits, $\alpha$-nickel with low hydrogen content and $\beta$-nickel richer in hydrogen [9] [10]. $\alpha$-nickel is a solid solution with less than 3 atm. % of hydrogen. This small amount of hydrogen gives a minimal lattice expansion - it is hard to detect other than by electrochemical techniques. $\beta$-nickel is an interstitial hydrogen alloy with greater than 60 atm. % hydrogen considered to occupy the octahedral voids leading to a lattice constant increase of 5.6%. At room temperatures this hydride is unstable reverting to $\alpha$-nickel within hours. $\alpha$-nickel, will form during nickel electrodeposition under most electrochemical conditions. Due to the negligible amount of hydrogen it contains it’s properties are very similar to those of pure nickel [9]. $\beta$-nickel is formed only when there is a plentiful supply of hydrogen. Therefore at the start of a current transient $\beta$-nickel is formed but as hydrogen is used up and becomes in short supply $\alpha$-nickel continues to form by three dimensional growth and progressive nucleation, which is controlled by mass transport. $\beta$-nickel is preferentially formed at high overvoltages (hydrogen adsorption is high), low pH values and at low solution temperatures. $\beta$-nickel is less likely to form when hydrogen evolution can take place not only on the Ni deposits but also on the electrode material i.e. Class III inert material of Table 1.2.

The large number of adsorbed species on a nickel surface leads to inhibition of the growth which manifests itself as preferential growth along specific crystal directions and hence texturing of the crystal structure of the deposit is observed. It has been shown by Amblard et al.[11] that this texturing has a strong dependence on the pH at which the deposition occurs. Their relation is shown in the phase diagram of pH vs current density (Figure3.27), which is quite similar to the Winand’s diagram discussed in Chapter 1.
At low current densities and low pH values, the surface of the electrode is covered in an adsorbed layer of hydrogen which inhibits growth in all directions but less so in the [110] direction giving rise to $<110>$ texturing of the deposit. As the current density or the pH increases, the electrode surface advances and hydrogen adsorbents are not replaced. Hydrogen evolution causes a resultant pH rise near the cathode which may cause precipitation of the alkaline salt Ni(OH)$_2$. This is a black amorphous non-conductive salt and is found to precipitate from solutions at pH >7 [12]. If the local pH near the cathode rises to this value, Ni(OH)$_2$ will precipitate on the surface. In this case Ni(OH)$_2$ strongly inhibits growth, but less so in the [211] direction giving $<211>$ texturing of the deposit. At higher current densities and assuming that the pH of the solution remains acidic the electrode surface becomes covered with the intermediate $Ni(OH)_{ads}$ and growth is not hindered by any species directly related to the hydrogen evolution. This mode of growth is known as the free growth mode, the texture of which is in the 100 direction. However work by Koslov et al. [15] predicts that for thin deposits in the free growth mode, initial texture of electrodeposited fcc metals is always in the [111] direction; while as the deposition thickness increases, then the...
texture is seen. In extremely acidic solutions where hydrogen evolution will be substantial, the gaseous hydrogen on the surface will determine the crystal growth directions of the codepositing nickel and <210> texture is seen.

From the above discussion an essential component of the nickel electrolyte is a buffer which will maintain a low pH at the cathode and prevent the precipitation of nickel hydroxide. Boric acid is often used for such a purpose. It is known to reduce the local cathode pH from 12 to 5 [13]. The mechanism of such an effect is unclear as the pK$_a$ of boric acid suggests that direct dissociation cannot account for such a change. It is suggested that boric acid complexes with the nickel in which $H^+$ is a happy by-product [14]:

$$B(OH)_3 + Ni^{2+} + H_2O \rightarrow Ni[B(OH)_4]^+ + H^+$$  \hspace{1cm} (3.9)

Nickel is normally deposited from highly concentrated nickel salt solutions because under such conditions the partial current of the nickel deposition is much larger than that of the mass transport controlled hydrogen evolution, leading to high current efficiency. The nickel partial current remains kinetically controlled over a wider potential range allowing higher quality deposits to be achieved. Elevated temperatures also allow for increased current density without loss of current efficiency or deposit quality. Current efficiency for nickel deposition increases as the overpotential or current increases as these have no effect on partial current due to the hydrogen reaction.

There are many reports on the structural, mechanical and electrical properties of nickel electrodeposits in the literature [10] [16] [17]. The most studied of these effects are texturing of the deposit and the effect on the deposit grain size. However, very little has been reported on the magnetic properties of electrodeposited nickel and how these are effected by the electrodeposition process.
The work presented in this chapter first extends the previous study of the magnetic field effects on electrodeposition to that of nickel deposition. Chronoamperometry is used to investigate the effect of the magnetic field on the diffusion process and on the convection-controlled steady state limiting current. Following from this, the properties of electrodeposited nickel are studied. Nickel is deposited from three different baths and the crystal structure, morphology, resistance and magnetic properties of the deposits are compared. The saturation magnetisation is studied in detail for one such bath, the citrate bath. It is hoped that this work will determine any material characteristics which are unique to the electrodeposition process.
3.2 Magnetic Field Effects on the Nickel Electrodeposition.

3.2.1 Introduction

A magnetic field is expected to affect the deposition of nickel by the same forces that are explained in details in Chapter 2. Work carried out by Devos et al. [18] [19] has assigned the magnetic field effect on the nickel system to a knock-on effect of the increased rate of hydrogen evolution caused by induced convection in the system. This increases the pH rise at the electrode, encouraging the formation of nickel hydroxide which partially passivates the electrode surface and accounts for the observed reduction in current in an applied magnetic field. This work was carried out in the Watts bath, a highly concentrated nickel salt solution, where the nickel reaction process is kinetically controlled. Here we intend to look at the effect of a magnetic field in a more dilute nickel solution where the reduction of the ions will, at high overpotentials become mass transport controlled. It is hoped to establish the dominant forces involved in such a system.

3.2.2 Experimental

The experimental set-up and techniques used were exactly the same as those described in detail in Chapter 2. The electrolyte used was a dilute nickel solution 50 mM Ni$_2$SO$_4$·7H$_2$O, 0.04 M H$_3$BO$_3$ (pH= 4.5). The working electrode used was nickel.

3.2.3 Results

The voltammogram for a nickel working electrode in 50 mM NiSO$_4$ and 0.04 M H$_3$BO$_3$ indicated a rest potential of -260 mV rel Ag/AgCl both with and without an applied magnetic field. The nickel voltammogram shows two very distinctive regions as highlighted in Figure 3.28.
Region 1 corresponds to hydrogen ion reduction, which becomes mass transport controlled and Region 2 to nickel and, eventually, water reduction. At very low overpotentials, $\eta<600\text{mV}$, no detectable dependence of the steady state limiting current on the applied magnetic field is seen (Figure 3.29(a)). At such an overpotential the hydrogen evolution reaction is partially activation controlled. At slightly higher overpotentials $800<\eta<1000\text{mV}$, it was obvious that Cottrell behavior is not occurring (Figure 3.29(b)). An induction time for nucleation of 1-2 seconds is observed at the start of the current transients after which the current rise is in keeping with progressive nucleation and growth i.e. diffusion is not planar but spherical. Fitting these transients to Equations (1.30) and (1.31) it is found that they agree quite well with the Scharifker Hill model for progressive nucleation at short times but not for longer times, where the current should follow Cottrell behavior the current deviates. This is due to a kinetic contribution to the current which is better modelled by D’Ajello et al. [20]. No effect of a magnetic field is seen on the magnitude of the limiting current.
Figure 3.29. Current transients both with and without an applied magnetic field at a nickel working electrode for 50mM NiSO$_4$ and a potential step of (a) 400mV and (b) 800mV.

Figure 3.30. The experimental data of Figure 3.29(b) above (a) with no field and (b) with a magnetic field. The fits for progressive and instantaneous nucleation for each data set are also shown.

At intermediate overpotentials, $1200 < \eta < 1400$ mV, the most striking effect of the magnetic field on the current transients is the difference in shape of the curve, as shown in Figure 3.31. Those plated without a magnetic field show perfect Cottrell behavior. However those plated in a field seem to show little change in current with time. At these potentials, nickel reduction should be mass transport limited and the results show that the steady-state limiting current is increased when a magnetic field is applied. At high overpotentials, $\eta > 1600$ mV,
Cottrell behavior is seen both with and without a field and the steady state limiting current does increase on the application of a magnetic field. However the slopes are not equal as is seen in Figure 3.32. Their corresponding diffusion coefficients are an order of magnitude apart. A summary of the enhancement found at each potential step is given in Figure 3.33.

Figure 3.33. Current enhancement in 0.5 T field over the range of potential steps for 50mM NiSO₄.

3.2.4 Discussion

The effect of applying a magnetic field during the electrodeposition of nickel onto a
Figure 3.32. (a) Current time response to -2000 mV potential step both with and without and applied magnetic field. (b) Cottrell plot of the same data showing the corresponding diffusion coefficients

<table>
<thead>
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<th>Enhancement at max. step</th>
<th>21±1%</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
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</tr>
<tr>
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</tr>
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<tr>
<td>Rest Potential (mV rel. Ag/AgCl)</td>
<td>-260</td>
</tr>
<tr>
<td>Threshold of Enhancement(mV)</td>
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</tr>
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<td>$x_m$ for Salt (mol m^-3)</td>
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</tr>
<tr>
<td>$j_L$ for B= 0 T (A m^-2)</td>
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</tr>
<tr>
<td>Diffusion Coefficients m^2s^-1</td>
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</tr>
<tr>
<td>Conductivity of soln. $\sigma(\Omega m)^{-1}$</td>
<td>10</td>
</tr>
</tbody>
</table>

Table 3.8. Summary of chronoamperometric data for 50 mM Nickel sulphate solutions in a field of 0.5T when the maximum potential step is applied. Other relevant parameters are included.

nickel electrode involves the consideration of not only the magnetic forces acting on the electrolyte species and the current, but also the effect of an electrode which will be magnetized once placed in a magnetic field. The field at the surface of the electrode will be the demagnetization field of the nickel electrode. For a sheet of nickel of dimensions 1 cm^2 × 0.025 cm the demagnetization field would be expected to be 0.03 T, which would fall off to near zero within 5 mm giving a field gradient of 6 T m^-1. The roughness of the surface however will greatly increase the field gradient near the electrode surface. As no effort was made to achieve a smooth surface, roughness would be expected on a scale of 10 $\mu$m leading to
a field gradient of 1,000 T m$^{-1}$. This would be expected to have a large influence on the movement of ions near the electrode. The effect of a magnetic field on the deposition of nickel is unusual when compared with results for the other metals: with nickel a change in the Cottrell slope is seen at high overvoltage. At intermediate overvoltages Cottrell behaviour, i.e. planar diffusion with growth of a diffusion layer, is observed in the absence of a magnetic field but is not observed when a magnetic field is applied. These results may be explained when consideration is given to the magnetic field gradient which will affect the ion transport. Diamagnetic water will be repelled from the electrode by a large body force ($10^4$ Nm$^{-3}$) acting in the proximity of the electrode. This will considerably increase convection near the electrode.

At low overpotentials, $\eta < 600$ mV (Figure 3.29(a)), no effect of the field is seen. The current is low and hydrogen reduction is the primary reaction. At potential values $800$ mV $\leq \eta \geq 1000$ mV, progressive nucleation and growth of the deposit is seen. The reaction rate is under mixed control of electron transfer kinetics and mass transport of ions. Hence the magnetic field enhances the current only slightly. As the overpotential is increased, $\eta \geq 1200$ mV, mass transport is now controlling the reaction rate. The magnetic field’s induced convection increases the transport of hydrogen ions and nickel ions to the electrode and the steady-state reaction rate is seen to increase. The growth of the diffusion layer with time however, is not seen in the current transient obtained at these potentials when a magnetic field is applied. This effect may be attributed to the induced convection caused by the field gradient which will occur once the field is applied - there should be no time delay for this to set in as is the case for natural convection. At high overpotentials the reaction rate is such that the convection induced by the field gradient will not sufficiently replenish the ions at
the electrode and the growth of a diffusion layer is observed (Figure 3.32). The production of nickel hydroxide at a large rate can cause significant passivation of the electrode surface. If there is increased convection the OH\(^-\) ions can be transported away from the electrode surface reducing passivation and thereby increasing the active area of the electrode. This will reduce the effective diffusion coefficient calculated from the Cottrell equation. The presence of diamagnetic hydrogen bubbles on the electrode surface will also be decreased in the presence of a field gradient increasing the active surface area.

\[
j = \frac{I}{A} = \frac{nFzc\sqrt{D}}{\sqrt{\pi t}}
\]  

(3.10)

According to Equation (3.10) the changes in the effective diffusion coefficient from \(1\times10^{-9}\) to \(2\times10^{-10}\) with the application of a magnetic field corresponds to an active area that is twice as big in an applied magnetic field than when no field is applied. An inability to determine the active surface area makes any absolute measurement of the diffusion coefficient impossible.
3.3 Characterization Techniques

3.3.1 Scanning Electron Microscopy (SEM)

SEM is a well established diagnostic technique used to examine surface morphology. The resolution of electron microscopy can be down to 10 nm and a higher depth of focus is achievable compared to optical microscopy. The technique consists of bombarding the sample with a beam of highly focused monochromatic electrons. The secondary electrons emitted due to the interaction of the beam with the surface are detected as the beam is rastered across the surface. Non-conducting samples may be coated with a thin layer of gold by sputtering in order to prevent the build-up of charge on the surface. In addition to providing information about the morphology of the surface, detection of other products of the interaction between the beam and the surface may be used to identify the chemical species present. The detection of back scattered electrons provides information about the atomic mass distribution at the surface. Heavier atoms produce more back scattering leading to brighter areas on the image, while lighter atoms show up as darker areas. Scanning Electron Microscopy (SEM) was performed at the TCD Centre for Microscopy Analysis on a Hitachi S3500N microscope. The resolution of the microscope is in the sub-\( \mu m \) range. The morphological information about the nickel electrodeposits allows a particle size determination and identification of features which will depend on the electrodeposition parameters.

