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Electrodeposition of coercive
ferromagnetic films

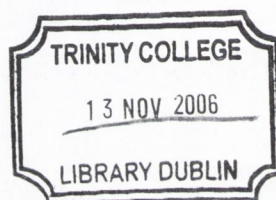
by

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***A thesis submitted for the degree of Doctor of Philosophy
in the University of Dublin***

Department of Physics
Trinity College Dublin

April 2005.



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Declaration

This thesis is submitted by the undersigned for examination for the degree of Doctor of Philosophy at the University of Dublin. It has not been submitted as an exercise for a degree at any other university.

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Gerardo Márcos Menéndez

April 2005

Summary

The need for even more compact and low power consumption devices has been the driving force for microelectromechanical systems (MEMS). Also the integration of MEMS into current state of the art silicon technology has set the boundaries for the preparation of these devices. Any candidate device to be manufactured using silicon technology should be integrated at the last step of production to minimize the cost. To achieve, the maximum annealing temperature should not exceed about 300 °C. Many integrated circuits (CMOS) deteriorate above this temperature.

There are several approaches to address the preparation of MEMS devices from the materials point of view, which include ferroelectric, piezoelectric, magnetic, and thermoelectric materials. The present thesis work concentrates on magnetic materials for microelectromechanical systems. Besides the low temperature requirements, most of the devices in MEMS technology require thick films (20 to 500 μm). Some of the basic devices include micromotors, microswitches and magnetic circuits to produce field bias, which are described in Chapter 1. To address the preparation of magnetic material for MEMS we have developed novel electrodeposition techniques to produce ordered $L1_0$ fct phases of FePt, CoPt, FePd and Co-rich Pt containing P.

The MEMS device, focus has been mainly on micromotors, and in particular on the preparation and characterization of the rotor. To magnetically pattern rotors, we studied techniques using pulsed magnetic field, static magnetic field and a method using the dependence of the coercivity of the tetragonal CoPt phase on composition. The latter

method was demonstrated by electrodepositing into porous alumina membranes, with porous size in the range 100-200 nm.

Another topic, arising from the electrodeposition of ferromagnetic metals, was the effect of magnetic field effect on the rest potential. This was examined for the metals Fe, Ni, Co, Zn, Mn, Cu, Cr, Al and stainless steel in the second part of this thesis. We have explicitly demonstrated that is corrosion-related and can occur in any systems where corrosion is mass-transport controlled. It does not require either a ferromagnetic electrode or diamagnetic solution. The Lorentz force was identified as the main driving force behind the phenomenon. This force typically acts to enhance the mass transport of the cathodic reaction during corrosion, therefore shifting the rest potential anodically.

The thesis is divided into chapters as follows: the first two chapters cover an introduction to basic MEMS devices, electrochemistry, corrosion, a literature review of $L1_0$ and Co-rich permanent magnets and the experimental techniques used in the work. Chapter 3 presents the magnetic results obtained for electrodeposited FePt, FePd, CoPt and CoPt(P) alloys. The preparation of the rotor is described in chapter 4, where several magnetizing devices and techniques have been exploited. Chapter 5 is devoted to the rest potential of transition metals. Chapter 6 proposes some future work.

The main results are the successful electrodeposition of $L1_0$ FePt, FePd and CoPt, with coercivities of 1.5 T, 0.15 T and 1.3 T, respectively. Also, the room-temperature electrodeposition of coercive $Co_{80}Pt_{20}(P)$ yields values of 0.35 T for 50 μm thick film. These results fulfil the basic requirement for magnetic MEMS application: thick films and low processing temperatures. In addition, the electrodeposition technique has been extended to membrane templates. A novel idea for the preparation of magnetic patterns using dual coercivity has been demonstrated by depositing CoPt into alumina membrane templates.

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Chapter 1

1 Introduction

A description of the current needs of micro-electromechanical system (MEMS) technology, which is one of the main driving forces of this work, will be discussed. There are several approaches for the preparation of MEMS devices from the materials point of view, which include ferroelectric, piezoelectric, magnetic, and thermoelectric materials. This work is focussed only on the magnetic approach. This chapter shows what the current needs of MEMS technology are and describes important basic devices.

The technique which shows many features compatible with MEMS is electrodeposition. Therefore, basic concepts of electrodeposition are introduced without going into mathematical derivations since there is plenty of available literature on this topic. Materials which are good candidates for the electrodeposition of permanent magnets are reviewed and compared: FePt, CoPt, FePd, CoPd and Co-rich alloys. The literature survey covers a wide range of preparation techniques, organized chronologically and by magnetic material.

The studies of rest potential shift dependence on magnetic field for transition metals are the second main topic of this thesis. The rest potential shift is correlated to corrosion to a certain level and corrosion has the same basic nature as electrodeposition. A discussion of corrosion is also included with emphasis on galvanic cells. From the magnetic point of view the relevant magnetic forces are introduced.

1.1 Permanent magnet films for micro-electromechanical systems (MEMS)

The demand for wireless network technology such as mobile phones and laptops continues to grow. As the wireless networks advance, new challenges emerge for mobile phone and communication designers. RF (radio frequency) MEMS may help engineers to add new capabilities and improve power efficiency while keeping wireless devices small and affordable. About 75 % of the components in a mobile phone are passive elements such as inductors, resistors and variable capacitors. Reliable MEMS versions of variable inductors and capacitors would make wireless devices more power efficient.

What other market demands are driving the need for squeezing more functionality into a mobile handset? In the near future, wireless networks will enable wireless devices to receive streaming video or music as well as "Web" content. "World" phones will have to contend with an increasing number of bands or modes. Handsets may also be expected to integrate short-range wireless technologies to enable wireless connection to other devices such as laptops, printers or cameras thereby suppressing the need for cables in the office or home. A user could then print or save the picture taken with their mobile phone camera, use mobile phone for storing data and many other possibilities.

Current dual-mode or tri-mode phones require separate PA (power amplification) circuits for each mode. An integrated MEMS solution would need only one power amplifier, which would save both physical space and money. In this context there is the need for a "tunable" voltage control oscillator (VCO) that could select among the various frequencies – from 900 Mhz to 2.4 Ghz – that different transmission technologies require.

Such a tunable MEMS VCO would eliminate the need for multiple VCO circuits and be more space efficient.

A simple metallic MEMS switch would allow a phone to work with as many as five different bands or transmission modes. The switch would also save circuit board by reusing hardware. In order to incorporate MEMS technology into the already existing silicon technology, the integration process should allow MEMS to be directly deposited on top of a mobile device's integrated circuit board, requiring a low processing temperature.

From the magnetic materials point of view, in order to meet the requirements for MEMS it is necessary to develop new permanent magnet film based devices and processes which could be used in micro-motors, micro-generators, sensors and read heads and help significantly reduce the size, weight, and cost of these devices. These elementary devices would feed as an input to the more complex MEMS devices.

One of the first goals is focussed on the development of nanostructured magnetic material. The key point is to develop new low temperature processes compatible with microelectronics environment. The knowledge of the deposition and characterization of permanent magnetic films is essential for the future design of MEMS devices. The objectives can be summarized as follows.

a) Preparation of optimized permanent magnets (hard phase) with tailor-made properties by tuning the nanostructural characteristics such as grain size. Special importance is given to developing a new and novel low temperature process for preparation of hard permanent magnetic films with magnetic properties comparable or superior to bulk permanent magnets.

b) To prepare, characterize and understand the magnetic properties of permanent magnets down to submicron.

For permanent magnets of sizes larger than 10 μm , the magnetic properties may not differ from those of the bulk material except for the effect of the demagnetizing field, which can be calculated. For smaller sizes, the surface and internal structure can strongly modify the magnetic properties like the coercivity.

c) The third objective of this work from the MEM's point of view is to prepare 'demonstrator parts': a permanent magnet to be used as a bias field for magnetoresistive sensor (GMR/MR) and a rotor which can be used in micro-motors and micro-generators. With the knowledge obtained from objective a) and b), small permanent magnets will be prepared which can be used in industrial fabrication processes.

GMR/MR sensors are usually composed of a Wheatstone bridge structure using NiFe/Ag multilayers obtained by sputtering deposition. The integrated permanent magnet is needed to bias the sensor up to a few tens of mT in order to reach a relatively wide operational magnetic field (± 2 mT or more) range with good linearity. Magnets for this application demand thicknesses up to 20 μm with a lateral dimension of 50 μm . The micro-rotor requires films with thickness greater than 50 μm .

The integration of small permanent magnets in microsystems imposes some constraints, depending on the target application. Read head biasing (GMR/MR sensor) requires thin films of small size, while micro-motors require thicker films and large lateral sizes. The diagram below (Fig. 1) shows the possible techniques for the deposition and patterning of permanent magnets as a function of the lateral size and thickness.

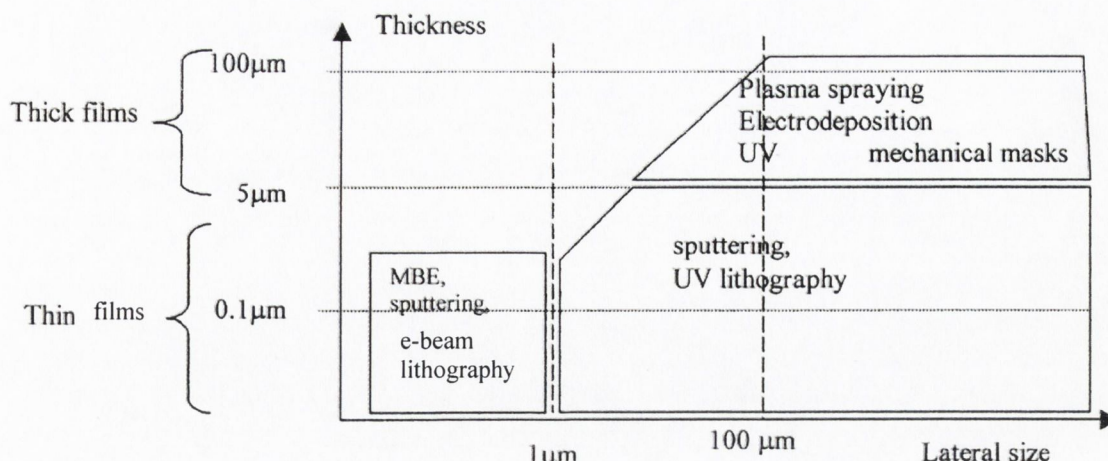


Figure 1. Diagram showing the most suitable deposition and patterning techniques according to the target device dimensions.

As can be seen from the diagram in Fig. 1 the electrodeposition and plasma spraying are the most promising candidates for the deposition of thick films.

1.1.1 Applications

1.1.1.1 Microswitches

Microswitches devices are one of the many applications that require a technological breakthrough in the preparation of permanent magnets without a post-annealing process. When a call is made to a mobile phone the internal circuits switch on to deliver power to the RF amplifiers and other parts. This switching device is generally made of a few milli-Watts transistor which is required to drive a few hundreds of mA during its operation and it dissipates energy. All of the commercial mobile phones available today make use of such a

switching device. Because of the current specification and the need for heat dissipation, the size of the transistor does not allow its integration in large numbers. This sets a need for a smaller and lower energy loss switching device for wireless as well mobile phone technology.

A strong candidate to replace the electronic switch (transistor) would be a mechanical switch, which could operate without dissipating energy. A switching device based on permanent magnets is shown in Fig. 2. In Fig. 2, there are two fixed magnets (A and C) and a mobile magnet (B). Let us suppose that all three magnets are magnetized in the positive direction of x and the initial state of the system has magnet A attached to B, thereby having the magnetization as shown. When a field gradient ∇B_x is applied the interaction with all magnets will pull them to the right. The attractive force between two permanent magnets in contact is $F = 0.5 \mu_0^{-1} A (B_r)^2$, where B_r is the remanence and A is the cross-section of the interface, whereas the field gradient force is $F_{\nabla B} \sim m \nabla B$, where m is the magnetic moment. For a contact with dimension $50 \mu\text{m} \times 50 \mu\text{m}$, $B_r = 0.8 \text{ T}$, the attractive force is about $0.6 \times 10^{-3} \text{ N}$. When the field gradient force overcomes the attraction between magnets A and B, magnet B detaches from A and attaches to C, the second steady state. When magnets B and C are attached, if the magnetic field gradient $-\nabla B_x$ is applied, magnet B will detach from C and attach to A, the first steady state. Therefore, by switching the magnetic field gradient from positive to negative it is possible to have two steady state configurations for this system, which can be used as a basic construction for the preparation of a magnetic switch. Yet, electrical functionality needs to be added.

The magnetic field gradient necessary to switch the magnets can be obtained by pulsing a current through a wire near the magnets. Permanent magnets are preferred to soft magnets because of the magnetic remanence, which is responsible for the attachment between the magnets once the external field gradient is removed. The fact that the magnets remain attached after the removal of the external field gradient means that no power is consumed during the steady state of the operation of the switch.

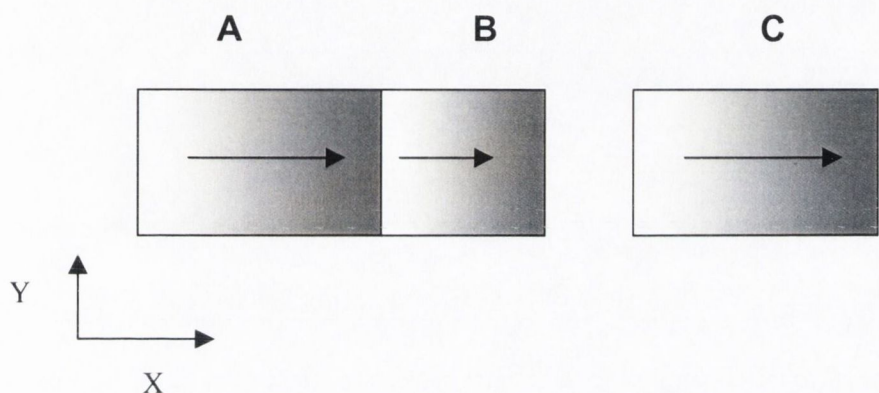
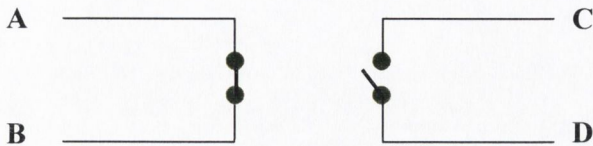
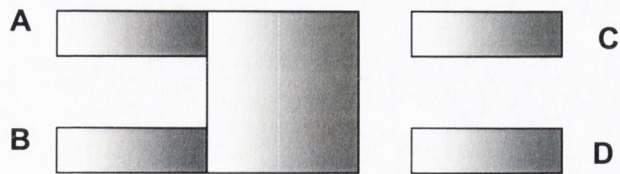


Figure 2. A mechanical switch based on permanent magnets without electrical functionality. Magnets A and C are fixed and B is mobile. The two steady states “A” attached to “B” and “B” attached to “C”.

After adding electrical functionality to the magnetic switch the top view of the magnets and the electrical diagram are shown in Fig. 3, as well as the logic table.



Magnetic Pulse	A-B	C-D
$+\nabla B_x$	off	on
$-\nabla B_x$	on	off

Figure 3. Top view of the magnetic switch, electrical diagram of the switch and the logic table of the magnetic switch.

The maximum magnetic field required to change the configuration state of the switch depends on the magnetic force between the poles and should not be bigger than the coercive field of the magnets.

1.1.1.2 Magnetic bias

The magnetic read head based on magneto-resistive (MR) sensor usually requires a magnetic bias in order to improve linearity and reduce noise. In fact, if no bias field is applied to the sensor the magnetic domain configuration may be random and a multidomain structure is formed. So far, magnets with small coercivity (0.1 T) are fully integrated to the MR sensor for read heads, but for other applications, which require material with higher coercivities, the magnets may be prepared separately in a process that requires annealing at high temperature.

A simplified diagram of a MR sensor is shown in Fig. 4. The two permanent magnets produce a bias field over the sensor reducing noise and improving linearity. When a H_y field is applied to the sensor, the resistance and therefore the electrical current changes.

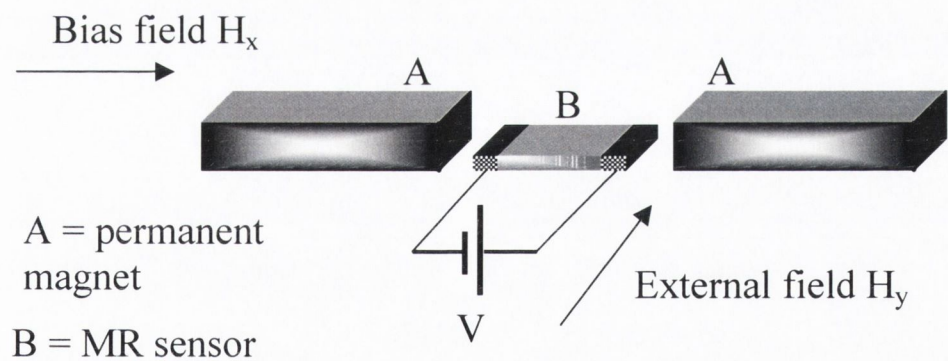


Figure 4. Schematic diagram of a MR sensor with a bias field produced by two permanent magnets. The sensor, during its operation, is polarized by a potential V .

Fig. 5 shows the typical behaviour of a MR sensor as function of the bias field (H_x) and the magnetic field, H_y . For small bias fields the magnetic structure of the sensor is a multidomain. Therefore the external field H_y changes the domain structure, producing an erratic dependence of the resistance on the field. When the bias field is large enough to produce a monodomain, the external field (H_y) rotates the domain coherently producing a smooth reversal rotation, resulting in a smooth change in resistance.

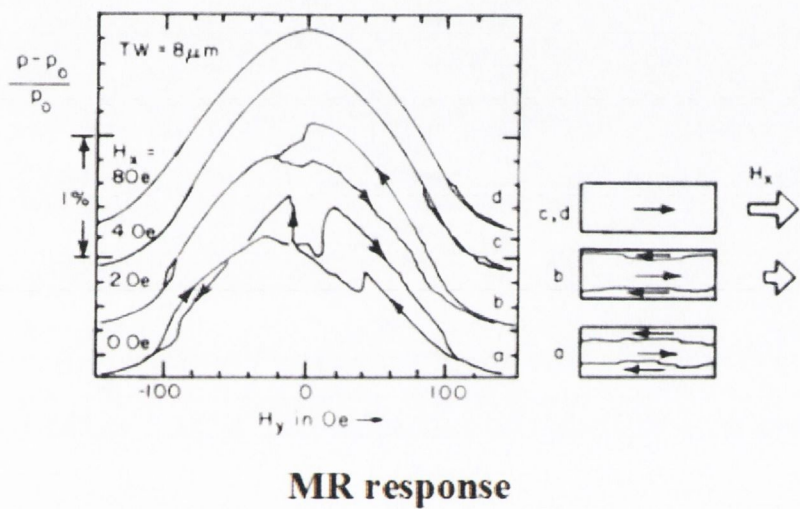


Figure 5. Magnetoresistance dependence on the bias field (H_x) and external magnetic field (H_y) from Rezende¹.

1.1.1.3 Motors and generators

Motors and generators are two sides of the same electromechanical transducer device. A motor converts electrical energy into mechanical energy and vice versa for the generator. The conversion of electrical energy into mechanical energy occurs through the interaction between a magnetic field and a magnetic dipole. In the case of a motor, a coil carrying an electrical current produces the magnetic field and the dipolar field is produced by a permanent magnet or vice versa.

The generator makes use of the movement of a permanent magnet relative to a coil, which results in a change of magnetic flux in the coil and induces an electrical potential according to Faraday's law:

$$E = -d\Phi/dt \quad (1)$$

Where Φ represents the magnetic flux and E is the electrical potential.