3.3.2 Energy Dispersive X-Ray Spectrometry (EDX)

The bombardment of a sample by electrons leads to the emission of x-rays. The energy spectrum of these emitted X-rays may also be measured and the peaks assigned to particular elements. The area under the peaks gives an estimate of the percentage composition of the
surface. Lateral resolution of \( \approx 5\mu m \) and detection of X-rays emitted 3\( \mu m \) below the surface is achievable. Heavy elements are best detected by this method as they produce high energy X-rays; lighter elements, such as O, H, N and C are harder to detect due to the low energy of their X-rays. EDX was performed at the TCD Center for Microscopy with a PGT-Imix EDX system with a germanium detector that was attached to the Hitachi microscope. System standards were used in the quantitative analysis of all heavy elements. EDX was the main tool used to determine the composition of the nickel electrodeposits. The precision of the data is considered to be 1\% or less for heavy elements. Most samples were characterized at three points on the surface. The average of the composition at these points, with their standard deviation is used as a measure of uniformity - it is this value that is represented in the error bars.

3.3.3 Auger Electron Spectroscopy (AES)

The Auger effect is the emission of a second electron after high energy radiation has expelled another. The first electron emitted leaves a hole which is filled by an electron of a higher orbital thereby releasing energy. This energy may then cause another electron to be ejected. This electron is known as an Auger electron, and its energy is dependent on the atom from which it originates. Each element has its own signature energies for Auger electrons and detection of the energies of Auger electrons from a sample allows the identification of the atoms present. The advantage of AES is that it can detect all elements with a high degree of accuracy, however Auger electrons from the surface of the sample can only be detected. Compositional depth profiles can be obtained by progressively removing the sample surface with Ar ion etching. AES spot analysis and depth profiles were carried out by Prof. N. Brown and Dr. C. Anderson at the University of Ulster Surface Science Laboratory using a
3.3.4 Powder X-ray Diffraction (XRD)

This technique developed by Debye and Scherrer uses monochromatic x-ray radiation and a powdered sample to determine crystal structure. When the sample is bombarded with x-rays it will have at least some crystallites oriented so as to satisfy the condition for constructive interference of reflected radiation given by Bragg’s law:

\[ 2d \sin \theta = n \lambda \]

where \( d \) is the spacing between lattice planes, \( \theta \) is the angle of incidence of the radiation, \( \lambda \) is the wavelength of radiation and \( n \) is an integer. As illustrated in Figure 3.34 the diffracted angle, \( \theta \), makes an angle \( 2\theta \) with the incident beam.

![Figure 3.34. Diffraction of X-rays from a crystal](image)

For this reason, X-ray diffraction patterns are represented as plots of intensity against \( 2\theta \). From the angles of high intensity reflection, the spacing between the planes can be determined. As each structure will have a signature diffraction pattern, by comparing the diffraction pattern to the large database, the Joint Committee on Powder Diffraction Standards (JCPDS), phases present in a sample can be identified. From the positions of the peaks, lattice spacings can be determined. If a specific crystal structure is known or assumed, these
spacings can be associated with particular lattice planes and the lattice parameter can be determined. For a cubic structure, the lattice spacings are given by:

$$d_{hkl} = \frac{a}{(h^2 + k^2 + l^2)^{1/2}}$$  \hspace{1cm} (3.11)

where $d_{hkl}$ is the lattice spacing of (hkl) planes and $a$ is the lattice parameter. Only phases present in the sample of 5% or greater of total phases present can be detected in a X-Ray diffraction pattern. Diffraction patterns were taken in air using a Siemens D500 diffractometer with a 40 kV Cu anode to generate Cu-Kα radiation, $\lambda = 0.154$ nm. Samples were mounted on a silicon slide using double-sided adhesive tape. $\theta/2\theta$ step scans were taken using 0.01° steps and a 2 s count time for each step. The range of angles scanned was from 5-140°. Lattice parameters were calculated using AUTOX - lattice search program. Due to an offset in the position of the sample a correction factor of 1.001 was applied to the derived lattice parameter. This value was obtained by comparing the lattice parameters from XRD data obtained from a sample mounted in the correct position to that mounted with the position-offset. For a particular sample set due to an interest in the phases present more rigorous Rietveld refinement of the XRD data was carried out. It was found that the lattice parameters determined from the Rietveld fitting were larger than those derived from the AUTOX program. This was attributed to the range of the variable parameters during the Rietveld fitting - absolute values being more reliable from the AUTOX program. Broadening of the diffraction lines as a result of crystallite size, $D_v$, and strain $\varepsilon_{str}$, was also investigated. These are expected to follow the Equations (3.12) and (3.13).

$$D_v = \frac{k\lambda}{\beta_{size} \cos \theta}$$  \hspace{1cm} (3.12)

$$\varepsilon_{str} = \frac{\beta_{strain}}{4 \tan \theta}$$  \hspace{1cm} (3.13)
where $D_v$ is the volume weighted crystallite size, $k$ is the Scherrer constant (usually $k=1$),

$\lambda$ is the wavelength of the radiation, $\beta$ is the integral breadth of the reflection in radians $2\theta$ and $\varepsilon_{str}$ is the weighted average strain. $\beta_{size}$ and $\beta_{strain}$ are the broadening contributions due to the crystallite size and strain respectively. A third contribution being due to the instrument, $\beta_{inst}$. $\beta_{obs}$ is the total observed broadening. The linear relationship of the broadening components, $\beta_{obs} = \beta_{size} + \beta_{strain} + \beta_{inst}$, is not necessarily true, often they add by raising to the power of two, the method depending on the shape of the reflections Lorentz, Gaussian or in some cases a mixture of two (known as Voigt). Reflection breadths were calculated using the pseudo-Voigt method in Origin software giving a full width at half maximum for the reflection and also a mixing parameter of Lorentz and Gaussian contribution to the peak shape. The resultant contributions to broadening were calculated using the BREADTH method as introduced by Davor Balzor [21]. Instrumental broadening, which would be $\approx 0.05^\circ$ for the monochromatic X-rays used was not accounted for as broadening in our samples was of a factor of 10 greater than this. Also knowledge of relative changes in strain was sufficient.

The crystallite size determined from these patterns are domains of coherent diffraction and do not correspond to the particle sizes determined from SEM micrographs. Extended defects, such a stacking faults, in the sample will effect this crystallite size. Strain, or deformation of the sample is detected when non-uniform strain is present - defect such as vacancies and interstitials are the main causes. The expected crystal structure of nickel is face-centred cubic with a lattice parameter of 3.5238Å [22] and density of 8912 kg m$^{-3}$ at 298 K [23].
3.3.5 Resistivity Measurements

Resistivity of a sample, $\rho$, is defined as $\frac{RA}{L}$, where $R$ is the Resistance, $A$ is the cross-sectional area and $L$ is the length of the sample. Resistance of the sample was determined using the DC four probe Van der Pauw Method. Four pressure contacts were made at the corners of the rectangular sample as shown in Figure 3.35.

![Figure 3.35. Schematic diagram showing the contacts, M, N, O, P to a sample for Van der Pauw resistivity measurements. Voltage and current measurements were taken between adjacent points](image)

Two resistance measurements were taken, $R_1$ and $R_2$ where $R_1 = \frac{I_{MN}}{V_O - V_P} = \frac{I_{NM}}{V_P - V_O}$ and $R_2 = \frac{I_{MP}}{V_N - V_P} = \frac{I_{PM}}{V_P - V_N}$. $V_O - V_P$ and $V_P - V_O$ were determined by measuring the voltage over a range of applied currents. The average of the resulting slopes gave $R_1$. A similar technique was used to determine $R_2$. The measurements were done with a Keithley sourcemeter 2400 Series. Thickness, $d$, of the samples was determined from SEM micrographs with an accuracy of 1 $\mu$m. The Van der Pauw relation was used to determine the resistivity, $\rho$:

$$\rho = \frac{\pi d}{\ln 2} \frac{R_1 + R_2}{2} f$$

(3.14)

where $f$ is a function only of the ratio $R_1/R_2$. This function is given in reference [24]. This method is useful is to determine relative magnitudes of resistance rather than absolute values, as relying on the function $f$, as determined in the above reference, introduces significant errors. Nickel is expected to have a resistivity in the range of $(6.8 - 9.9) \times 10^{-8}$ $\Omega$ m at 20°C.
Resistance of samples was also measured as a function of temperature. During this process the sample had four bolted tantalum contacts on each corner. The sample was placed on a ceramic plate over a hotplate in a chamber. This chamber was evacuated using a roughing pump. Resistance measurements were taken with a Keithley sourcemeter 2400 which was interfaced with a computer that recorded the resistance as a function of time. The direction of the applied current was varied and the resistance measurement taken as an average. The amplitude of the current applied depended on the sample ranging between 2A and 0.2A. The hotplate temperature was controlled by a variable power supply. The temperature was monitored with a thermocouple placed beside the sample - readings were taken by hand. The sample was heated to 300°C, held there for 30 min and then allowed cool back down to room temperature. Resistivity of a metal is expected to increase with temperature according to $\rho(T) = \rho_o(1+\alpha T)$ or $d\rho/dT = \rho_o \alpha$. The rate of change in resistivity is not constant with temperature varying from $0.0385 \ \Omega \ m \ K^{-1}$ at 27°C to $0.0905 \ \Omega \ m \ K^{-1}$ at 327°C for nickel.
3.4 Magnetic Properties of Nickel and Measurement Techniques

Nickel is a ferromagnetic metal. Its electronic structure defines it to be a strong ferromagnet with a fully polarized spin up 3d band and partially-filled 3d spin down band, \([\text{Ar}]3d^83d^{4.4}4s^{0.3}4s^{0.3}\). This is illustrated in Figure 3.36.

![Energy diagram for spin up, \(\uparrow\) and spin down, \(\downarrow\), electrons of the d-band of nickel resulting in its strong ferromagnetism.](image)

The resultant net magnetic moment is \(0.6157\mu_B\) per atom [23] (55.09 emu/g, 6170 G or 0.617 T) and experimentally is known as the saturation magnetisation. As the nickel is heated, disorder induced within the sample will destroy its ferromagnetic properties - this occurs at its Curie temperature of 354.4 °C or 627.4 K [23]. The magnetic susceptibility, \(\chi\), is the response of material to an applied magnetic field, \(\chi = M/B\) where \(M\) is the magnetisation of the sample and \(B\) is the applied magnetic field. A large change in the measured susceptibility is seen at the Curie Temperature. Nickel is a soft magnetic material meaning that it loses much of its magnetisation once the applied magnetic field is removed. This loss of magnetisation is due to the easy formation of magnetic domains within the sample which result in a zero net magnetisation. The ease at which nickel is magnetized depends
on the orientation of the applied magnetic field relative to the crystallographic directions. Particular crystalline directions are easier to magnetize, namely the [111] direction while others are more difficult, namely the [100] direction.

A magnetic field applied to a nickel sample will affect its resistance. The magnetic field distorts the electron clouds affecting the cross-section for scattering of the conduction electrons. This is illustrated in Figure 3.37. The maximum increase in resistance is seen when the field is in plane with the current ($\theta = 0^\circ$, $180^\circ$ or $360^\circ$) while resistance is at a minimum when the field is applied perpendicular to the current ($\theta = 90^\circ$ or $270^\circ$). The Anisotropic magnetoresistance (AMR) is usually presented as a percentage change of resistance. According to Bozorth [26] the AMR of pure nickel is $\approx 3\%$.

$$AMR = \frac{R_0 - R_{90}}{R_0} \times 100$$ (3.15)

AMR can be identified by two distinctive measurements. A constant field can be applied to the sample, the direction of which is rotated relative to the current flow. This results in a sinusoidal variation of the current with field direction and Equation (3.15) above is used to determine the percentage of the AMR effect. Alternatively, an increasing field can be applied in a fixed direction, $0^\circ$ or $90^\circ$, and the change in resistance is monitored. This allows a determination of the field dependence of the AMR effect.
The magnetic properties of interest for the nickel samples prepared by electrodeposition were the saturation magnetisation, the AMR and the Curie temperature. The saturation magnetisation was measured in two ways depending on the mass of the samples. For large masses a Vibrating Sample Magnetometer (VSM) was used while for samples of smaller mass a Superconducting Quantum Interference Device (SQUID) was used. In-house purpose built set-ups were used to measure the AMR and the AC susceptibility.