A diagram of a typical motor/generator is shown in Fig. 6, from Yamashita². Basically, the motor consists of a rotor, a stator and the coils. Here, the rotor is made of permanent magnetic material (NdFeB) and it is divided into sectors, also called poles, which are each magnetised in opposite directions. The number of poles and the diameter of the rotor define the maximum torque of the motor- the bigger the number of poles the bigger the torque. As the number of poles is increased it becomes more difficult to magnetically pattern the rotor.

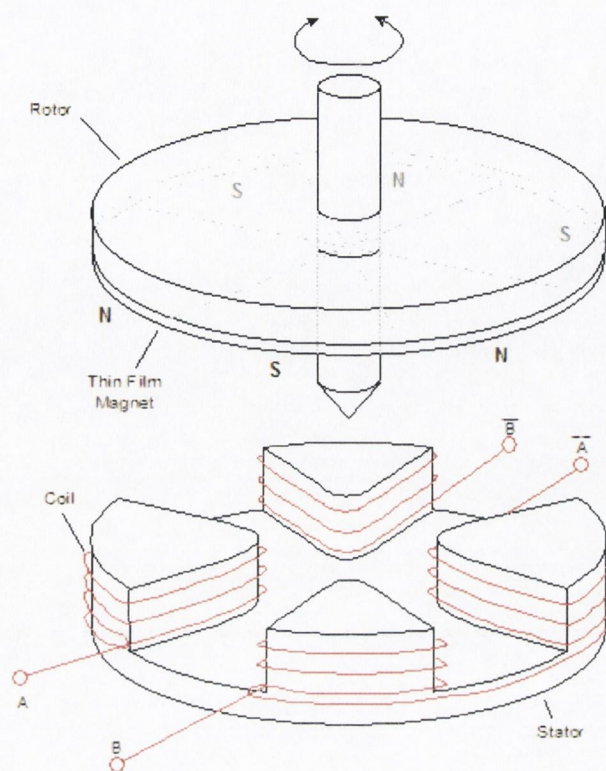


Figure 6. Schematic of a milli-sized motor using a 20 μm NdFeB film from Yamashita et al. (1991). The diameter of the rotor is 5 mm.

In order to reduce the size of the motor and generator and maximize the torque, the number of poles per unit area should be maximized. From the technical point of view the issue here is how to prepare and magnetically pattern small poles.

1.2 Kinetics of heterogeneous electron transfer

When an electrode is placed in an electrolyte solution, thermodynamic equilibrium is achieved between the electrode and the solution. In this situation reduction and oxidation reactions are balanced. The interface is in dynamic equilibrium as illustrated in Fig. 7.

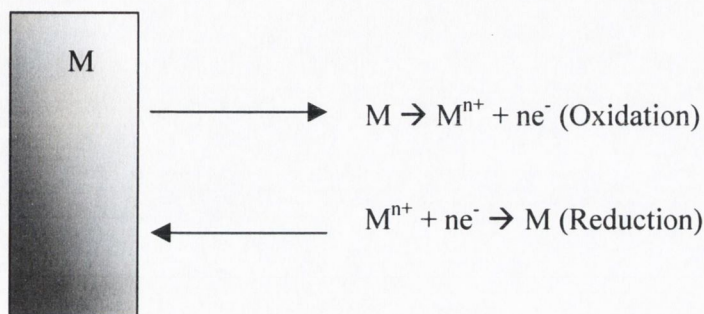


Figure 7. Dynamic equilibrium in a heterogeneous interface (electrode/electrolyte solution). M, ($M \rightarrow M^{n+} + ne^-$) and ($M^{n+} + ne^- \rightarrow M$) are the metal electrode, oxidation reaction and reduction reaction, respectively.

The current density across the interface electrode/electrolyte is written as:

$$J = nF[k_c C_0(O) - k_a C_0(R)] \quad (2)$$

Where n , F , k_c , $C_0(O)$, k_a and $C_0(R)$ are the number of electrons transferred per atom, the Faraday constant, the reaction rate constant of reduction, the concentration of oxidizing species at the electrode surface, the reaction rate constant of oxidation, and the concentration of reducing species at the electrode surface respectively. At dynamic equilibrium the forward and backward reaction are balanced and the net current is zero.

Using activated complex theory, with the Arrhenius formula for the dependence of the rate constant on the Gibbs free energy of activation, we can obtain the following expressions for the reaction rate:

$$K_c = K_0 \exp[-\alpha_c nF (E-E^0)/RT] \quad (3)$$

$$K_a = K_0 \exp[\alpha_a nF (E-E^0)/RT] \quad (4)$$

Where K_0 is the standard electrochemical rate constant for the reaction, E^0 is the formal potential (standard reduction potential), R is the gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$) and α_c and α_a are the cathodic and anodic charge transfer coefficients. Inserting (3) and (4) in (2) we get:

$$J = nFK_0 \{ C_0(O) \exp [-\alpha_c nF (E-E^0)/RT] - C_0(R) \exp [\alpha_a nF (E-E^0)/RT] \} \quad (5)$$

This equation describes the current-potential characteristics of the electrochemical reaction. Kinetic parameters can be obtained from an experimental current-potential curve for certain oxidation-reduction reactions. At equilibrium we have that $E = E_{eq}$, the net current is equal to zero, from thermodynamic assumptions $\alpha_c = \beta$, $\alpha_a = 1-\beta$ and the electrode surface concentrations are equal to those at bulk solution, then after rearranging the expression we obtain the Nernst equation:

$$E_{eq} = E^0 + (RT/nF) \ln [C_\infty(O)/C_\infty(R)] \quad (6)$$

The Nernst equation describes the equilibrium potential of an electrochemical system as a function of the concentration of oxidized and reduced species in solution.

Current exchange density, J_0 , is defined as the magnitude of either the cathodic or the anodic current density at equilibrium. Using $\eta = E-E_{eq}$ and combining with (5) we obtain:

$$J = J_0 \{ [C_0(O)/C_\infty(O)] \exp (-\alpha_c nF\eta/RT) - [C_0(R)/C_\infty(R)] \exp (\alpha_a nF\eta/RT) \} \quad (7)$$

When the surface concentrations of oxidized and reduced species do not deviate much from the bulk solution concentrations, i.e. at low potential and a stirred solution, this equation reduces to the Butler-Volmer equation:

$$J = J_0 \{ \exp (-\alpha_c n F \eta / RT) - \exp (\alpha_a n F \eta / RT) \} \quad (8)$$

The Butler-Volmer equation describes the current density from the kinetic parameters of the reaction. It assumes that the reacting ions are supplied to the electrode surface faster than they can be consumed. However, when a large overpotential is applied the rate of reaction is faster than the rate that the ions arrive to the surface. The reaction rate is no longer dependent only on the kinetics but also on the mass transport of the ions from the bulk solution to the interface region where they react. As the ions have to reach the surface in order to react we can write a general equation that takes into account the mass transport and the kinetics as:

$$1/J = 1/J_k + 1/J_L \quad (9)$$

Where J , J_k and J_L are the total current density, the kinetic current and the mass transport limiting current, respectively. The limiting current depends on the diffusion layer thickness (δ) as:

$$J_L = n F D C^\infty / \delta. \quad (10)$$

Where D is the diffusion constant. The thickness of the diffusion layer (δ) is controlled by mass transport through three different mechanisms: migration, diffusion and convection, which will be discussed in the next section.

1.2.1 Mass transport

Mass transport in an electrolyte can occur by three main processes: migration under the application of an electrical field, diffusion of ions due to concentration gradients and convection within the system.

1.2.1.1 Migration

When an electrical field is applied, ions experience an electrical force $F_m = neE$. The ions gain a steady state velocity, v_s , rather than an acceleration due to collisions with other ions in solution.

$$v_s = \pm \mu E$$

Where μ is the mobility of the ion in solution. The flux of ions is given by $J = nDC^\infty \nabla V / RT$, where ∇V is the gradient of the electrical potential in the electrolyte. Usually, due to the use of a supporting electrolyte, the conductivity of the solution is such that the gradient of potential in the solution is negligible, consequently the migration has a small effect and can be neglected.

1.2.1.2 Diffusion

The electrochemical reaction that occurs at the electrode consumes or creates ions. Consequently, a gradient of concentration is formed between the surface electrode and the bulk solution. This region is known as the diffusion layer. The force per unit volume acting

on these ions is $F_D = (RT/C)\nabla C$, where ∇C is the concentration gradient. The flux of ions, ϕ , due to the gradient is written according to Fick's law

$$\phi = -D \nabla C \text{ and} \quad (11)$$

$$-D \nabla^2 C = dC/dt \quad (12)$$

which can be rearranged to give

$$\nabla C = (C^0 - C^\infty) (\pi D t)^{-0.5}. \quad (13)$$

Assuming that the kinetic of the reaction is fast enough, then for instance the reduction at the electrode surface is such that $C^0 \sim 0$ and the current density turns out to be

$$J = -nFC (D/\pi t)^{0.5} \quad (14)$$

This equation is known as the Cottrell equation. If we assume that the concentration gradient is linear over the thickness of the diffusion layer, δ (the Nernst diffusion layer model), then since $\phi = J/nF = -D\Delta C/\delta$ and substituting J from the Cottrell's equation leads to an expression for δ

$$J = -nFCD/\delta \text{ and } \delta = (\pi t D)^{0.5} \quad (15)$$

This shows how the diffusion layer thickness varies with time. Eventually, the spread of the concentration gradient is halted by convection within the solution and a steady state for the limiting current density is reached. Then, 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 condition.

1.2.1.3 Convection

There are two important forms of convection: natural, due to density differences in the solution and forced, due to stirring of the solution for example. The forces causing convection will depend on the source. Natural convection is 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 from the relative movement of neighbouring layers in a fluid has a force, $F_{cV} = \eta \nabla^2 v$, where η is the viscosity of the electrolyte and v is the velocity. A hydrodynamic boundary layer, δ_H , will be established near the electrode as a result of velocity gradients due to convection and the boundary condition that fluid velocity is zero at the electrode surface. In this region the fluid velocity differs from the bulk (main stream) fluid velocity.

The hydrodynamic boundary layer δ_H is defined as the distance from the electrode within which velocity gradients occur. Beyond this, the velocity of the fluid is considered constant. This main stream fluid velocity, U , increases the concentration gradient of the reducing species close to the electrode by narrowing the diffusion layer.

The diffusion layer thickness can be related to U by³:

$$\delta \approx D^{1/3} \nu^{1/6} (x/U)^{0.5} \approx 0.1 \delta_H$$

Where x is the distance to the leading edge of the electrode. From this equation it is reasonable to assume that there is negligible convection within the Nernst diffusion layer. The diffusion layer thickness illustrated in Fig. 8 (from Gileadi⁴) is typically 10^{-4} m whereas the hydrodynamic boundary layer δ_H is typically 10^{-3} m. Forced convection can therefore be used to control δ , hence the limiting current J_L .

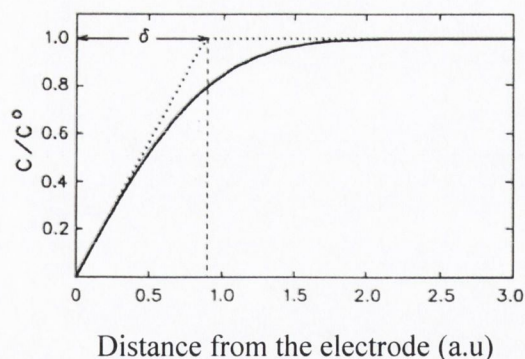


Figure 8. Concentration profile showing the Nernst diffusion layer thickness from Gileadi.

1.2.2 The standard reduction potential and Nernst equation

The Nernst equation gives the equilibrium potential across an interface due to the two-way reaction of the metals ions as shown Fig. 7.

$$E_{eq} = E^0 + (RT/nF)\ln [Q] \quad (16)$$

Where $Q = C_{\infty} (O)/C_{\infty} (R)$ is the reaction quotient. At diluted solutions $C_{\infty} (O)$ and $C_{\infty} (R)$ can be interpreted as the bulk concentrations. However, at higher concentration the ion-ion interaction needs to be taken into account and the activities of the ions are instead used to determine the reaction Q .

Because an electrochemical system always has a two electrode reactions associated with it, the reduction and oxidation processes, the standard reduction potential of a single process cannot be measured directly. Only the potential difference can be measured, therefore a standard electrode reaction must be considered as a reference. A standard electrode reaction is $2H^+ + 2e^- \rightarrow H_2$, which is called the standard hydrogen electrode

(SHE). The standard reduction potential tells us the thermodynamic favourability of a reaction, which is a useful tool for oxi-reduction in chemical reactions. Fig. 9 shows the measurement of the reduction potential of a Cu electrode vs. SHE. The standard reduction potential is defined for 1 M of the ions in a solution at normal conditions of temperature and pressure. Table 1 shows some standard reduction potentials for common reactions.

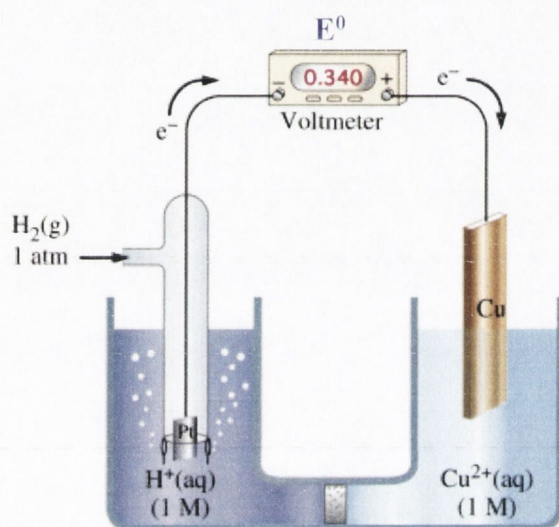


Figure 9. Measurement of the standard reduction potential of a Cu electrode vs. the standard hydrogen electrode (SHE).

Table 1. The standard reduction potential for some metals/metal ions in aqueous solution.

Reaction	Standard reduction potential vs. SHE (V)
$\text{Fe}^{3+} + 3\text{e}^- \rightarrow \text{Fe}$	-0.036
$\text{Fe}^{2+} + 2\text{e}^- \rightarrow \text{Fe}$	-0.409
$\text{Pd}^{2+} + 2\text{e}^- \rightarrow \text{Pd}$	0.83
$\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$	0.8
$\text{Au}^+ + \text{e}^- \rightarrow \text{Au}$	1.68
$\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$	0.34
$\text{Co}^{2+} + 2\text{e}^- \rightarrow \text{Co}$	-0.28
$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$	-0.8277

1.2.3 Tafel Plots

The current at a heterogeneous interface (electrode/solution) is described by the Butler-Volmer, equation (8). At large negative overpotential the anodic current becomes negligible and we have:

$$j = j_0 \exp (-\alpha_c n F \eta / R T) \tag{17}$$

Taking the logarithms of both side we obtain the Tafel relation:

$$\text{Log } j = \text{log } j_0 - \alpha_c (n F \eta / 2.3 R T) \tag{18}$$

In the same manner for large positive overpotential

$$\text{Log } j = \text{log } j_0 + \alpha_a (n F \eta / 2.3 R T) \tag{19}$$

Hence the parameters j_0 , α_c , α_a may be determined from a Tafel plot of $\text{log } j$ against η .

A schematic Tafel plot is shown in Fig. 10. In a typical Tafel plot, deviations from linearity at low overpotential are due to the contribution from the back reaction. At high overpotential, mass transport effects cause a levelling off of the current response.

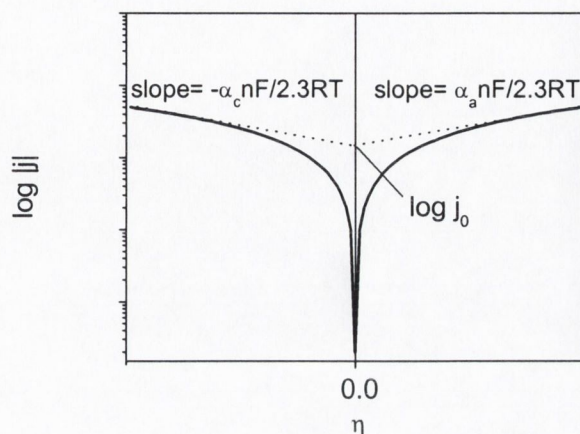


Figure 10. Tafel plot for cathodic (left) and anodic (right) branches for $\alpha_c = \alpha_a$.

1.2.4 Rotating disc electrode (RDE)

The rotating disc electrode consists of a metallic electrode, encased in an insulating sheath, which may be rotated about its own axis in a fluid. Electrical contact is made via brushes in the shaft of the electrode body. The velocity of the hydrodynamic layer at such an electrode is well defined, so that mathematical solution of the convective diffusion equation is made possible. Essentially, the fluid is flung radially outwards by the centrifugal force and fresh solution is sucked up from below to produce the flow pattern as shown in Fig. 11.

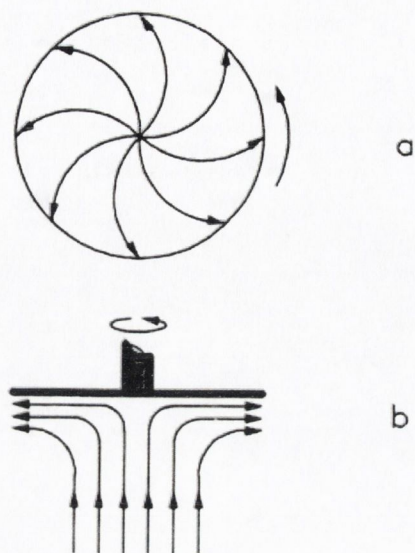


Figure 11. Motion of the liquid at the surface of an RDE: (a) tangential motion at the plane of the electrode and (b) perpendicular motion towards the electrode, from Gileadi.

The rotating disc electrode is an example of a hydrodynamic system, where the rate of mass transport may be increased by forced convection. It is commonly used to determine kinetic parameters as mass transport effects may be neglected at high rotation rates (> 10000 rpm).

Since the flow in the RDE is laminar, it is possible to calculate rigorously the rate of mass transport. The corresponding equation for the limiting current density, developed by Levich, is

$$I_L = 0.62 nFD^{2/3} \nu^{-1/6} \omega^{1/2} C^0 \quad (20)$$

Where D , ν , ω , C^0 , are the diffusion constant, viscosity, angular velocity in radians per second and the bulk concentration. A plot of the limiting (I_L) current vs. $\omega^{1/2}$ allows the extraction of the diffusion coefficient. A comparison to the limiting current equation using the diffusion layer leads to:

$$\delta = 1.61D^{1/3}\nu^{1/6}\omega^{-1/2} \quad (21)$$

As can be seen the rotating disc electrode is a tool which allows us to access, in a controlled manner, the thickness of the diffusion layer.

1.2.5 Electrodeposition of alloys

In contrast to the electrodeposition of a single metal, the electrodeposition of alloys from a single bath usually presents difficulties associated with the need for a stable bath of mutually soluble salts.

When considering only the equilibrium potential of each metal involved in the electrodeposition of an alloy, it is natural to expect that the less noble metal (smaller standard reduction potential) will deposit at more negative potentials and the composition of the alloy will directly depend on the bulk concentration of the metal salts in solution. This is known as normal co-deposition. This can be further refined to consider where mass transport controls the rate as regular co-deposition and where kinetics controls the rate as irregular co-deposition. On the other hand, when the electrodeposition of the less noble metal is favoured we have what is called anomalous co-deposition. Additionally, it is also possible to deposit an alloy component where at least one metal cannot be electrodeposited

alone. This is known as induced co-deposition. An example of this is Ni-Mo, where Mo does not deposit on its own.