### 3.4.1 Vibrating Sample Magnetometry (VSM)

Room temperature vibrating sample magnetometry (VSM) was performed in a bench-top magnetometer where the variable field was created by two concentric Halbach cylinders. The magnitude of the field was changed by rotating the cylinders so that the vector sum of their fields added to the desired applied field, up to a maximum of 1.1 T. The sample was vibrated at 29.4 Hz along the bore of the cylinders (H \( \perp \) bore). This induces a voltage in a set of quadrupole pick up coils, also inside the bore, which can be converted into a magnetic moment after calibration with a nickel standard.

![Schematic of Halbach cylinder based VSM used for magnetic characterization](image)

Figure 3.38. Schematic of Halbach cylinder based VSM used for magnetic characterization
3.4.2 Superconducting Quantum Interference Device (SQUID)

Nickel samples with small mass do not produce a strong enough signal for VSM measurement and are therefore characterized using a Quantum Design Magnetic Properties Measurement System (MPMS), better known as a SQUID magnetometer. In this system, a superconducting magnet, a superconducting quantum interference device (SQUID) detection system and a high-performance temperature control system are integrated. This allows for rapid precision measurements over a temperature range of 1.9 to 400 K, in fields up to 5 T. Automatic control and data collection are provided for the system by a computer and two independent subsystem controllers.

Functional components of the system, shown in Figure 3.39, include a temperature control module, superconducting magnet system, SQUID detector system, sample handling system, and a gas handling system. These components are all contained within a liquid nitrogen-jacketed liquid helium dewar. The liquid helium provides refrigeration for the superconducting components as well as providing for operation at low temperatures.

The field in the system is automatically changed by the MPMS control system when a magnetic field value is specified. The magnetic field generated by the superconducting solenoid is controlled through careful monitoring of the current supplied to the solenoid. The field is sustained by trapping a persistent current in the solenoid. The field is then changed either by injecting or removing current to get the desired field. In low resolution mode the field is controlled to within $10^{-5}$ T, while in high resolution it is controlled to within $10^{-6}$ T.
The sample response is detected by a longitudinal SQUID system. This detection system comprises of SQUID sensing loops, a superconducting transformer and the SQUID sensor and control electronics. The SQUID sensing loops are configured as a highly balanced second-derivative coil set with a total length of approximately 3 cm. The coils are designed to reject the field from the superconducting magnet to a precision of approximately 0.1%, making the SQUID detector relatively insensitive to drifts in the magnet. The coils measure the sample response to sensitivity of $10^{-11}$ J T$^{-1}$.

Measurements were performed using the Reciprocating Sample Option (RSO) sample handling system, rather than the standard DC (extraction) system. For this option, the sample is vibrated in the field, in the same way as in a VSM, but this time the vibration direction is parallel to the field direction. The main advantage of this option is shorter measurement times compared to the DC system. Magnetisation data for the samples were
collected at 300 K in fields up to 5 T.

3.4.3 AC Susceptibility

In AC susceptibility measurements the initial susceptibility is determined by a small low frequency (1000 Hz) alternating field of $10^{-5} \text{T}$. A precisely balanced pair of concentric or coaxial pick-up coils is used with driving coils to generate the field, so that no emf is induced in the absence of a sample. The magnetisation of the sample is detected by a pair of pick up coils, high signal to noise ratio is achieved with the use of a lock-in amplifier. The real and imaginary parts of the susceptibility, $\chi = \chi' + i\chi''$, are deduced from the response in phase and out of phase with the applied field. Therefore relative changes in the susceptibility as a function of temperature allow the deduction of the Curie temperature of the sample and the sharpness of the transition. The experimental set-up for such a measurement is shown in Figure 3.40. This apparatus in our laboratory was operated by Plamen Stamenov.

![Figure 3.40. Schematic diagram of the high temperature ac-susceptibility rig](image)
During measurement, samples were heated to above their Curie temperature, 355°C. Nickel electrodeposits were measured by this technique a total of three times. This allowed the effect of heat treatment on the sample’s Curie temperature to be determined.

3.4.4 Anisotropic magnetoresistance (AMR)

Anisotropic magnetoresistance (AMR) of the samples was determined using four in-line contacts to the sample. A magnetic field of up to 2 T produced by a MULTIMAG, a permanent magnetic flux source, could be rotated about the direction of the current flow. Changes in resistance of the sample was again measured by a Keithley sourcemeter 2400. Resistance was measured as a function of the angle between field and current for a fixed field of 2 T and also as a function of field strength at fixed angles 0° and 90°.
3.5 Electrodeposition of Nickel from Sulphate, Citrate and Watts Baths

Nickel electrodeposits were produced from three baths: a simple sulphate bath, a citrate bath and a typical Watts bath. Their magnetic and structural properties were studied and compared. The sulphate bath is a very rudimentary bath containing a high concentration of nickel sulphate and boric acid as a buffer. The Watts bath is a standard bath for the electrodeposition of nickel, consisting of a high concentration of nickel sulphate, boric acid which acts as a buffer and nickel chloride which is used to increase the conductivity of the solution and also helps the efficient dissolution of the nickel anode, which in an industrial setting would allow for plating over an extended period of time. The citrate plating bath investigated is derived from the Ni-Cu alloy plating bath where the citrate serves as a complexing agent shifting the rest potentials of the constituent reduction processes towards each other. The citrate would be expected to shift the rest potential of the nickel reduction to a slightly more negative value. The presence of citrate avoids the precipitation of hydroxides, hence the use of boric acid is unnecessary. The increased temperature of the bath will increase the uniformity of the current distribution. This is particularly important for alloy plating. For this reason also the configuration of the citrate bath is different from the Watts and sulphate baths as seen in Figure 3.41. In the citrate bath the cathode is placed at the centre of a nickel ring anode while for the sulphate and Watts bath the anode and cathode are parallel. Magnetic, electrical and structural properties of these deposits were investigated.

All depositions were carried out potentiostatically at -1.0 V rel to the reference electrode in a standard three electrode cell. The reference electrode was a 3 M Ag/AgCl electrode - all
potential values referred to are relative to this electrode. Details of each plating bath used are shown in Table 3.9. All solution were made up with 0.2μm filtered water and where appropriate the bath was heated by placing it in a temperature controlled water bath. The tantalum substrate was activated by acid treatment immediately before deposition, after which it was rinsed in 0.2μm filtered water. It was then attached to a copper electrode with silver paint for good electrical contact and fixed firmly in place with kapton tape, this also defined the working electrode area. The acid treatment allowed the deposits to be peeled off from the substrate after deposition eliminating interference of the measured properties by the substrate. The area of the working electrode exposed was < 1 cm². Linear sweep voltammograms were taken for each bath at a sweep rate of 20 mV/sec. Electrochemical procedures were carried out using a EG&G 263A potentiostat which was interfaced to a PC.

<table>
<thead>
<tr>
<th>Sulphate bath</th>
<th>Citrate bath</th>
<th>Watts bath</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrolyte</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.14 M NiSO₄·6H₂O</td>
<td>1.14 M NiSO₄·6H₂O</td>
<td>1.14 M NiSO₄·6H₂O</td>
</tr>
<tr>
<td>0.4 M H₃BO₃</td>
<td>0.2 M C₆H₅Na₃O₇·2H₂O</td>
<td>0.15 M NiCl₂·6H₂O</td>
</tr>
<tr>
<td></td>
<td>0.034 M NaCl</td>
<td>0.65 M H₃BO₃</td>
</tr>
<tr>
<td>Plating Conditions</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-1 V for 600 sec</td>
<td>-1 V for 600 sec</td>
<td>-1 V for 600 sec</td>
</tr>
<tr>
<td>50 ml electrolyte</td>
<td>250 ml electrolyte</td>
<td>50 ml electrolyte</td>
</tr>
<tr>
<td>C.E: glassy carbon</td>
<td>C.E: Nickel outercircle</td>
<td>C.E: Nickel</td>
</tr>
<tr>
<td>W.E: Ta (acid treated)</td>
<td>W.E: Ta (acid treated)</td>
<td>W.E: Ta (acid treated)</td>
</tr>
<tr>
<td>100 rpm magnetic stirrer</td>
<td>No stirring</td>
<td>No stirring</td>
</tr>
<tr>
<td>Room temp</td>
<td>pH=4.5</td>
<td>Room Temperature</td>
</tr>
</tbody>
</table>

Table 3.9.Details of the plating baths used for nickel deposition and the relevant parameters. The voltage given is rel. to Ag/AgCl reference electrode

3.5.1 Comparison of Electrochemical Characteristics.

The linear sweep voltogramms for each bath are shown in Figure 3.42. A sharp rise in the current transients is seen in the cathodic current for all baths after a current plateau. This rise can be assigned to the onset of nickel reduction. The current prior to this is due
Figure 3.41. Cells used for the deposition of nickel (a) from a Watts and sulphate solution, (b) from the citrate solution to hydrogen evolution which has reached diffusion control. The onset potential for nickel reduction is estimated to be: for the citrate bath -1.05 V rel Ag/AgCl, Watts baths -0.91 V rel Ag/AgCl and the sulphate bath -0.79 V rel Ag/AgCl. Increasingly cathodic values indicate the increased inhibition of the reduction process in the respective baths. A larger hydrogen evolution current in the citrate bath is also noted. This larger current was still observed when no nickel ions are present in the solution confirming, that the increased current is not related to a nickel deposition process.

Figure 3.42. Linear sweep voltammograms for each of the three baths. Sweep rate 20 mV/sec.
A potential of -1.0 V rel to Ag/AgCl applied for 600 sec was used to prepare the nickel electrodeposits from each of the baths. Typical current transients are shown in Figure 3.43. The current transients are similar to those investigated by D’Ajello [20] which indicates progressive nucleation that is partially controlled by the reaction rate at the electrode as would be expected for nickel electrodeposition. It is also noticed that the deposition rate increases in the order sulphate, Watts to citrate bath. Deposition was also carried out in the presence of magnetic field at -1V and no effect was seen on the deposition rate, indicating that kinetic control of the system is dominant for these electrodeposition parameters. Deposits were bright and typically \( \approx 1 \) mg in mass and of thickness \( \approx 2-3 \mu m \). The current efficiencies of the sulphate, citrate and Watts bath were 97\%, 94\% and 99\% respectively.

![Figure 3.43. Typical current transients during nickel deposition from various baths.](image)

### 3.5.2 Characterization of Deposits

#### Morphology of Deposits and Crystal Structure

Typical SEM micrographs of deposits from each bath are shown in Figure 3.44. It can be seen that granular aggregated particles are deposited. The size of these particles is larger.
for citrate deposition, indicating a lower nucleation rate relative to growth.

Figure 3.44. SEM micrographs of electrodeposited Nickel (a) from sulphate bath (b) from citrate bath and (c) from Watts bath.

For nickel from the citrate bath, the composition as determined by EDX analysis was, pure nickel other than impurities of 0.7 wt % Cu and 0.05 wt % Co. No other heavy element impurities were detected. Lighter elements, which are less reliably detected from EDAX analysis accounted for less than 1 wt %. Nickel from the Watts bath showed, on average, 0.03 wt % Cu and 0.01 wt % Co; lighter impurities were again less then 1 wt %. Nickel from the sulphate bath showed, on average, 0.08 wt % Cu and 0.01 wt % Co; lighter impurities were again detected to be less than 1 wt %. Due to concern about the carbon content in the nickel electrodeposited from the citrate bath I refer to Auger analysis which was carried out in relation to other work. The analysis was carried out on a Ni-Cu electrodeposit of low copper content so it would be expected that the carbon content is similar to that of pure nickel deposition. The depth profile of a single point on the sample surface is shown in Figure 3.45
Figure 3.45. Auger depth profile for nickel-copper electrodeposited from the citrate bath.

The average carbon content of the sample is shown to be 7±3 atm %. Contamination from the Auger analysis chamber is considered to be 2 atm % for both oxygen and carbon yielding 5 ±3 atm.% carbon that is associated with the nickel deposit which persists throughout the depth profile of 0.3μm. This corresponds to an average carbon content of 1 ±0.5 wt % in the deposit from the citrate bath. No oxygen was detected from the deposit.

The crystal structure of all deposits was found to be face centered cubic with a 111 texture dominating all samples. The crystallite size estimated from the peak broadening and Equation (3.12) was in the 20 nm range for all deposits. This implies that the particles observed in the SEM micrographs are polycrystalline.
Figure 3.46. X-ray diffraction patterns for electrodeposited nickel from each bath studied.

<table>
<thead>
<tr>
<th>Nickel source</th>
<th>111: 200: 220</th>
<th>Lattice parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Citrate bath</td>
<td>1: 0.79: 0.15</td>
<td>3.517 Å</td>
</tr>
<tr>
<td>Watts bath</td>
<td>1: 0.40: 0.15</td>
<td>3.516 Å</td>
</tr>
<tr>
<td>Sulphate bath</td>
<td>1: 0.61: 0.63</td>
<td>3.515 Å</td>
</tr>
<tr>
<td>Powder [22]</td>
<td>1: 0.42: 0.21</td>
<td>3.524 Å</td>
</tr>
</tbody>
</table>

Table 3.10. Summary of data from X-ray diffraction patterns of nickel.