For normal co-deposition, when less noble and more noble metal ions are present in solution and the potential is varied towards more negative values, four regions can be identified: a kinetic and mass transport limited region for more noble metal ions and a kinetic and mass transport limited region for less noble metal ions, respectively as illustrated at Fig. 12. Yet in Fig. 12, B and D are the products of the reduction of A (more noble) and C (less noble) ions, respectively. There are, in this simplified analysis, two important regions, which affect the composition of the alloy. The first corresponds to an intersection region where the more noble metal ion is mass transport limited and reduction of the less noble metal is kinetically controlled. In this case the final composition of the alloy can be controlled by changing the potential or at fixed potential enhancing the mass transport of the more noble metal towards the electrode. Once the potential is kept constant in this region, changes in mass transport can only affect the reaction rate of the more noble metal. On the other hand, if the mass transport is kept constant, changes in potential will only affect the rate of deposition of the less noble metal. Therefore, the composition of the alloys can be controlled in two different manners without changing the bath composition.

The second region corresponds to both metal ions having the reduction rate controlled by mass transport. In this case, the composition of the alloy does not depend on the mass transport, therefore the composition cannot be changed by means of stirring or variation of the potential, but by changing the concentration of the ions in solution. Despite the fact that the composition cannot be changed in this region, the deposition rate can be since it depends on the limiting current by the following expression:

$$I_L = nFDC^0/\delta \quad (22)$$

Where n = valence number, F = Faraday constant, D = diffusion coefficient, C^0 = the bulk concentration and δ = Nernst diffusion layer thickness.

In this situation, changes in the thickness of the diffusion layer affect the limiting current, thereby increasing the reduction rate (deposition rate).

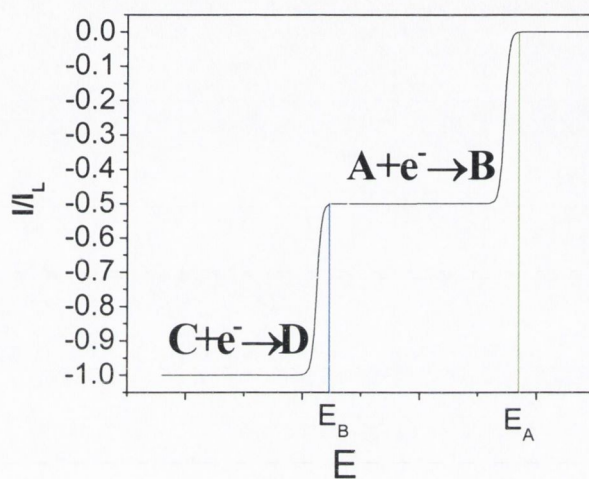


Figure 12. Electrodeposition of alloys. A, C, B and D are the more noble and less noble ions and their reduction product, respectively.

Unfortunately, the partial currents during deposition are not always non-interacting. They can be coupled. When this is the case, the partial current of one reduction reaction may be reduced in the presence of the other reaction. Competitive absorption of intermediates in the electrode surface is likely to cause this inhibition; one intermediate may become dominant. Additionally, some reductions may chemically change the environment near the electrode affecting the kinetics of the other reaction. If this is the case

and the reaction is mass transport limited so are the reactions affected by the chemical changes. The most common example of this is the effect of hydrogen evolution, which increases the pH near the electrode according to the following reaction:



This changes the deposition kinetics of the other reactions taking place often by the formation of a metal hydroxide at the cathode. If the hydrogen formation is mass transport controlled then so too is the alloy deposition process.

Complexing agents are ions which bond usually to metal ions to form a new ion. They are highly soluble in a broader range of pH than the metal ions to which they bonded, thereby minimizing the effect of pH changes. Consequently, they have a substantial effect on co-deposition. They can change the charge transfer kinetics and they also prevent metal hydroxide formation, thereby reducing the effect that hydrogen evolution has on the co-deposition process. An example of a complexant is vitamin C, technically known as ascorbic acid. When used in solutions containing Fe ions it prevents hydroxide formation up to a pH as high as 12 depending on concentration, iron hydroxide usually precipitates below a pH of 7. Whenever the metal ions compete for complexing agents the rate of deposition of one will affect the other.

The complex ion issues, electrochemical interaction, electrochemical properties and interacting chemical properties are some of the difficulties which make prediction of composition and of plating parameters an experimental science.

1.2.6 Corrosion

Most corrosion reactions are electrochemical in nature. In the process one atom loses electrons and forms an ion. Electrochemical corrosion requires a medium to transport electrons, which can be a solid, a fluid or plasma of ionised gas in space (shuttle glow).

The electrical circuit that is formed is called an electrochemical cell or galvanic cell which is composed of four components: a) the anode which gives up electrons, b) the cathode which receives electrons, the cathode de-ionizes an element to produce what is called the reaction byproduct, c) a closed electrical circuit for the flow of electrons and d) an electrolyte between anode and cathode which supplies and receive ions.

The chemical reaction is composed of two so-called half-cell reactions, the oxidation and the reduction reactions. Both reactions occur at the same time and are inseparable.

The oxidation reaction, also called the anode reaction, forms ions and releases them into the electrolytic solution, while the free electrons flow in the opposite direction towards the cathode. The release of elements leads to corrosion. The reaction is written as:



Where the metal M oxidizes into an ion.

The reduction reaction, also called the cathode reaction, combines electrons with ions to form elements or reduce the oxidation number of the ion. When the ions are reduced to metal we call the process electrodeposition.

Every metal has a different tendency to give up electrons in a particular chemical environment, which is associated with the standard reduction potential. The potential in

which the metal has equal tendency of giving or receiving electrons is called the half-reaction potential.

1.2.6.1 Passivation and breakdown

A piece of aluminum placed in dilute nitric acid corrodes but no corrosion is observed when aluminum is placed in highly concentrated nitric acid solution. This is due to passivation, a phenomenon known for over 200 years. The passivation of Al in nitric acid occurs for concentrations around 35 vol. %.

When a piece of iron is placed in a dilute solution of sulphuric acid and its potential increased in the anodic direction, the rate of dissolution increases, reaches a maximum, and then decreases to almost zero. Further increase of the potential has little effect on the current in the passive region until passivity breaks down, and the current rises rapidly with potential. This sequence of events is illustrated in Fig. 13, from Gileadi. The potential in which the anodic dissolution current has its maximum value, and beyond which it starts to decline rapidly, is called the primary passivation potential E_{pp} and the corresponding current is called i_{crit} . In the passive region, which may extend over half a volt or more, the current is nearly constant. It starts to rise again at the so-called breakdown potential (E_b), above which pitting corrosion occurs, along with oxygen evolution and electrochemical dissolution of the passive film.

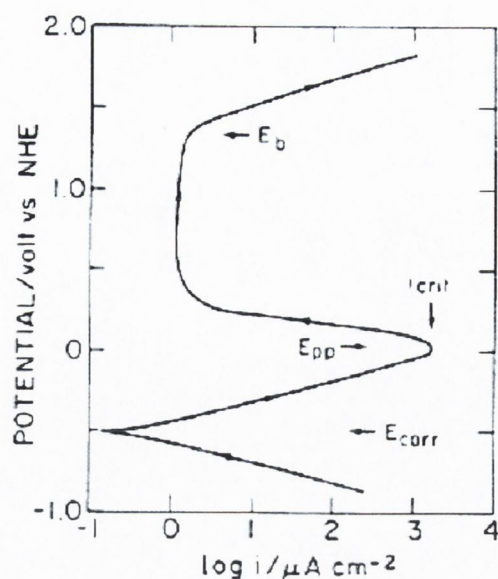


Figure 13. Schematic representation of corrosion and passivation of iron in sulphuric acid from Gileadi. The primary passivation potential E_{pp} and the corresponding critical current density for corrosion i_{crit} are shown. Breakdown of the passive film occurs at potentials more positive than E_b .

1.2.6.2 Anodes and cathodes in corrosion

There are several types of metallurgical galvanic cells which are naturally formed when two or more dissimilar materials have electrical contact: grain-grain boundary cells, multiple-phase cells (eutectics, dispersion-strengthened and aged materials), impurity cells (intermetallics, dispersions), rivets and bolts, welding, soldering, brazing. Single element materials such as Fe also show dissimilarities since their microstructure is constituted of non-uniform grains.

The grain boundaries are often more anodic than the grain crystal itself. This leads to preferential corrosion of the grain boundary area in a chemically active environment. The corrosion propagates along the grain boundary to form substantial cracks, which weaken the material. In some alloys and metals the grain boundary is cathodic and the grain is anodic, which leads to corrosion of the grain next to the grain boundary (Fig. 14). One application of the grain-boundary corrosion process is the visualization of the grain boundaries of polished surfaces by etching them. As the grain boundary has higher energy, atoms are readily removed and grooves are formed. The grooves deflect incoming light which leads to a dark line visualization.

As grain boundaries produce galvanic corrosion cells, a fine grain structure is more sensitive to the environment than a large or single crystal structure. This is one of the reasons for using single crystal turbine blades, which are exposed to very corrosive combustion gases.

Many of the high performance magnets such as SmCo and NdFeB are extremely vulnerable to chemical attack. They have a microstructure rich in grain boundaries and their components corrode very easily. It is common practice to add a protective layer of Ni or Cr to permanent magnets produced from SmCo and NdFeB.

Other galvanic cells include steel screws in brass (marine) hardware, Pb-Sn solder around copper wire, steel pipes connected to copper plumbing. Building codes require teflon connectors between city water pipes and the copper tubing in houses. Teflon is an electrical insulator and thus breaks the electron flow between copper and steel.

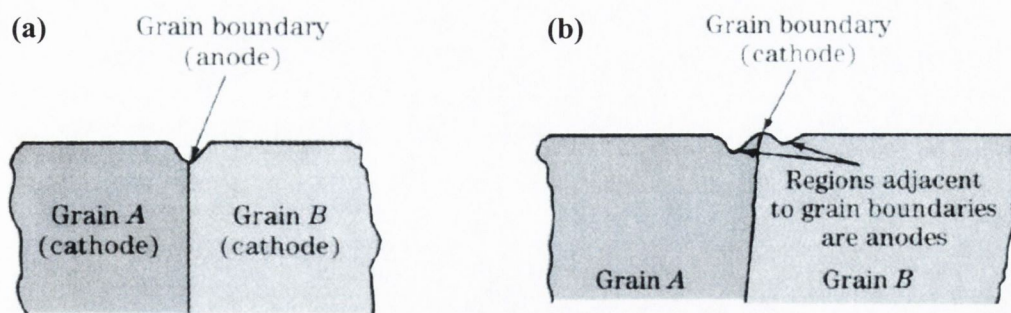


Figure 14. The formation of a galvanic cell between grain and grain boundaries. An anodic (a) and cathodic (b) grain boundary.

1.2.6.2.1 Concentration and oxidation corrosion

Concentration cells arise from differences in electrolyte compositions, when a gradient in ion concentration is present. At higher concentrations the metal becomes a cathodic electrode and is protected; at lower concentrations the same metal becomes an anodic electrode and corrodes.

Oxidation corrosion also develops in an environment with oxygen deficiency. Metal parts with inaccessible surface locations with low oxygen become anodes. The inaccessible or covered surface then corrodes.

1.2.6.2.2 Stress Corrosion

Stress cells involve dislocation, grain boundaries and highly stressed or pre-stressed regions in the material.

Cold deformation creates dislocations that become anodic surfaces, whereas the unchanged metal serves as cathode. The electrode potential of a deformed metal is more anodic than that of an annealed metal. Highly stressed regions are more anodic than the less stressed areas.

Fine grain materials are more anodic than large grain size materials. Fine grain size regions which have a larger ratio of grain boundary area to volume and a specific surface energy, are more anodic than large grain size regions, which have a smaller ratio of grain boundary area to volume (and low surface energy). Welded regions often have varying grain size, thus they corrode more easily.

1.2.6.3 Corrosion measurements

There are three methods commonly used to determine the corrosion rate: the polarization resistance, Tafel extrapolation and weight loss methods. In the polarization resistance technique the sample potential is scanned over a very small range relative to the open circuit potential (typically ± 20 mV vs. E_{∞}), and the resulting current is measured. Over this range, the current vs. voltage curve is roughly linear. From the slope one obtains the polarization resistance per unit area, R_p , which is used to calculate J_{corr} and thus the corrosion rate using the Stern-Geary equation:

$$J_{\text{corr}} = (1/R_p) (\alpha_a \alpha_c) / [2.303 (\alpha_a + \alpha_c)] \quad (25)$$

where α_a and α_c are the anodic and cathodic Tafel slopes, respectively, which must either be estimated or determined from another experiment.

The behaviour of two metals that are galvanically coupled can be estimated by superposition of the cathodic polarization curve of the less-active (more noble) metal on the anodic polarization curve of the more-active metal. The current at which the two curves intersect is the galvanic current, which is proportional to the galvanic corrosion rate of the anode, provided that the ohmic drop in solution is negligible and that the current distribution is uniform.

The precision of the Stern-Geary equation relies on the accuracy of the coefficients α_a and α_c , which are usually obtained from Tafel plots. In turn, the coefficients obtained from Tafel plots carry a certain inaccuracy due to solution resistance (ohmic drop). As long as it is applicable, the weight loss technique is the most simple and reliable method to determine the corrosion rate and can also serve to determine the coefficient of the Stern-Geary equation $(\alpha_a \alpha_c) / (\alpha_a + \alpha_c)$.

1.3 Magnetic forces in fluids

1.3.1 Lorentz force

The force resulting from the interaction between a magnetic field and a moving charge or current density is expressed by the Lorentz force:

$$F_L = J \times B \quad (26)$$

Where J is the current density in $A\ m^{-2}$, B is the applied field in Tesla and F_L is the Lorentz force per unit volume $N\ m^{-3}$. This force acting in moving ionic solution leads to convection. For example for $j = 50\ A\ m^{-2}$, $B = 0.5\ T$, $F_L \sim 25\ N\ m^{-3}$.

1.3.2 Electrokinetic magnetohydrodynamic force⁵

An electric field applied parallel to the electrode surface interacts with the charge in the diffusion layer, inducing a flow of these charges. This effect is known as electro-osmotic motion. Boundary conditions force the flow velocity to be zero at the surface, therefore the flow velocity increases with distance from the electrode surface. Viscous forces oppose the flow, allowing a steady state velocity to be reached. The relative motion of the two phases, the electrode and the electrolyte, is known as an electrokinetic effect. Because the electrokinetic force arises due to the charge in the diffusion layer, any process which modifies the structure and charge distribution, such as contact adsorption of ions, or the concentration of the electrolyte, will modify this force.

Olivier⁶ et al. proposed that a magnetic field applied parallel to the electrode will act on the diffuse charges, via the Lorentz force, and create an electric field parallel to the electrode surface. They suggested that this electric field will then induce electro-osmotic motion giving rise to convection in the diffuse layer and thereby increasing the current. This they called the electrokinetic magnetohydrodynamic effect.

$$F_{EK} = (\sigma_d E_{//}) / \delta_H \text{ as a body force acting in the diffuse layer} \quad (27)$$

Where σ_d is the charge density of the diffuse layer, $E_{//}$ is the induced nonelectrostatic field and δ_H is the boundary layer thickness. Using $\sigma_d = 10^{-1}\ C\ m^{-2}$, $E_{//} = 10\ V/m$ and $\delta_H = 10^{-2}\ m$, the magnitude of F_{EK} is $10^2\ N\ m^{-3}$.

1.3.3 The concentration gradient force $F_{\nabla C}$

The magnetic energy density can be written as:

$$E = -C\chi_m B^2/2\mu_0 \quad (28)$$

Where C is the concentration in mol m^{-3} , χ_m is the molar susceptibility of the ion in $\text{m}^3 \text{mol}^{-1}$ and μ_0 the permeability of free space, $4\pi \times 10^{-7} \text{ A m}^{-1}$. Using $F = -\nabla E$ and taking only the term with ∇C (the other term will be discussed in another section), we obtain:

$$\mathbf{F}_{\nabla C} = (\chi_m B^2/2\mu_0) \nabla C \quad (29)$$

For example, when $\chi_m = 10^{-8} \text{ m}^3 \text{mol}^{-1}$ in 0.1 M (10^2 mol m^{-3}) solution and the diffusion layer thickness $\delta = 1 \times 10^{-4} \text{ m}$, $B = 1 \text{ T}$ then $F_p = 4000 \text{ N m}^{-3}$.

1.3.4 The field gradient force

The second term of the magnetic force which derives from the magnetic energy density (equation (28)) is

$$F_{\nabla B} = (C\chi_m B \nabla B)/\mu_0 \quad (30)$$

This magnetic force is generated when the magnetic field is not uniform. For positive values of $B\nabla B$, paramagnetic ions are attracted and diamagnetic ions are repelled. For example, in a 1 T field, with field gradient of 1 T m^{-1} , for a paramagnetic ion with $\chi_m = 10^{-8} \text{ m}^3 \text{mol}^{-1}$ in 0.1 M solution, $F_{\nabla B} = 1 \text{ N m}^{-3}$. One of the most successful applications of this force is the construction of oxygen sensor⁷. The sensor is used to measure real time oxygen

levels in combustion systems in order to determine combustion efficiency, information which can be used to feedback the combustion process. Oxygen needs to be at a certain level in order to minimize the emission of the poisoning CO.

1.3.5 Hydrodynamic damping force

For very conductive electrolytes, the motion of an electrolyte in a magnetic field will induce an electric field, $\mathbf{v} \times \mathbf{B}$, then the current in the electrolyte can be written as $\sigma (\mathbf{v} \times \mathbf{B})$, where σ is the conductivity of the solution in ($\text{Ohm}^{-1} \text{ m}^{-1}$). Consequently a current moving in a magnetic field will induce motion according to the Lorentz equation:

$$\mathbf{F}_d = \sigma \mathbf{v} \times \mathbf{B} \times \mathbf{B} \quad (31)$$

This force acts to impede or damp the velocity ($\sim 10^{-1} \text{ m s}^{-1}$) in the transverse direction while velocity in the longitudinal direction is unaffected. This force is negligible in aqueous solutions where the conductivity is low; about $10^2 \text{ Ohm}^{-1} \text{ m}^{-1}$. The use of static magnetic fields to control the convection during the growth of crystals from conducting molten salts relies on this damping force⁸.

1.4 Structure and phase diagrams of Fe-Pt, Fe-Pd, Co-Pt and Co-Pd

Equiatomic FePt, CoPt and FePd belong to a special class of magnets with the structure $L1_0$. These alloys form tetragonal phases which show high anisotropy. The $L1_0$ structure is an ordered structure corresponding to a stacking sequence A-B where A corresponds to a layer of atoms of Fe or Co and B correspond to atoms of Pt for example. The uniaxial anisotropy is along the c axis. When Pt randomly occupies the layers of Fe and vice versa the disordered phase is formed and the lattice parameter c becomes equal to a. In this situation the anisotropy is very small in the structure and the magnetic properties correspond to a soft material. As an example, the structure of the FePt ordered phase is represented in Fig. 15. The magnetic properties of the bulk samples are shown in table 2⁹.