The thickness of the samples suggest that substrate issues should not affect the crystal texture. The relative intensities of the dominant X-ray peaks are shown in Table 3.10 When the intensities are compared with those expected from a non-textured powdered sample it is seen that weak texturing of the polycrystalline deposits was obtained. The preferred orientations are 200 for the citrate samples, 200 and 220 for the sulphate sample and no preference for the Watts samples. Relating these to Amblard’s phase diagram, Figure 3.27, it could be suggested that the free growth mode seems to be in operation for the citrate bath, where adsorbents are not inhibiting the crystal growth. This would also explain the larger particle size in the citrate bath deposit morphology. The sulphate bath deposit texture suggests an interference of adsorbed hydrogen with the texture formation.
Saturation magnetisation values obtained from SQUID measurements of the deposits are shown in Figure 3.47. Previous measurements of the magnetisation gave values below that expected for nickel (40-45 Am$^2$ kg$^{-1}$). The error associated with these values is small (±0.05 Am$^2$ kg$^{-1}$) due to the minimal error of the SQUID (±10$^{-10}$ A m$^2$) and the mass measurements (±0.002 mg). These measurements were checked and confirmed by D. Gamet in LETI - CEA, Grenoble, France three months after the data was gathered. When the samples were remeasured 9 months later their values had increased to above that of nickel. Samples which were later freshly prepared in exactly the same manner were measured and yielded magnetizations which were again low but much closer to the literature value for nickel. All crystallographic and composition data of the samples indicated similar properties - it is these results that are summarized in Table 3.11. From these results it can be seen that the magnetisation is a little high for the Watts and sulphate baths while the opposite is true for the citrate bath. The higher magnetisation might be partially explained by the presence of cobalt or iron in the deposits however the EDX analysis only detects 0.01 wt % - 100 times this amount would be needed to explain the increased magnetisation.
Figure 3.47. Magnetisation curves for nickel electrodeposits (a) immediate measurement of initial samples (points) and measurements 9 months later (solid lines) of the same samples (b) Nickel electrodeposits - immediate measurements deposited by the same method as (a).

AMR values of \( \approx 2\% \) are obtained for nickel electrodeposited from the Watts and sulphate baths while the slightly higher values of \( 2.9 \pm 0.1\% \) was obtained for nickel electrodeposited from the citrate bath. Typical AMR measurements are shown in Figure 3.48. The values obtained compare quite favorably to AMR values on 99.99\% nickel of \( 1.4 \pm 0.1\% \) obtained for thin films [27] and also from 99.99\% Advent Nickel Film (Cat No: Ni188411 0.125mm thick). It is below the value of 3\% reported by Bozorth [26]. Resistivity of the samples was estimated using the previously described Van der Pauw method and the thickness of the samples was determined using SEM. These results are included in Table 3.11 and are within the range expected for nickel. The effect of heat treatment on the resistance was also investigated by monitoring the resistance of the sample while it was heated. The results are shown in Figure 3.49. It can be seen that heating the sample significantly reduces the resistance of the citrate deposit while others are relatively unaffected.
Figure 3.48. AMR curves for nickel electrodeposits from (a) sulphate (b) citrate (c) Watts and (d) AMR for commercial nickel.

Figure 3.49. Variation of resistance with time as sample is heated to 300 °C which is maintained for 30 min and then allowed to cool.

From the data summarized in Table 3.11, it is noticed that there is an unusually high saturation magnetisation for the nickel deposited from the sulphate and Watts baths. The effect of crystal structure of electrodeposits on their magnetisation has already been reported
for Co-Ni-Fe system where saturation values higher than predicted by the Slater-Pauling curve have been reported. The high values have been linked to the fcc-bcc interface within the deposits which effect the magnetisation.

![Image](image.png)

Table 3.11. Summary of properties of electrodeposited Nickel.

<table>
<thead>
<tr>
<th></th>
<th>Sulphate</th>
<th>Citrate</th>
<th>Watts</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma_s$ (±0.05) Am²kg⁻¹</td>
<td>56</td>
<td>51</td>
<td>57</td>
</tr>
<tr>
<td>Resistivity ×10⁻⁸ Ω.m</td>
<td>20</td>
<td>40</td>
<td>30</td>
</tr>
<tr>
<td>AMR at 2 T (±0.1%)</td>
<td>1.9%</td>
<td>2.9%</td>
<td>2%</td>
</tr>
<tr>
<td>$\Delta R$ % after heat treatment</td>
<td>+4%</td>
<td>-25%</td>
<td>-7%</td>
</tr>
</tbody>
</table>

The characteristics of the nickel deposited from the citrate bath are different from those of nickel deposited from the sulphate and Watts bath. Its magnetisation is lower, the AMR is higher and a large decrease in resistance is seen on heat treatment. The deposition took place at higher temperatures where there is a higher growth rate which may increase the likelihood of the formation of a metastable phase. Such a metastable state has already been found in as-deposited copper [29]. The grain size of as-deposited copper increases by an order of magnitude within hours of deposition. This results in a 20% reduction of resistivity, removal of stress and decrease in hardness. The initial stability of the smaller grains has been assigned to the pinning of the grain by defects such as vacancies or impurities. Further investigations were therefore carried out on nickel electrodeposited from the citrate bath.
3.6 Nickel Electrodeposited from Citrate Bath.

Nickel was deposited from the citrate bath under similar conditions to those described in Table 3.9. A higher potential of 1.1 V rel. Ag/AgCl was used in order to provide deposits which were thicker, $\approx 10\mu m$, and therefore easier to handle. Galvanostatically deposited samples were also investigated. These were deposited at -50 mA/cm$^2$. Current efficiency was high, at 99-100% according to weights of samples measured compared to the charge passed. These samples were characterized both before and after a heat treatment of 300°C for 30 minutes in vacuum. In order to determine reproducibility of properties, 4 samples were deposited potentiostatically and 4 galvanostatically.

3.6.1 Characterization of Deposits

Crystal Structure and Morphology

SEM micrographs of deposits are shown in Figure 3.50. It can be seen that the granular morphology of the nickel electrodeposits described previously (Figure 3.44(b)) has been replaced with a finer structure of agglomerates reflecting the increase in growth rate. Cross-sectional micrographs confirm the similar granular aggregates albeit on a smaller scale to those previously described. EDX analysis of the deposits showed no change before and after the heat treatment with impurities of 0.2 wt % Fe and 0.1 wt % Co.
Figure 3.50. Micrographs of nickel electrodeposits (a) as deposited (b) after heat treatment (c) cross section showing granular structure.

X-ray diffraction patterns from the samples show an fcc structure with some texturing in the [200] direction. This is similar to the texturing of the previous sample however in this case the texturing is much stronger. The crystalline structure and texture is unaffected by the heat treatment, however as is shown in Table 3.12, the full width at half maximum of the XRD peaks shows a reduction upon heat treatment. This reduction can be assigned to a change in strain and crystallite size, an estimate of which is given using the BREADTH program. This was done for three samples before and after the heat treatment. The average results are presented in Table 3.12.

Figure 3.51. X-ray diffraction patterns for as deposits and heat treated samples, fcc indices are shown.

115
Table 3.12. Summary of properties obtained from the X-ray diffraction. Standard deviations are shown in brackets. This method gives an estimate of strain and crystalline size only.

### Magnetisation

Typical magnetisation measurements are shown in Figure 3.52 before and after heat treatment. Data collected over four samples were averaged and compared before and after heat treatment. This was also done for samples deposited galvanostatically, these results are shown in Table 3.13. Experimental errors are $<\pm0.3\ \text{Am}^{-2}\text{kg}^{-1}$, standard deviation is $<2\ \text{Am}^{-2}\text{kg}^{-1}$. A rise of 8% is noted in the values, bringing the values in-line with what is expected of pure nickel.

![Magnetisation curves of a nickel as-deposited and after heat treatment.](image)

Table 3.13. Magnetisation data averaged over four samples.
The evolution of the electrodeposits may be followed in measurements of the AC susceptibility as a function of temperature. The sample was cycled three times from 20 to 400°C. Each cycle took 20 minutes. The Curie temperature, $T_C$, estimated by extrapolating $\chi''$ to zero, also evolves on thermal cycling from 335°C (608K) on first heating to 354°C (627K) on the third run, whether heating or cooling.

Figure 3.53. Magnetic susceptibility measured at 1 kHz for a nickel deposit (a) first heating/cooling cycle and (b) third heating/cooling cycle.

**Resistance**

The lack of reproducibility in the Van der Pauw technique did not allow for the detection of changes in resistivity due to heat treatment. Resistivity measurements that were carried out on the samples were all of the order of $10 \times 10^{-8} \ \Omega \ \text{m}$. However the in-situ evolution of resistance with temperature was measured. These measurements of resistance, as deposits are heated to 300°C, are shown in Figure 3.54. It can be seen that a fresh deposit shows a reduction of resistance of 20% after heat treatment. It is interesting to note that this change is not seen for a deposit which had been made two months previously. This suggests that the effect of heating on the sample can also occur at room temperature over time.
When the resistance of a fresh sample was monitored over an extended period of time (2 days) no change was seen in the resistance.

![Figure 3.54. Change in resistance of nickel, electrodeposited from a citrate bath at -1.1 V, on heating to 300°C for 30 minutes and then allowed to cool to room temperature.](image)

3.6.2 Discussion

The properties of nickel electrodeposited from a citrate bath are unusual. Its magnetisation and Curie temperature are low in the as-deposited state however a mild heat treatment restores their expected values. Defects in the crystal, which are removed during heat treatment are likely to be the cause. Hydrogen would be considered the most likely cause as nickel is known to easily absorb hydrogen into the interstitial positions of the lattice forming the α—nickel and β—nickel as mentioned in the introduction. The amount of hydrogen needed to explain the reduced moment is 5 atomic %. This is greater than that of α—nickel. If hydrogen was present in the samples then two experimental observations would be expected. Firstly heating of the sample would cause an outgassing of hydrogen from the nickel. In order to test this the sample was placed, under slight vacuum to prevent oxidation, in a sealed tube. This was then heated to 400 °C. A piezo-detector was attached
to register the change in pressure with temperature and the results recorded. The detector was accurate enough to register an increase in pressure. However the increase observed was due to thermal expansion on heating rather than hydrogen outgassing. The pressure change expected from 5 atm. % hydrogen in the sample of 3.5mg calculated from the ideal gas law (PV=nRT) is shown in Figure 3.55 - no outgassing was observed from the sample.

Figure 3.55. Data obtained from thermo piezo analyzer compared with that required to explain reduction in magnetisation of electrodeposited nickel.

Secondly, the hydrogen would also be expected to occupy the interstitial sites of the nickel lattice causing it to expand. The lattice parameter would be expected to expand by 0.004 Å with 5 atm. % hydrogen [30]; this is not observed. The same reasoning would rule out any nitrogen which could have been adsorbed during the deposition. Other defects possible are light element impurities such as carbon or oxygen present in the sample as substitutional or interstitial defects. The presence of nickel vacancies and nickel interstitials may also effect the magnetisation of the samples.

The effect of these defects on the magnetisation of nickel has been evaluated by Dr. Sanvito, in the local spin density approximation using the SIESTA code [31]. The calculated moment for the full 32 atom cell was $19.08\mu_B$ ($0.5963\mu_B$ per atom) or $56.72\text{Am}^2\text{kg}^{-1}$. The
Table 3.14. Reduction of saturation magnetisation for defects. Concentration of defect is one in 32 atoms.

<table>
<thead>
<tr>
<th>Defect</th>
<th>$\Delta\sigma_s$/ Am^2kg^{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni vacancy</td>
<td>1.5</td>
</tr>
<tr>
<td>Ni divacancy</td>
<td>2.9</td>
</tr>
<tr>
<td>Ni interstitial</td>
<td>3.0</td>
</tr>
<tr>
<td>C substitutional</td>
<td>2.4</td>
</tr>
<tr>
<td>C interstitial</td>
<td>5.7</td>
</tr>
</tbody>
</table>

Change observed experimentally of $\approx 5$ Am^2kg^{-1} was seen on heat treatment of 300°C for 30 minutes. Assuming that the defects are removed by a thermally activated diffusion process through the lattice to the grain boundaries, then the diffusion length ($\sqrt{D}\,t$) from the centre of a grain to its edge $\approx 20$ nm according to Table 3.12. The activation energy of the process can be estimated from $D = \nu a^2 e^{E_A/kT}$ where $\nu$ is the attempt frequency $\approx 10^{-13}$ and $a$ is the jump distance equal to the lattice parameter $3.5 \times 10^{-10}$m. The estimated activation energy is then 1.5eV. The energy associated with such a process at room temperature is 0.7eV. Defects therefore need to fill two requirements: reduce the magnetisation of nickel by 5 Am^2kg^{-1} ($=0.05\,\mu_B$) and have an activation energy of diffusion between 0.7 and 1.5eV. Table 3.14 summarizes the reduction seen of the saturation magnetisation for each defect according to the SIESTA calculations. While the activation energy of nickel vacancy diffusion ($\approx 1$ eV) is suitable, four nickel vacancies would be needed in the 32 atom cell to explain the reduction in magnetisation - an implausible scenario. The effectiveness of a nickel divacancy in reducing the moment is no better: it is equivalent to two independent vacancies. The presence of two nickel interstitials in the 32 atom cell would reduce the moment sufficiently, however this concentration of defects is unlikely. Also, the activation energy for interstitials is expected to be as low as 0.1eV [32] implying that the defect would run out of the electrodeposit very quickly at room temperature. The presence of carbon in the deposits has little effect on the magnetisation when it substitutes in a nickel lattice site. However, if the carbon takes up an interstitial octahedral site, as shown in Figure 3.56, the increased proximity to the nickel...
ions results in a significant reduction in the magnetisation of the sample.