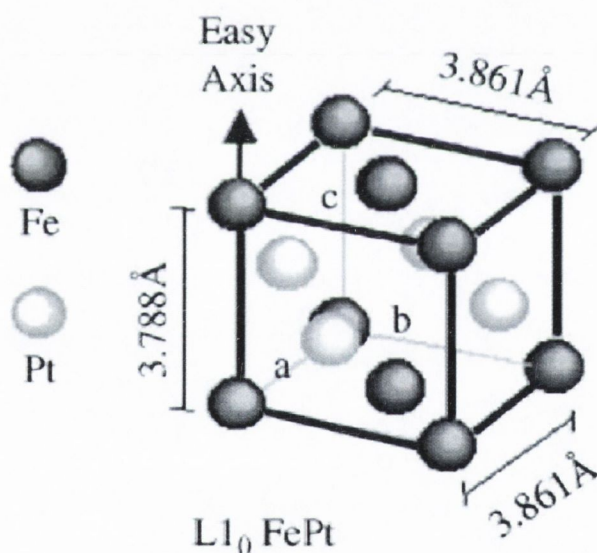


Figure 15. Model structure of tetragonal FePt also known as the $L1_0$ phase.

Table 2. Intrinsic magnetic properties of ordered 3d alloys of typical bulk permanent-magnet.

Alloy	T_c (K)	$\mu_0 M_s$ (T)	K_1 (MJm ⁻³)	$\mu_0 M_r$ (T)	H_c (KA m ⁻¹)	Lattice parameters (nm)	
						a	c
FePd	760	1.38	1.8	0.95	160	0.3852	0.3723
FePt	750	1.43	6.6	1.04	390	0.3852	0.3713
CoPt	840	1.00	4.9	0.65	360	0.3803	0.3701

The phase diagrams of FePt, FePd, CoPt and CoPd¹⁰ are shown in Fig. 16, 17, 18, 19, respectively. The range of compositions which form the tetragonal phase for FePt, FePd and CoPt are 34-59 at. % Pt, 50-60.5 at. % Pd and 41-75 at. % Pt, respectively. Since Fe forms the L1₀ tetragonal phase with Pd and Pt (FePd, FePt), it is natural to think that the same type of structure would be formed if we replace Fe by Co. In fact, there is an L1₀ CoPt phase but there is not an L1₀ CoPd phase as can be seen in the phase diagram (Fig. 19). CoPd alloys are included in the Co-rich alloys and not in the L1₀ family. When Co and Pd are mixed together they segregate into Co and Pd phases.

In order to minimize the time required to obtain the ordered phase in bulk samples it is common practice to homogenize the sample. This procedure is carried out by annealing the sample at temperatures higher than the melting point of the tetragonal phase and quenching the sample in water. As the cooling rate is significantly high the sample only forms a very homogenous disordered phase which then can be heat treated to form a highly homogenous tetragonal L1₀ phase. The homogenisation temperatures, according to the phase diagram, are about 1300 °C, 640 °C and 825 °C for FePt, FePd and CoPt, respectively.

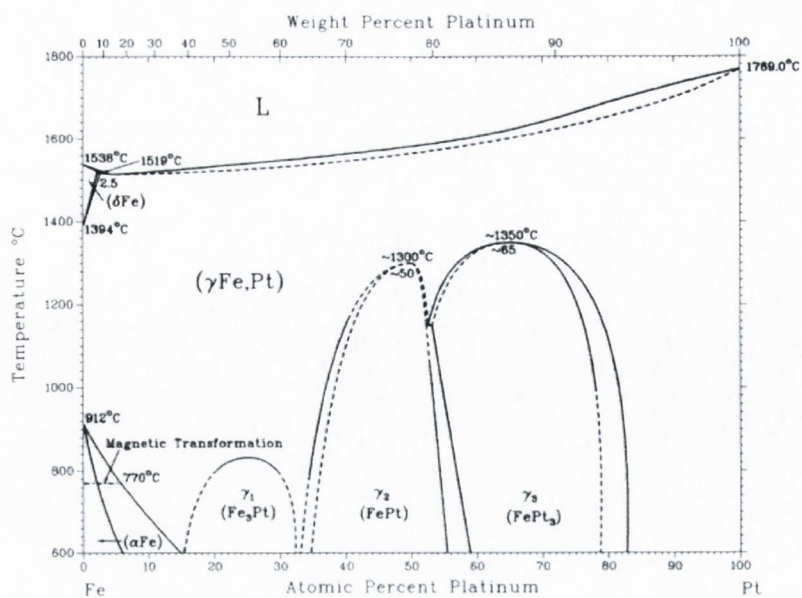


Figure 16. Phase diagram of FePt, the tetragonal phase is formed in the range 34-59
at. % Pt.

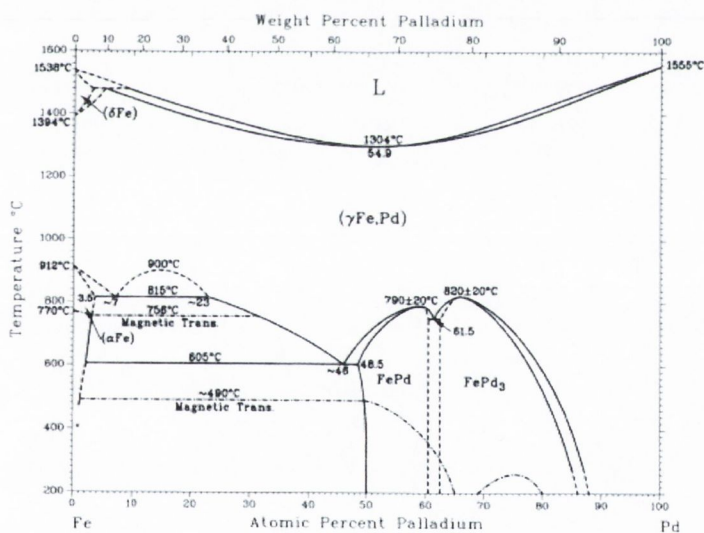


Figure 17. Phase diagram of FePd, the tetragonal phase is formed in the range 50-60.5
at. % Pd.

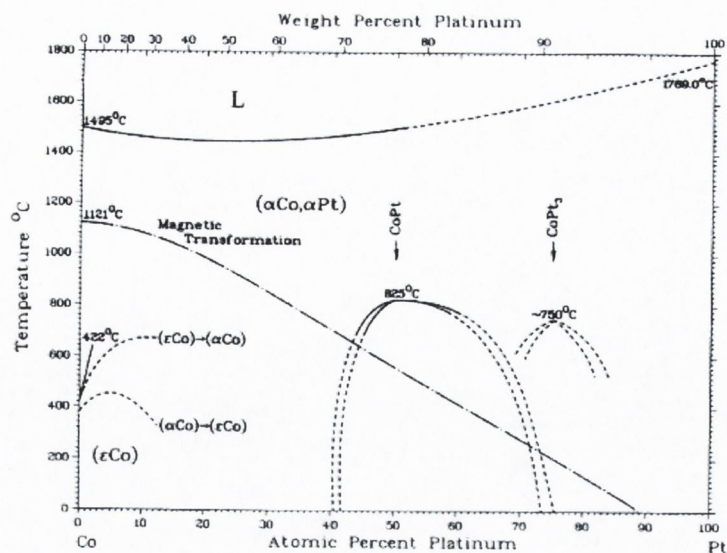


Figure 18. Phase diagram of CoPt, the tetragonal phase is formed in the range 41-75 at. % Pt.

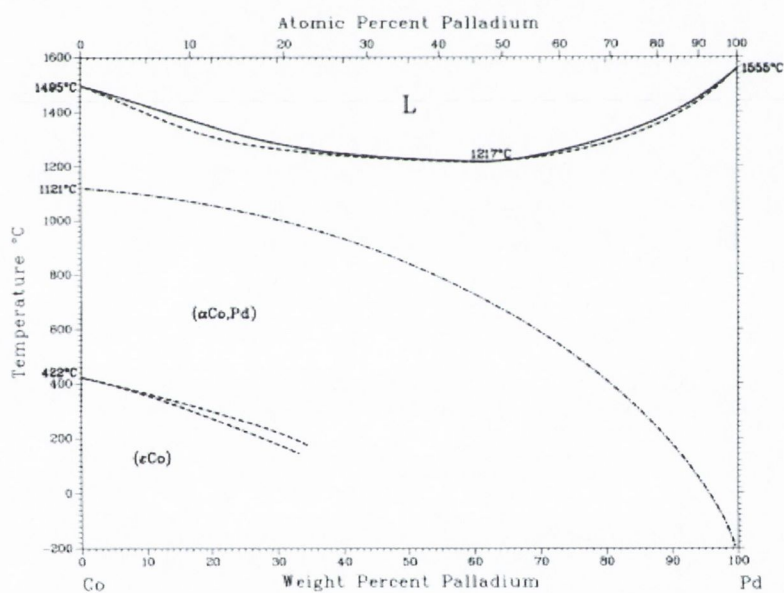


Figure 19. Phase diagram of CoPd. Co and Pd do not form any common phase, when mixed the alloys segregate into Co and Pd.

1.4.1 Literature review

1.4.1.1 Fe-Pt

Most studies about FePt alloys reported in the literature were focussed on media recording applications. Thin and ultrathin films are prepared as alloys or multilayers usually by sputtering^{11, 12, 13, 14, 15, 16, 17, 18, 19}, electron-beam evaporation^{20, 21, 22, 23} (e-beam) and pulsed laser deposition (PLD)²⁴. Bulk materials have been prepared by arc-melting²⁵ and room-temperature cold-deformation^{26, 27}. A common feature of these techniques is the requirement for the films to be either deposited onto a heated substrate or post-annealed in order to develop a crystalline structure. The effect of additives in FePt alloys has been studied by many authors.

In 2002, Chen et al. studied the effect of the addition of Nb on the magnetic properties of $(\text{FePt})_{100-x}\text{Nb}_x$ $0 < x < 2.1$ at. %. They reported an increase in the energy product, which was associated with a better loop squareness and a decrease in coercivity. The coercivity decreases as Nb concentration increases.