Figure 3.56. Fcc crystal structure of nickel showing interstitial carbon in the octahedral site.

One carbon interstitial to 32 nickel atoms (3 atm.%) reduces the magnetisation 5.71 Am²kg⁻¹. Auger analysis of the electrodeposits support the idea that carbon is present in the as-deposited films at this level (Figure 3.45).
3.7 Conclusions

Magnetic field effects on the chronoamperometry of nickel are more complicated than for the other metals discussed in Chapter 2 because of the action of the magnetic field gradient force and the coevolution of hydrogen. The origin of the magnetic field gradient forces lies in the roughness of the electrode. A definite effect on the diffusion process is observed - whether this is due directly to the gradient force or the passivation of the electrode is unclear. The absence of diffusion-controlled evolution of the current in a magnetic field when intermediate potentials are applied suggests that the gradient force is affecting ion transport.

Nickel electrodeposits from the simple sulphate and traditional Watts bath produce properties comparable to those of bulk nickel. A face-centred cubic crystal structure with little or no crystalline texture is observed, a slightly higher than expected magnetisation is measured and an AMR of <2% is obtained. These properties are stable upon heat treatment and are in accordance with values expected of nickel. Nickel deposited from the citrate bath however has a lower magnetisation and Curie temperature in the as-deposited state. These properties are restored upon mild heat treatment. The resistance of the nickel is seen to drop upon heat treatment. The type of defect which could be responsible for such an effect is limited by the low activation energy required to remove it and also its stability at room temperature. Despite the expected effect of adsorbed hydrogen on nickel no experimental evidence was found to suggest it is present in significant quantities. Carbon positioned in octahedral sites of the nickel can explain the observed moment reduction.

This work serves to illustrate that the electrodeposition, even though carried out at near room temperatures, is a process which can produce material that is not in equilibrium. The electrodeposited nickel is in a metastable state which a mild heat treatment can eliminate.
The presence of defects in the as deposited material, will under certain conditions, modify the properties of the material. Magnetic properties of the material are an ideal indication of their presence.
### Appendix A

**List of Symbols**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\chi_m$</td>
<td>Molar susceptibility (mol m$^{-3}$)</td>
</tr>
<tr>
<td>$j_L$</td>
<td>Steady state limiting current density (A m$^{-2}$)</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>Conductivity of solution ($\Omega$ m)$^{-1}$</td>
</tr>
<tr>
<td>$\eta$</td>
<td>Overpotential (V)</td>
</tr>
<tr>
<td>$j$</td>
<td>Current density A m$^{-2}$</td>
</tr>
<tr>
<td>$I$</td>
<td>Current (A)</td>
</tr>
<tr>
<td>$A$</td>
<td>Area (m$^2$)</td>
</tr>
<tr>
<td>$n$</td>
<td>Valence of ion</td>
</tr>
<tr>
<td>$F$</td>
<td>Faraday’s constant (96485.309 C mol$^{-1}$)</td>
</tr>
<tr>
<td>$c$</td>
<td>Concentration in bulk (mol m$^{-3}$)</td>
</tr>
<tr>
<td>$D$</td>
<td>Diffusion coefficient m$^2$s$^{-1}$</td>
</tr>
<tr>
<td>$t$</td>
<td>Time (s)</td>
</tr>
<tr>
<td>$d$</td>
<td>Spacing between lattice planes (m)</td>
</tr>
<tr>
<td>$d_{hkl}$</td>
<td>Lattice spacing of (hkl) planes (m)</td>
</tr>
<tr>
<td>$\theta$</td>
<td>Angle of incidence of the radiation (°)</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>Wavelength of radiation (m)</td>
</tr>
<tr>
<td>$D_v$</td>
<td>Volume weighted crystallite size</td>
</tr>
<tr>
<td>$k$</td>
<td>Scherrer constant (usually $k=1$)</td>
</tr>
<tr>
<td>$\beta_{size}$</td>
<td>Broadening due to crystallite size (°)</td>
</tr>
<tr>
<td>$\beta_{strain}$</td>
<td>Broadening due to strain (°)</td>
</tr>
<tr>
<td>$\beta_{inst}$</td>
<td>Broadening due to instrument (°)</td>
</tr>
<tr>
<td>$\beta_{obs}$</td>
<td>Total observed broadening (°)</td>
</tr>
<tr>
<td>$I_{MN}$</td>
<td>Current through points M and N (A)</td>
</tr>
<tr>
<td>$V_P$</td>
<td>Voltage at point P (V)</td>
</tr>
<tr>
<td>$R$</td>
<td>Resistance (Ω)</td>
</tr>
<tr>
<td>$\rho$</td>
<td>Resistivity (Ω m)</td>
</tr>
<tr>
<td>$\chi$</td>
<td>Magnetic susceptibility</td>
</tr>
<tr>
<td>$\nu$</td>
<td>Attempt frequency (s$^{-1}$)</td>
</tr>
<tr>
<td>$a$</td>
<td>Jump distance (m)</td>
</tr>
<tr>
<td>$E_A$</td>
<td>Activation energy (J atom$^{-1}$)</td>
</tr>
<tr>
<td>$\sigma_s$</td>
<td>Saturation magnetisation Am$^2$kg$^{-1}$</td>
</tr>
<tr>
<td>$\mu_B$</td>
<td>Bohr magneton (9.2740154 $\times$ 10$^{-24}$ J T$^{-1}$)</td>
</tr>
</tbody>
</table>
References


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[32] Correspondance with Prof. A. P. Sutton, Department of Materials, Oxford University.
Chapter 4

Properties of Electrodeposited Nickel-Copper
4.1 Introduction

Nickel copper alloys have been of interest for many years due to the improved mechanical properties of the alloy when compared with the parent metals; higher tensile strength, malleability and ductility [1]. The superior corrosion resistance of Monel metal (67 % nickel, 30% copper, 1.5% iron, small content of carbon, manganese, silicon and other elements) in environments such as sea water allow its use in many marine structures and seawater treatments. The high electrical resistance of Constantan (48 % nickel, 52 % copper) coupled with its low temperature coefficient make it an ideal material for use as resistance wires at low temperatures. Despite early work on the electrodeposition of the alloys a commercial plating process for Ni-Cu has never been developed; the main obstacle being the large difference in the rest potentials of the metals, making homogenous alloys of high copper content difficult to produce with high efficiency [2]. In recent years there has been renewed interest in nickel-copper electrodeposition due to the Giant Magneto-resistance (GMR) effect, of 3-6%, observed when nickel-copper alloy is plated as a component of a multilayered system, which has possible application in magnetic sensors [3] - [6]. Electrodeposition of GMR structures would provide a method of fabrication that is relatively simple and inexpensive. The Ni-Cu system is particularly suited to multilayer GMR structures because a nickel rich magnetic layer and copper nonmagnetic layer can be easily plated from a single bath by pulsing the potential of deposition.

The metallurgical nickel copper alloy system is very simple. The metals are completely soluble as seen in the phase diagram in Figure 4.57. Both have fcc crystal structures which are maintained in the alloy. The lattice parameter increases linearly from 3.52 Å to 3.61 Å with the addition of copper to nickel [7]. Diamagnetic copper is transformed to be paramag-
netic on the addition of 0.8 to 0.9% nickel. 56% nickel is required for the alloy to exhibit ferromagnetism at ordinary temperatures. Both the Curie temperature and the magnetisation increase linearly with the addition of nickel to copper from this point [9].

![Phase diagram of nickel and copper showing complete miscibility. Curie temperature for relevant alloys also shown [8].](image)

The electrochemistry of nickel and copper is dominated by the fact that copper is substantially more noble than nickel. The rest potential for copper is +0.337 V rel. SHE while that for nickel is -0.250 V rel. SHE. The implication for alloy deposition is that the copper reduction rate is controlled by mass transport to the cathode at the potential where codeposition of nickel becomes possible. This can be compensated for by using a high concentration of nickel relative to copper allowing the deposition of Ni-Cu alloys with low copper content. However, if the copper content is increased the resulting large current will cause dendritic or powdery copper growth. The reduction rates of nickel and copper ions from a single bath are considered to be largely independent of each other [10].

In order to overcome the problem of producing homogenous Ni-Cu alloys where the copper content is appreciable, a complexing agent can be used. These organic ligands complex with metal ions in solution modifying their concentration and changing their electrochemical
behavior increasing the range of parameters under which codeposition can occur. A range of complexing agents are used for Ni-Cu codeposition: ammonia, cyanide, oxalate, thiosulfate, pyrophosphate and citrate. Citrate is a particularly suitable complexing agent as this produces good quality nickel-rich alloys with a high current efficiency. The citrate ion acts not only as a complexing agent but also as an effective buffer, brightener and levelling agent. The low toxicity of the citrate bath is also an advantage [7]. Despite the use of citrate, the regimes under which copper and nickel deposit are still different as was demonstrated by Landolt [11]. The nickel deposition rate is activation controlled while that of copper is controlled by mass transport. Investigations by Ying [12] have shown that in the citrate system there is a potential region where codeposition of Ni-Cu alloys is possible. The lower limit is determined by the onset of nickel reduction and the upper limit is set by the water reduction reaction (-0.83V SHE), both of which reduce the current efficiency to below usable levels. Ying considered deposition from a citrate bath where the concentration of citrate was high enough to ensure that all metal ions were complexed. Podlaha et al. considered the situation where this is not the case [13]. They found that copper deposited from the complexed ion does so at a slower rate than that of uncomplexed copper due to the decreased diffusion coefficient. The nickel deposits more easily from the uncomplexed ion, the presence of the complexant reducing the nickel partial current. The overall effect of the citrate was a lowering of the reaction rates. In such a system, it was also found that the nickel and copper partial currents were not completely independent due to the complexing equilibria with the citrate ion.

Much of the research on the electrodeposition of Ni-Cu bulk alloys has concentrated on the alloy’s electrochemical and mechanical properties in the region of the Monel alloy
There is little to read on the magnetic properties of electrodeposited ferromagnetic Ni-Cu alloys (Ni ≥ 60%). These properties have only been studied briefly in relation to the AMR and GMR properties of Ni-Cu/Cu multilayers [15]. Other electrodeposited ferromagnetic alloy systems have been studied extensively. The Ni-Fe-Co system has produced very interesting magnetisation results where the saturation magnetisation was claimed to be beyond that predicted in the Slater-Pauling curve. The high magnetisation values are linked to a hybrid crystal structure (fcc/bcc) which is stabilized due to the unique features of the electrodeposition process [16] - [18].

The investigations reported in this chapter explore the magnetic and structural properties of electrodeposited nickel-copper alloys. It was hoped to establish if there is any effect of the electrodeposition process on the magnetic and other properties of Ni-Cu, such as an increase in moment above the Slater-Pauling curve. To this end, nickel copper alloys are potentiostatically deposited from three highly concentrated nickel solutions: a simple sulphate bath, a citrate bath and a Watts bath. The effect of copper concentration in the electrolyte on the alloy composition is investigated. The alloys that have been produced are in the nickel-rich region with 90-100% Ni. It would also be expected that any forced convection in the system will increase the rate of the copper reduction process which is mass transport controlled. With this in mind the effect of applying a magnetic field during the electrodeposition process on the alloy composition and properties has been investigated and compared with the effect of electrolyte stirring.
4.2 Experimental Method

The nickel-copper alloys were prepared from three baths similar to those used to deposit nickel in the previous chapter with the addition of various concentrations of copper sulphate. The bath conditions were summarized in Table 4.15. The reference electrode used for all baths is Ag/AgCl/3 M KCl. The cell geometries were identical to those in the previous chapter as shown in Figure 3.41. All solutions were made with 0.2 \( \mu m \) filtered water. For the citrate bath, where plating was done at the elevated temperature of 50° C, the temperature was controlled by placing the electrochemical cell in a temperature controlled water bath. All deposition was carried out potentiostatically at -1 V rel Ag/AgCl electrode as this was found to give a more uniform deposit than galvanostatic deposition. The tantalum working electrode was placed in 50% HCl for 10 minutes prior to deposition when it was then rinsed in filtered water and attached to a copper sheet with silver paint and fixed in place with kapton tape, which also defined the working area.

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Sulphate bath</th>
<th>Citrate bath</th>
<th>Watts bath</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1.14 M NiSO4.6H2O</td>
<td>0.2 M C6H5Na3O7.2H2O</td>
<td>1.14 M NiSO4.6H2O</td>
</tr>
<tr>
<td></td>
<td>0.4 M H3BO3</td>
<td>0.034 NaCl</td>
<td>0.15 M NiCl2.6H2O</td>
</tr>
<tr>
<td></td>
<td>0.0-0.04 M CuSO4</td>
<td>0.0-0.04 M CuSO4</td>
<td>0.65 M H3BO3</td>
</tr>
<tr>
<td>Plating Conditions</td>
<td>-1V for 600sec</td>
<td>-1V for 600sec</td>
<td>-1V for 600sec</td>
</tr>
<tr>
<td></td>
<td>50ml electrolyte</td>
<td>250ml electrolyte</td>
<td>50 ml electrolyte</td>
</tr>
<tr>
<td></td>
<td>C.E: glassy carbon</td>
<td>C.E: Nickel outercircle</td>
<td>C.E: Nickel</td>
</tr>
<tr>
<td></td>
<td>W.E: Ta (acid treated)</td>
<td>W.E: Ta (acid treated)</td>
<td>W.E: Ta (acid treated)</td>
</tr>
<tr>
<td></td>
<td>100rpm magnetic stirrer</td>
<td>No stirring</td>
<td>No stirring</td>
</tr>
<tr>
<td></td>
<td>Room temp</td>
<td>50°C</td>
<td>Room Temperature</td>
</tr>
<tr>
<td></td>
<td>pH=4.5</td>
<td>pH=4.5</td>
<td>pH=4.5</td>
</tr>
</tbody>
</table>

Table 4.15. Details of the plating baths used for nickel deposition and the relevant parameters. The voltage given is rel to Ag/AgCl reference electrode. C.E.: counter electrode, W.E.: working electrode.

Once the deposition was complete, the working electrode was immediately removed from the plating bath and the deposits were peeled from the tantalum substrate. They were then rinsed with filtered water, acetone and water again. The morphology and composition of
the deposits were characterized using SEM and EDX analysis. X-ray diffraction patterns were used to determine crystallographic properties, the SQUID magnetometer was used to obtain magnetisation curves and the in-house AMR set-up was used to measure the anisotropic magnetoresistance. AC susceptibility measurements were carried out on all samples prepared from the citrate bath. These techniques are described in detail in the previous chapter; Sections 3.3 and 3.4.
4.3 Nickel-Copper Electrodeposited from the Sulphate Bath

The linear sweep voltammograms taken for various concentrations of copper ions are shown in Figure 4.58. These results illustrate clearly the different behaviour of the nickel and copper reduction reactions. Copper reduction begins at about -0.15 V and increases within a relatively short voltage range to a limiting value due to the low concentration of copper ions in solution. The copper limiting current increases as the copper ion concentration increases. Nickel reduction begins at -0.8 V and the current depends linearly on the potential over the remaining potential range. The high concentration of nickel in solution ensures that its reduction process is kinetically controlled. The copper content of the alloy is controlled by the copper ion concentration in solution. The deposition potential of -1 V, shown in Figure 4.58, corresponds to a nickel partial current of -138 Am⁻². When this is compared to the limiting current of copper at Cu²⁺ concentrations of 0.035M and 0.008M this would yield alloys of 90% and 94% nickel respectively. However, the presence of Cu²⁺ reduces the nickel partial current at any given potential, the effect being greater with greater copper

Figure 4.58. (a) Linear sweep voltammograms for nickel sulphate and boric acid solution with added copper sulphate concentration as indicated. (b) Detail of copper reduction region. Sweep rate 20mV/sec
concentration. This maybe due to the reduction of active sites available for nickel reduction. The current transients during the deposition processes are shown in Figure 4.59. At this.

![Graph showing current transients for deposition of Ni-Cu at -1 Vrel. Ag/AgCl. Solution contains 1.14 M nickel sulphate and 0.4 M boric acid plus the indicated copper sulphate concentration.](image)

Figure 4.59. Current transients for deposition of Ni-Cu at -1 Vrel. Ag/AgCl. Solution contains 1.14 M nickel sulphate and 0.4 M boric acid plus the indicated copper sulphate concentration.

deposition potential, the pure nickel current is not larger than the current when Cu$^{2+}$ ions are present and increases slowly with time. For intermediate copper ion concentration the current achieves a steady state limiting current more quickly, hence there will be a small composition gradient on the substrate side of the deposit, where a nickel-rich film gradually increases in copper content. The current efficiency of the deposition reduces as the copper content of the bath increases; for a pure nickel bath current efficiency is 97%, while for a bath containing 0.01 M CuSO$_4$ the current efficiency is reduced to 90%. For the bath containing 0.04 M CuSO$_4$ the current efficiency is as low as 28%, however the total mass of these deposits may not have been measured due to their powdery nature. If we assume a compact deposit, which as we will see later is not always the case, the thicknesses of the deposits are 2.8 µm, 2.3 µm and 1 µm respectively in actuality they are much thinner than this when prepared from a bath of high copper content. Current efficiencies determined from

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the more accurate quartz crystal microbalance yielded values of 60% for 0.002 M and 0.003 M CuSO₄ in the solution.

4.3.1 Morphology and Composition of Deposits

The effect of copper sulphate addition to the nickel sulphate bath, shown in Figure 4.60, was striking. Pure nickel deposits were smooth, however once the Cu²⁺ concentration exceeded 0.015 M copper-rich components were seen. The morphology of the deposits becomes progressively rougher with increasing [Cu²⁺] and eventually dendritic and fractal growth occurs. This explains why the error of such values are higher. These deposits are powdery, making current efficiencies and thickness difficult to determine. The composition

![Figure 4.60](image-url)
of the samples, determined from EDX analysis, indicated that the rougher fractal growth was richer in copper content. This fractal growth leads to less uniformity of the copper deposition. A clear distinction between copper rich and poor phases appears first from a bath of 0.02 M CuSO$_4$ and then grows steadily. Due to the thin deposits the X-rays were detected not only from the deposits but also from the sample holder which was primarily carbon and aluminium. This made the detection of impurities unfeasible. All weight percentages referred to are normalized to consider only the nickel and copper content. The detection of carbon and aluminium increases as the copper content of the deposits increases due to the thinner deposits, which are powdery and porous. The variation of composition in the deposit cross-section was investigated using EDX for a sample prepared from a bath with 0.01 M Cu$^{2+}$ concentration. This is shown in Figure 4.61. The thickness of the sample was close to the resolution of the SEM and the spot size for EDX resolution was also a limitation to accuracy. However, it can be seen that a nickel-rich surface is present and that the copper content increases with thickness. The presence of these two phases was further investigated by X-ray diffraction.

![Figure 4.61. (a) SEM micrograph showing the cross-section of a deposit from 1.14 M NiSO$_4$, 0.4 M H$_3$BO$_3$ and 0.01 M CuSO$_4$ (b) variation of copper content with thickness. Composition of the two phases at the surface shown in red.](image-url)
4.3.2 Crystal Structure

The X-ray diffraction patterns also highlighted the onset of a copper-rich phase. This can be clearly seen in the (111) reflection of the X-ray patterns in Figure 4.62. A broadening of the peaks can be seen at their low angle edge for deposits plated from solution with 0.015 M CuSO$_4$ or greater. Eventually a distinctive shoulder on the peak is observed. The broadness of this shoulder indicates a quite disordered phase which, due to its position, is compatible with a copper rich phase.

![X-ray diffraction pattern](image)

Figure 4.62. X-ray diffraction pattern of Ni-Cu deposited from electrolyte of 1.14 M NiSO$_4$, 0.4 M H$_3$BO$_3$ and CuSO$_4$ as indicated. The expected peak positions for pure nickel and copper are also shown.

Rietveld refinement of the X-ray diffraction data confirmed the presence of two phases. While it is unable to distinguish between the copper and nickel content within the phases due to their similar scattering factors, it does reveal that $\approx$40% of the deposit consists of a copper-rich phase and $\approx$60% of a copper poor phase. This ratio is constant for all samples with two phases (i.e. deposited from a bath with 0.015 to 0.04 M CuSO$_4$). The corresponding lattice parameters, also determined by the Rietveld fitting are shown in Figure 4.63. The
Figure 4.63. Lattice parameters as a function of copper sulphate concentration in the plating bath. The presence of two phases and their corresponding lattice parameters are indicated from the Rietveld and for single phase deposits from the AUTOX program.

AUTOX program determines lattice parameters more accurately but is unable to do so for two phases. The lattice parameters for those alloys with a single phase are also shown in Figure 4.63. The lattice parameter is seen to be below that expected for nickel. For low copper content the lattice parameter increase linearly with copper content, obeying Vegards law. Deviation is observed marking the onset of two phases: the copper-rich phase having as expected a larger lattice parameter than that of the copper-poor phase. An fcc crystal structure is found for all deposits; there was no detection of hydroxide, oxides or other crystalline compounds. As can be seen from Figure 4.64, little texturing of the deposits was observed, relative intensities becoming more similar to that of powder with the addition of copper.
4.3.3 Magnetic Properties

Magnetisation data for the nickel copper electrodeposits were obtained using a SQUID magnetometer, due to the small masses of the samples (~1.2 mg). The error associated with these values is small (±0.05 Am^2 kg^-1) due to the minimal error of the SQUID (±10^-10 A m^2) and of the mass measurements (±0.002 mg). The saturation magnetisation values are plotted as a function of both copper concentration in the solution and the % wt. of copper in the deposits in Figure 4.65. The main feature to note is the reduced magnetisation of pure nickel and low copper content deposits in comparison with bulk values. The values are as much as 30% below what would be expected from their copper content. As has already been mentioned, impurities in the deposits were not quantifiable from the EDX analysis however, the impurity content of the deposits would have be ≈20% to allow for such a reduction. X-ray diffraction did not detect any significant amount of impurity.
In contrast however the deposits with higher copper contents have higher than expected values of saturation magnetisation. This could be accounted for by an over-estimation of copper content of the deposits due to the presence of copper rich components. When these samples were remeasured after 13 months a dramatic increase in their magnetisation was observed (Figure 4.66). Anisotropic magnetoresistance data of deposits at room temperature in a magnetic field of 2 T are shown in Figure 4.67. A maximum value of 2.5 ± 0.1 % is achieved for a sample with 10 wt. % Cu. This value compares well with AMR values of 1.2 ± 0.1 % previously reported for electrodeposited nickel copper alloys [19] and can be compared to the GMR effect of 2-3% found in the Ni-Cu/Cu multilayer system [6].

4.3.4 Effect of Convection and Magnetic field on Electrodeposit

It would be expected that any forced convection in the system would increase the rate of copper reduction, which is mass transport controlled, leaving the nickel reduction rate unaffected. For this reason the effect of both mechanical stirring and application of a
Figure 4.66. Saturation magnetisation data from Figure 4.65 with data from same samples remeasured 13 months later.

magnetic field to the cell have been investigated. The electrodeposition process is identical to that described in Table 4.15 for the sulphate bath. The rotation rate of the magnetic stirrer was varied from 0-300 rpm. The effect of a magnetic field was investigated by placing the entire cell in the bore of a permanent magnet with a maximum field strength of 0.5 T, perpendicular to the current flow. The concentration of CuSO₄ in the electrolyte was 0.1 M as it was just beyond this concentration that copper growth became segregated. The morphology and copper content of the deposit are shown in Figures 4.68 and 4.69 and the X-ray diffraction patterns are shown in Figure 4.70.
Figure 4.67. (a) Change in resistance with field applied parallel, $\parallel$, and perpendicular, $\perp$. (b) % AMR determined by rotation of a 2 T field about the direction of the current flow. Insert shows typical results.

Figure 4.68. Morphology of electrodeposits from bath containing 1.14 M NiSO$_4$, 0.4 M H$_3$BO$_3$ and 0.1 M CuSO$_4$ (a) no stirring (b) 100 rpm (c) 300 rpm and (d) B- field, no stirring.
It can be seen from the micrographs that the copper speckling is increased with stirring rate. The Ni-Cu sample deposited with no agitation shows few sites of copper rich growth and has a smooth morphology. The increased agitation increases dramatically the copper growth resulting in much rougher and non-uniform growth. The effect of the magnetic field on the morphology is comparable to that of 100 rpm stirring. However, when the composition of these prominent growth sites is investigated, as shown in Figure 4.69, the difference in copper content is more comparable with the case of no agitation. In the X-ray diffraction patterns the distinctive copper rich shoulder is observed only for an agitation rate of 300 rpm, but not for any other conditions.
Figure 4.70. X-Ray diffraction patterns of Ni-Cu electrodeposited from 1.14 M NiSO₄, 0.4 M H₃BO₃ and 0.1 M CuSO₄ with agitation as indicated.
4.4 Nickel-Copper Electrodeposited from Citrate Bath

The citrate bath used to codeposit the nickel and copper has a citrate concentration that is well below the total metal ion concentration in the solution. It would be expected that nickel deposition occurs from the uncomplexed nickel ion while that of copper occurs from the complexant. Linear sweep voltammograms for this bath are shown in Figure 4.71. A current plateau corresponding to copper reduction is not clearly observed indicating that copper reduction reaction is slower in the citrate bath than in the simple sulphate bath. A large increase in the magnitude of the current is seen when compared to the sulphate bath, this can be assigned to the higher operating temperature of the bath. The potential marking the onset of nickel reduction changes with copper addition to the bath from -1.05 V to -0.90 V. This is most likely due to the preferential complexing of the citrate with the copper ions.

Current transients for the deposition process for a number of copper concentrations are shown in Figure 4.72. The deposition rate is slowest for pure nickel and increases with increasing Cu$^{2+}$ concentration. All deposits were uniform, continuous, shiny and about 3
Figure 4.72. Current transients during potentiostatic deposition at -1 V for electrolytes as indicated.

µm thick. They appeared bright with a white nickel-rich finish on the undersurface, the top surface appeared increasingly coppery with increasing copper concentration in the bath. This may be due to a displacement reaction taking place between the nickel in the deposit and the copper ions in solution as discussed by Landolt [26] and in more detail by Toth-Kadar et al. [15]. The efficiency of the deposition process was greater than 90% for baths with low copper ion concentration but was found to decrease to 80% as the copper ion concentration increased.

4.4.1 Morphology and Composition

The morphology for a range of Ni-Cu deposits is shown in Figure 4.73. A granular or nodular growth is seen for all deposits; the size of these grains decreases with increasing Cu²⁺ concentration. Protrusions in the surface become more marked as the copper content increases. For larger copper content, as shown in Figure 4.73(d), speckled non-continuous growth is observed over a comparatively smooth underlayer.
Figure 4.73. SEM micrographs of Ni-Cu electrodeposited from a bath of 1.14 M NiSO$_4$, 0.2 M C$_6$H$_5$Na$_3$O$_7$, 0.034 M NaCl and (a) 0 M CuSO$_4$ (b) 0.01 M CuSO$_4$ (c) 0.02 M CuSO$_4$ (d) 0.04 M CuSO$_4$.

EDX analysis showed homogeneous copper content on the surface - the features did not seem to have a distinctive composition as was the case for Ni-Cu deposited from the sulphate bath. In order to determine the uniformity of the copper content with thickness, the % wt. Cu on the top surface and on the bottom surface is shown in Figure 4.74. A uniform cross-sectional composition is seen for electrodeposits from baths of 0.015 M CuSO$_4$ or less, beyond this a sharp increase in the copper on the top surface is observed. The thickness of these deposits allowed the determination of their heavy element impurities; cobalt content was seen to range from 0-0.08 wt. %, tantalum which was found in a small number of deposits was most likely due to poor cleaning, and other light element impurities such as carbon and oxygen were detected in minor amounts (<0.5 wt.% in all cases). As has already been stated, EDX is not suitable for detection of light elements. Due to the concern of carbon incorporation from the citrate and interest in the variation of copper content with thickness, Auger analysis was carried out on an electrodeposit from a bath containing 0.02 M CuSO$_4$. The results are shown in Figure 4.75.
Figure 4.74. % wt Copper in deposits as a function of copper sulphate concentration in plating solution. Copper content on the top and underlayers are shown as well as the average.

The initial large carbon content is attributed to contamination on the surface, 2 atm. % of carbon and oxygen is assigned to the chamber. The undersurface shows, after initial carbon contamination is removed, a slight increase in nickel content and a reduction of copper content with increasing thickness. This can be assigned to the initial depletion of the copper.
ion concentration at the electrode surface before more is supplied by diffusion towards the cathode. The top layer shows an extremely high amount of copper at the surface which falls to bulk value within 0.1 $\mu m$. The average percent of nickel, copper and carbon on the underlayer was 95.0, 3.5 and 1.5 wt. % respectively. The corresponding values on the top layer, disregarding the initial high copper content, were 95.0, 4.0 and 1.0 wt.% respectively. No oxygen contamination was noted. The corresponding value of the copper as determined from the EDX analysis on the same sample was 10 wt.%. As EDX analysis has a penetration depth of $\approx 1\mu m$, the Auger analysis suggests that this copper is present primarily within 0.1 $\mu m$ of the surface.

4.4.2 Crystal structure

All Ni-Cu electrodeposits from the citrate bath showed an fcc crystal structure. No texturing of the deposits were observed. The addition of copper to nickel had two effects; expansion of the lattice and a broadening of the peaks, indicating a decrease in the domain size of the samples. This is illustrated in the (111) X-ray reflection that is shown in Figure 4.76. The lattice parameter initially decreases with small additions of copper to the nickel ($\approx 1$ wt. %) and then begins to increase. The rate of increase is slower than expected from Vegard's law as shown in Figure 4.77. The deviation corresponds to the appearance of a copper-rich top surface, Figure 4.74, which indicates that the copper-rich surface phase is not detected in the X-ray diffraction pattern.

4.4.3 Magnetic Properties

The magnetisation of these samples was measured in the SQUID magnetometer at 300 K. The magnetisation data for all samples was found to be well below that expected from
Figure 4.76. The (111) reflection for nickel-copper deposited from bath of 1.14 M NiSO₄, 0.2 M C₆H₅Na₃O₇, 0.34 M NaCl with CuSO₄ as indicated.

their nickel content. The error associated with these values is small (±0.05 Am² kg⁻¹) due to the minimal error of the SQUID (±10⁻¹⁰ A m²) and the mass measurements (±0.002 mg). These measurements were checked and confirmed in LETI - CEA, Grenoble, France two months after the data was gathered. The samples were remeasured 6 months later and their values were restored to those expected; in some cases they exceeded the values expected as shown in Figure 4.78. Heat treatment of the samples (550°C for 10 min) also restored the magnetisation values to the expected values. X-ray diffraction patterns of the heat-treated samples showed a reduced broadness of the peaks. X-ray diffraction pattern of the samples measured after the 6 month period indicated no change in their crystal structure.
Figure 4.77. Lattice parameter of electrodeposited Ni-Cu as a function of copper salt in the bath and the average wt % of copper in the deposit.

Figure 4.78. (a) Magnetisation curves for two samples as-deposited, remeasured 6 months later, and for one, after a heat treatment. (b) The measured saturation magnetisation values of the samples as deposited, and remeasured 6 months later and for some after a heat treatment. The straight line shows the expected values.

Anisotropic magnetoresistance data for the samples are shown in Figure 4.79. Two types of measurements were made. First the direction of the field was kept constant, at 90° or 0° to the current flow, and the change in resistance as a function of applied magnetic field
was measured. Secondly, a constant field of 2 T was applied to the sample and the direction was rotated relative to the current flow. It is observed that the change in resistance from zero field to when the field is parallel to the current flow depends inversely on copper content, whereas the change observed when the field is applied perpendicularly is independent of the copper content of the deposit. This may be due to a GMR effect within the heterogenous deposit opposing the resistance increase. The observed change occurs at fields of 100 mT. The AMR for all deposits calculated from the rotation of a 2 T magnetic field at room temperature was \( \approx 2\% \) for all samples. Curie temperature of the samples was determined from the imaginary part of AC susceptibility measurements. This was done by heating the sample, in an evacuated capsule, to 675 K and using the AC susceptibility set-up as described in the previous chapter. The samples were heated and cooled three times in order to see if there was an effect of heat treatment on the \( T_c \) values. This effect of heating has already been mentioned for pure nickel deposits. No such effect was observed for the Ni-Cu deposits.

![Figure 4.79. (a) Resistance as a function of applied magnetic field parallel, \( \parallel \), and perpendicular, \( \perp \), to the current flow. (b) AMR calculated from a change in resistance as a function of direction of a 2 T field as shown in inset. All measurements at room temperature.](image)
Figure 4.80 shows the data for a pure nickel sample and a Ni-Cu electrodeposit. A sharp transition at $T_c$ can be seen for the pure nickel samples, whereas a very broad transition region is seen for Ni-Cu deposits. This indicates a variation in the composition of the Ni-Cu deposit. The maximum temperature reached before zero susceptibility, and the temperature at which the transition begins, are $T_{c_{\text{Max}}}$ and $T_{c_{\text{Min}}}$ respectively. These are determined from the 3rd cycle for all samples and the results are plotted in Figure 4.81.
Figure 4.81. Maximum and minimum transition temperatures for Ni-Cu electrodeposits from the 3rd heating cycle.

The minimum $T_c$ values correspond very well with the % wt. of nickel that is present in the samples. The maximum values suggest that there are nickel rich particles present in the deposits which have a higher transition temperature.

4.4.4 Effect of Convection and a Magnetic field on Electrodeposit Structure

As has already been discussed for electrodeposits from a sulphate bath, the effect of stirring is expected to increase the rate of reduction of mass-transport controlled species. Therefore the copper content would be expected to increase with an increase in stirring or with an applied magnetic field during the electrodeposition process. Is this the case for a citrate bath?

SEM micrographs show very similar morphology for samples prepared with a stirring rate of 100 rpm, no stirring and the application of a B Field. The morphology is much more speckled for deposits from the bath with 300 rpm stirring and this is confirmed by the increase in the copper content of the surface.
A common feature noted on the surface of the deposit prepared with an applied magnetic field is the tracks of presumably hydrogen bubbles as shown in Figure 4.83. The magnetic field will set-up convection parallel to the electrode surface. Areas of increased accessibility due to the flow of the electrolyte will have increased copper reduction rate while areas shadowed by the bubble will have a reduced copper reduction rate. This effect has also been observed by Devos et al. during the reduction of nickel from a Watts bath [20].
4.5 Nickel-Copper Electrodeposited from Watts Bath

The Watts bath is designed for nickel electrodeposition at high current efficiencies. Normally the bath operates at a high temperature, however we use it here at room temperature. It has a very similar composition to that of the sulphate bath, the chief modification being the addition of nickel chloride to the bath. This increases the conductivity of the bath and also the nickel ion concentration. The prospect of using this bath to produce Ni-Cu electrodeposits by the addition of various amounts of copper sulphate to the bath was examined.

Linear sweep voltammograms are shown in Figure 4.84. A distinctive current plateau is seen at low potentials which correspond to the mass transport limited copper reduction current. Again the presence of copper inhibits the onset of nickel reduction. Current transients are shown in Figure 4.85. The addition of Cu$^{2+}$ increases the current but a steady state current is not be reached, due to the absence of forced convection in the system. The efficiency of the plating process is 99% for pure nickel but reduces to 74% with 0.015 M...
CuSO₄ in solution.

Figure 4.85. Current transients during the electrodeposition of Ni-Cu from a Watts bath with CuSO₄ content as indicated.

4.5.1 Morphology and Composition

The appearance of the deposits changed from bright shiny nickel to dark powders on addition of very little copper sulphate to the electrolyte (0.007 M). The deposit thickness, assuming a compact structure, are 2-3 μm; however due to the dendritic growth observed these values would be an overestimate for deposits with higher copper content. The onset of poor morphology is shown in the SEM micrographs of the deposits by the appearance of small dendritic features on the sample surface. EDX analysis indicates that the composition of these dendrites is copper-rich however their fine structure makes it difficult to determine composition of the structures independent of the matrix.
Figure 4.86. SEM micrographs, (a)-(d), and corresponding copper compositions (e) of Ni-Cu electrodeposits from Watts bath with (a) 0 M, (b) 0.007 M, (c) 0.01 M, (d) 0.015 M CuSO₄.

4.5.2 Crystal Structure

XRD diffraction patterns of the samples indicate that the copper dendritic phase is not present in sufficient quantity to be detected by X-ray diffraction. The evidence of a copper phase appears only at the higher concentrations as shown in Figure 4.87. There is little shift in the peak positions with increasing copper content indicating a nickel-rich matrix of constant composition.

4.5.3 Magnetic Properties

Magnetisation measurement of the samples indicate values that decreased, as expected, with copper content. The absolute values however are ≈ 10% lower than those of bulk Ni-Cu. Impurities in the deposit as detected by the EDX analysis of carbon, sulfur and oxygen are no greater than 2 wt. %.
Figure 4.87. X-Ray diffraction patterns of electrodeposits from a Watts bath with copper ion concentration as indicated.

Figure 4.88. Room temperature magnetisation of Ni-Cu electrodeposited from a Watts bath. (a) An example of the curves obtained (b) The saturation values as a function of copper content.

As was found with Ni-Cu electrodeposited from the previous baths studied when the magnetisation of these samples was remeasured after 10 months the saturation values had increased substantially as shown in Figure 4.89.
Figure 4.89. Saturation magnetisation data as of Figure 4.88 with data of samples remeasured 10 months later.

4.5.4 Effect of Convection and a Magnetic field on Electrodeposit Structure

The effect of stirring on the electrodeposition of Ni-Cu from a Watts bath with 0.005 M CuSO₄ was investigated. The current density increased as the convection in the system increased. No effect of stirring on the copper content of the bulk deposit was observed rather there was an increase in the appearance of isolated dendritic structures which are rich in copper. These features were not found on an electrodeposit formed with no stirring, appeared near edges of electrodeposits formed with an applied magnetic field or 100 rpm stirring and throughout the deposit formed with 300 rpm stirring. These features are shown in Figure 4.90.
Figure 4.90. Morphology of electrodeposits from a Watts bath with 0.005 M CuSO₄ (a) no stirring, this surface is seen throughout all deposits with added features (b) features seen at edge of deposits when electrodeposited with an applied magnetic field or 100 rpm (c) example of copper rich dendritic growth observed with a stirring rate of 300 rpm during deposition. (d) similar effect seen during deposition with an applied magnetic field.

Figure 4.90(c) shows a feature which has been formed due a bubble on the surface with increased dendritic deposition due to enhanced flow at one side. EDX analysis confirms that the fern-like structures are copper rich while the centre eye is not. A similar effect is seen with the application of a magnetic field. The appearance of dendritic structures is increased at one side of the bubble track, again due to convection induced by the magnetic field.
4.6 Discussion and Conclusions

The electrodeposition of Ni-Cu from three distinctive baths has been investigated. All baths have a high nickel content and the copper content is varied in order to produce Ni-Cu of varying compositions. The simple sulphate bath operates at room temperature and the electrochemical behaviour of the system is predictable. Boric acid is used as a buffer and typical current densities of the baths are 120-140 A m\(^{-2}\). The citrate bath contains sodium citrate, which acts as both a complexant and a buffer, and sodium chloride which increases conductivity - it operates at the higher temperature of 50° C. The citrate ions reduce the rate of copper deposition but has no effect on the nickel deposition rate due to the high concentration of nickel ions. The higher temperature provides a higher reduction rate with typical current densities of 160-300 A m\(^{-2}\). The Watts bath, traditionally a pure nickel bath, differed from the sulphate bath in the addition of nickel chloride and an increase in boric acid concentration. These increase the conductivity of the electrolyte. The current densities during the depositions were 120-180 A m\(^{-2}\).

The sulphate bath produced Ni-Cu electrodeposits with segregated copper growth when the copper ion concentration exceeded 0.015 M. This copper growth was rough and dendritic in nature. X-ray diffraction patterns indicate that the lattice expanded with addition of copper. A nickel rich underlayer was formed, the copper content increasing with deposition thickness. Smooth deposits were obtained from the citrate bath for all copper concentrations with no inhomogeneity in the surface composition. A nickel-rich underlayer was again present and lattice expansion with increased copper content was noted, albeit to a lesser extent. A copper-rich surface, \(\approx 0.1 \, \mu\text{m}\), was also present for deposits with high copper content. This is probably due to a displacement reaction between nickel and copper ions occurring in the
time between the end of deposition and removal of the electrode from the bath. This is not seen for deposits from the Watts or sulphate baths due to the rough surfaces. Ni-Cu deposited from the Watts bath tolerated very little copper codeposition; dendritic features appeared with the addition of as little as 0.007 M CuSO₄. No increase of lattice parameter was observed indicating that the copper was predominantly present in the dendrites. This distinct effect must be assigned to the presence of the chloride in the solution, possibly increasing the conductivity of the solution and thereby increasing the importance of the primary current distribution which may be extremely non-uniform.

The magnitude of the anisotropic magnetoresistance (2%) is similar for deposits from the sulphate and citrate bath. A distinction between the two electrodeposits is seen in the increase in resistance as a function of magnetic field when the field is applied parallel to the sample: in the case of electrodeposits from the sulphate bath this is no different to the decrease in resistance when the field is applied perpendicular to the sample, for the citrate sample there in a systematically reduced enhancement of the resistance as the copper content increases. It has already been established that a copper rich layer is present on the surface. It is feasible that within this layer ferromagnetic nickel rich clusters may exhibit GMR and reduce slightly the AMR effect. The existence of nickel rich clusters in the deposits is confirmed by χ₀ studies which establish a Tc transition at near pure nickel values.

The saturation magnetisation values obtained for these deposits are peculiar: electrodeposits from all baths with a high nickel content had reduced saturation magnetisation, in comparison with bulk values. Impurities, which at a maximum are 2 wt.%, cannot explain such a reduction. The effect of time on these deposits is also startling, increasing the moments to values larger than those expected. These measurements have all been rechecked
and also a handful confirmed by independent measurement in France. The curves indicate that the deposits are fully saturated and while the masses of samples are quite small the sensitivity of the SQUID will still ensure sufficiently high accuracy measurement. There have been reports in the literature of the formation of Ni-rich segregations with large moments known as giant magnetic clusters but these are not expected to be stable at room temperature [21] [22]. It has also been suggested that the displacement reaction is responsible for the creation of regions of 'loose moments' which will exhibit superparamagnetic behavior [6]. However the saturation of the magnetisation rules out this possibility.

The effect of stirring on all baths increased the copper content of the alloy and also increased the roughness. The effect of an applied magnetic field during deposition is similar to that of gentle stirring - this is specifically highlighted by the enhanced copper deposition on one side of a bubble track. This confirms the magnetic field sets up convection in the system.

In conclusion it has been established that homogenous Ni-Cu alloys can be deposited with up to 10 wt. % and 14 wt.% Cu from the sulphate and citrate baths investigated. Homogenous nickel copper was not obtained from the Watts bath. An average AMR value of \( \approx 2\% \) was obtained for the deposits. Electrodeposits with high copper content from the citrate bath had a copper rich surface while from the sulphate bath rough dendritic growth was seen. The magnetisation of the electrodeposits were unstable, giving unusual magnitudes which changed over time suggesting that the samples had features not detected by any of the investigation techniques used in this study.
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Chapter 5

Conclusions and Future Work
5.1 Conclusions

Electrodeposition is an extremely versatile process for the fabrication of metals and alloys allowing straightforward and inexpensive preparation. It is a non-equilibrium processing technique that can produce nanostructures and high aspect ratio features. In this thesis the interdisciplinary area of magnetism and electrodeposition was studied from two separate perspectives - firstly the effect of an applied magnetic field on the deposition process and secondly the production of magnetic materials by electrodeposition. The effect of applying a magnetic field during the electrodeposition of numerous metals was investigated using chronoamperometry and the magnetic and structural properties of electrodeposited nickel and nickel-copper were studied. The results have been presented and discussed in detail in the preceding chapters. An outline of the conclusion drawn from this work is presented here.

5.1.1 Effect of a Magnetic Field on Electrodeposition

A number of conclusions can be drawn from the observed effects of an applied magnetic field on the chronoamperometry experiments carried out on silver, copper, bismuth and zinc solutions. Departure from planar diffusion occurs at earlier times with the application of magnetic field, while the diffusion coefficient of the ionic species is unaffected by the application the field. This confirms that convection is induced in the electrolyte by the action of the magnetic field and that this convection is stronger than natural convection. The steady state current enhancement that is observed in the presence of the field allows comparison of the magnetic field effect between each system studied. It was found that the enhancements of all the ions could be explained by considering the Lorentz force, the magnetic field gradient force, the magnetic damping force and the kinematic viscosity of the system. The paramagnetic gradient force was not considered significant because the
driving force for diffusion acts along the same concentration gradient and is many orders of magnitude larger. The current enhancement caused by applying a magnetic field parallel and perpendicular to the electrode surface was 55% and 10% respectively. This reduction in current enhancement illustrates the obvious importance of the Lorentz force in causing the current enhancement.

The magnetic field effect on the nickel reduction system was complicated by the magnetisation of the nickel working electrode. Current enhancement is observed signifying that induced convection is present. A nickel working electrode will have a large local field gradient: this would be expected to affect the concentration gradient of paramagnetic and diamagnetic ions in close proximity to the electrode, thereby affecting the mass transport process. At extreme over potentials (>2000mV) the effective diffusion coefficient derived from the slope of the Cottrell plot decreased by an order of magnitude with the application of a 0.5 T magnetic field. This may be explained by the increased active surface area available for reduction due to diamagnetic hydrogen gas being repelled from the magnetic surface and also increased convection near the surface which will reduce the formation of a passive nickel hydroxide layer.

An effect of magnetic field on the electrodeposition current was only detected for systems under mass transport control. No obvious effect on the electrode kinetics of any system was observed, although this was not investigated in great detail.

### 5.1.2 Characterization of Nickel Electrodeposits

Nickel electrodeposited from a saturated nickel solution, containing citrate ions and sodium chloride, exhibited saturation magnetisation values which were 8% or more below that expected for bulk nickel. A mild heat treatment of 300° C for 30 minutes restored
the magnetisation values to those expected. The resistance of the samples decreased upon a similar heat treatment while the Curie temperature increased. These unstable properties were not found in nickel deposited from the Watts or sulphate baths. Such a scenario is most likely to be due to defects which are trapped in the deposits during the deposition process but are released with such a mild heat treatment. Surprisingly outgassing of the sample did not produce hydrogen and other defects such as nickel vacancies and interstitials were found to be unable to account for the reduction in the magnetisation values. Local spin density calculations carried out using the SIESTA program by Dr. Sanvito showed that less than 3 atm. % of carbon present in the nickel in interstitial positions could be responsible for such a reduction.

Electrodeposition, being a non-equilibrium process, would easily facilitate the stabilization of defects not normally stable at room temperature and it is plausible that carbon is included from the citrate bath. Indeed evidence of such is found in Auger analysis. The activation energy of the defect, according to the heat treatment, would be 1eV. Magnetisation measurements of electrodeposits are an ideal way to detect such defects.

5.1.3 Characterization of Nickel-Copper Electrodeposits

Electrodeposition of Ni-Cu was carried out from three different baths; a sulphate, citrate and Watts bath. Compositional homogeneity on the surface of the electrodeposits was obtained for the citrate bath for all copper concentrations investigated and from the sulphate bath for electrodeposits with up to 10 wt % copper. Dendritic copper growth was obtained for Ni-Cu deposition from the Watts bath. A nickel-rich underlayer was a feature of all electrodeposits while a copper rich surface was present for deposits from the citrate bath. Anisotropic magnetoresistance for all deposits was found to be \( \approx 2\% \). AMR curves
obtained from Ni-Cu electrodeposited from the citrate bath suggested a GMR contribution. Curie temperature measurements of samples from a citrate bath indicated compositional gradients within the deposits, including pure nickel particles. All the electrodeposits were ferromagnetic, however the saturation magnetisation values were up to 30% lower that those expected from literature values of metallurgically prepared Ni-Cu alloys. After a substantial amount of time (≈ 6 months) the saturation magnetisation values were ≈130% their original values, bringing them, in some cases, above the literature values.

The effect of applying a magnetic field or stirring during electrodeposition was to increase the copper content of the electrodeposits. The effect of the field was equivalent to gently stirring (≤ 100 rpm). Hydrogen bubble tracks, with copper deposited preferentially on one side of the track, were seen for electrodeposits plated from the Watts and citrate baths with an applied magnetic field. This suggests again that the effect of an applied magnetic field is to induce convection in the electrolyte.
5.2 Future Work

The interesting and unusual effects of the magnetic field on the current transients for the nickel system merit further investigation. In order to confirm that the field gradient associated with the nickel electrode is responsible for the change in profile the comparison of the effects with the magnetic field applied perpendicular and parallel to the current flow should be investigated. The field gradient force should be similar in both cases however the effect of the Lorentz force will be greatly reduced, as observed for copper reduction. Because the field gradient at a ferromagnetic electrode depends directly on the surface roughness it would also be interesting to see if the changes in the current transient profile and the diffusion coefficient are also related to the electrode roughness. Similar investigation into the Fe/Fe$^{2+}$ system would also be interesting.

The effect of a magnetic field on nucleation and growth during electrodeposition would merit further investigation. The results presented in this work suggest that the magnetic field does not affect the diffusion coefficients of ionic species and therefore will not affect the growth process. The field may however affect the favourability of nucleation sites on the electrode surface via increased surface inhibition as has been suggested by Devos et al. [1]. There have also been reports in the literature on the effect of a magnetic field on the texture of deposits and on the grain size[2]. An ideal method for this investigation is electrochemical Atomic Force microscopy which allows in-situ studies of the nucleation and growth processes on electrode surfaces.

This work concentrates on the effect of magnetic field during the electrodeposition process, however it would be interesting to study the effect of field during the reverse process - corrosion. Rates of corrosion can often depend on the transport of aggressive or passivating
ions to and from corrosion sites. It is reasonable to expect that the Lorentz force acting on these ions will modify their mass transport rate and affect the corrosion rates accordingly. Work reported by Davenport et al.\cite{3} suggests that a magnetic field will only have a significant effect when the electrode is ferromagnetic, due to high field gradients at the electrode surface.

There is a drive in the magnetic recording industry to minimize the area required for data storage. In order to achieve a maximum areal density a material of high coercivity must be used. Electrodeposition provides an cheap and versatile method of production of these materials. The optimization of properties of electrodeposited magnetic materials such as Co/Fe-Pd/Pt alloys would represent a significant step towards this target especially if they can be patterned on the sub 100nm scale. These materials, when deposited as thick films, also have possible applications in microelectromechanical systems (MEMS).
References