Also in 2003, Hsu et al. studied the effect of a Ag underlayer in the magnetic properties of epitaxial FePt. They found that the films sputtered onto heated substrates exhibit a lower ordering temperature when using Ag as a seed layer. Film composition was $\text{Fe}_{55}\text{Pt}_{45}$, with thickness between 2.5-30 nm, Ag thickness (10-175 nm and a substrate temperature of $T_s = 25\text{-}300$ °C. The authors suggested that Ag acts as a seed to the epitaxial growth of FePt based on the fact that there is a small lattice mismatch between Ag and $L1_0$ FePt which is only 7 %. The authors found in plane coercivity of 0.4 T for 30 nm thick films sputtered onto substrates heated to 300 °C when using a 10 nm Ag seed layer on a Si substrate.

In 2003, Sato et al. studied the effect of a Ag seed layer in the $L1_0$ phase formation of FePt deposits. The films were prepared using e-beam evaporation and the substrate was NaCl. The authors claimed that Ag reduces the ordering temperature of FePt//NaCl. According to them, the ordering temperature was 673 K for an average 7 nm particle size. However, only a modest 0.1 T coercivity was obtained for samples containing 11 at. % Ag after annealing at higher temperature (600 °C). In conclusion the authors stated that the role of Ag additives on the promotion of atomic ordering remains an open question.

Some reports have specifically addressed the effect of additives on the reduction of the ordering temperature of the $L1_0$ FePt phase. Elements such as Cu, Ag, W, Ti by Kuo et al.²⁸ and Cr by Lee et al.²⁹ have been studied.

In 2002, Takahashi et al. reported that the $(\text{FePt})_{1-x}\text{Cu}_x$ ($x = 0, 0.04$) alloys have an ordering temperature smaller than that of pure FePt. By adding 4 at. % of Cu they reduced the ordering temperature from 500 °C to 400 °C with 1 hour annealing. They suggested that the decrease of the formation temperature of ordering is due to the enhanced kinetics of ordering as a result of higher diffusivity obtained from the alloy with a lower melting point. The authors also suggested that the chemical formula for FePtCu should be $(\text{Fe}_{1-x}\text{Cu}_x)\text{Pt}$ as Cu replaces Fe in the structure. Takahashi et al. during their conclusion referred to several other reports where other additives were studied. Other alloy elements have been studied for FePt, W, Ti by Kuo and Cr by Lee. W, Ti and Cr retard the grain growth but have no effect on the ordering temperature. Kitakami et al.³⁰, found that Sn, Pb, Sb and Bi additives in CoPt are effective at reducing the ordering temperature. Kitakami explained the ordering temperature reduction in terms of the enhancement in the diffusivity of Co and

Pt due to the vacancies left behind by the melting and segregation of the low melting point elements. These elements do not alloy with either Co or Pt.

Takahashi then concluded that the kinetics enhancement mechanism for Cu is different from that of Sn, Pb, Sb and Bi. Cu replaces Fe in the structure and reduces the melting point of the composed alloy, while the low temperature elements promote vacancies, which enhance diffusion. Coercivities up to 0.8 T were obtained for 300 nm thick films with composition $(\text{FePt})_{96}\text{Cu}_4$ after annealing at 400 °C for 1 hour (Fig. 20).

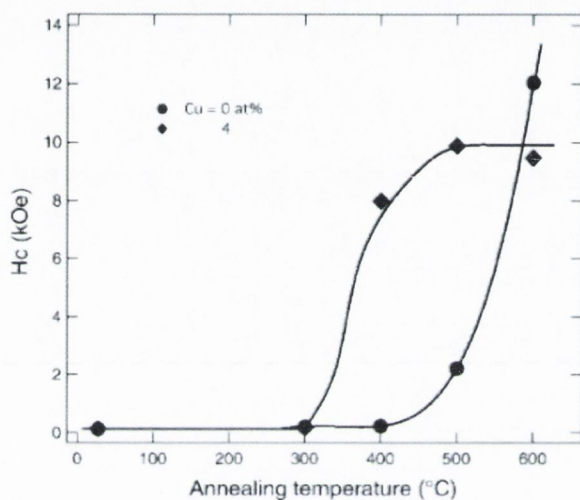


Figure 20. Coercivity dependence of FePt and $(\text{FePt})_{96}\text{Cu}_4$ on the annealing temperature from Takahashi.

In a recent publication a controversial issue was brought to light. In 2004, Wierman et al. claimed that Cu has no effect on the ordering temperature of FePt. They stated that the reduction of the ordering temperature is due to changes in composition rather than the effect of Cu addition itself. The authors present results where Cu atoms replace Fe and the ordering temperature is not changed. The magnetization and the coercivity diminish as Cu

is added. Therefore, they concluded that Cu does not change the kinetics of formation of the ordered phase as suggested by other authors. Additionally, the authors suggested that the changes in the ordered phase formation are rather associated with composition deviation from the equiatomic FePt. The lowest annealing temperature to show coercivity was 350 °C, as can be seen in Fig. 21.

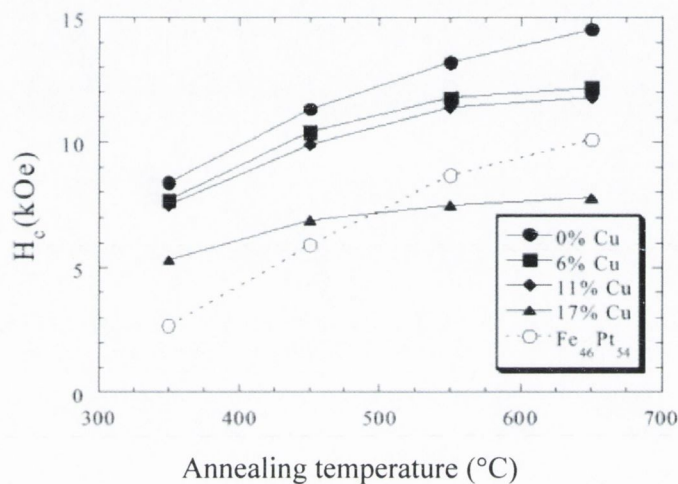


Figure 21. Coercivity dependence on annealing temperature of 50 nm $Fe_{50-x}Pt_{50}Cu_x$ ($x = 0, 6, 11, 17$ at. %) films from Wierman. Films were annealed for 10 min.

Colossal coercivities were obtained in a special situation where the ultrathin films were prepared by co-deposition of Fe and Pt using sputtering by Shima et al. and using PLD by Weisheit et al.. After growth at heated substrate, an array of well-separated nanoparticles was formed. Shima et al. found coercivities as high as 10.5 T at 5 K with these nanoparticles. The substrate was MgO (001) which was kept at 780 °C during the deposition. The combination of epitaxial growth and particle isolation lead to out of plane

room-temperature coercivity of 7.0 T for samples with 5 nm nominal thickness. The coercivity was found to reduce to 4.0 T as the nominal thickness was increased to 40 nm. Weisheit used the PLD technique to obtain coercivities as high as 5.6 T for a 40 nm thick film deposited on glass with an a MgO (001) seed layer. The substrate temperature was 800 °C during the deposition. The authors also found that the films grew epitaxially and formed well-separated nanoparticles.

In contrast to sputtered and e-beam deposition of FePt films, only recently, have FePt films been electrodeposited as a continuous film³¹ and into porous membranes³². To our knowledge our group was the first to report the electrodeposition of continuous films. Films were annealed to develop coercivity, which is associated with the formation of the L1₀ phase. Based on the electrochemical bath that we have first introduced there has been a remarkable improvement in the coercivity of electrodeposited films^{33, 34}. In addition to the interest in media recording and MEMS, there is also a renewed interest in shape memory alloys³⁵ and nanotubes³⁶ based on FePt. A summary of the magnetic properties of FePt is shown in table 1 and a comparison of the coercivity vs. the film thickness in Fig. 22.

Table 1. Magnetic properties electrodeposited (Ec), sputtered (Sp), e-beam evaporated (Eb), cold-deformation (Cd) and pulse laser ablazion (PLD) FePt alloys. All sputtered, e-beam evaporated and arc-melted samples were either prepared on heated substrates or with post-anneal. Symbols “-”, “//”, “⊥” stand for not reported, in plane and out of plane measurements, respectively.

Process code	Alloy	Alloying element (at. %)	Thickness (μm)	Coercivity (mT)	[Ms (T)]	References
Sp	FePtTa	20 Ta	0.01	500	0.5 -0.69	Shimatsu
Sp	FePtNb	0 Nb	-	650	0.980	Chen
Sp		2.1 Nb	-	270	1.5	“
Sp	FePtCu	0-4 Cu	0.3	800	0.753	Takahashi
Sp	FePtCu	0-4 Cu	0.3	1000	0.753	“
Sp	FePtCu	0-4 Cu	0.3	1000	0.753	“
Sp	FePtAg	-	0.03	400 (//)		Hsu
Sp	FePt	48 Pt	0.005	7000 (⊥)	1.44	Shima
Sp	FePt	48 Pt	0.04	4000 (⊥)	1.444	“
Sp	FePt	-	0.02	261	1.03	Lim
Sp	FePt	-	0.05	1400	1.25	Wierman
Sp	FePt	41 Pt	-	670 (⊥)	0.532	Lai

Sp	FePt	41 Pt	-	992 (⊥)	-	“
Sp	FePt	48 Pt	0.12	950 (/)	-	Bai
E-b	FePt	-	0.11	1200	-	Schwickert
E-b	FePt	-	0.05	150 (⊥)	-	Shima
E-b	FePt	56 Pt	< 0.02	550 (⊥), 460 (/)	-	Sato
E-b	FePd	58 Pd	< 0.02	330 (⊥), 340 (/)	-	“
E-b	FePtAg	11 Ag	-	100	-	Sato
PLD	FePt	-	0.04	5600	0.85	Weisheit
Cd	FePt	50 Pt	100	900	0.6-0.7	Hai ^{26, 27}
Ec	FePt	50 Pt	0.45	200	0.70- 0.90	Rhen
Ec	FePt	50 Pt	0.45	300	0.70- 0.90	“
Ec	FePt	50 Pt	-	1500	-	Rhen
Ec	CoPt	-	-	380	-	Huang
Ec	FePt	-	-	300	-	“
Ec	FePt	50 Pt	0.7	1100	0.4-0.6	Leistner

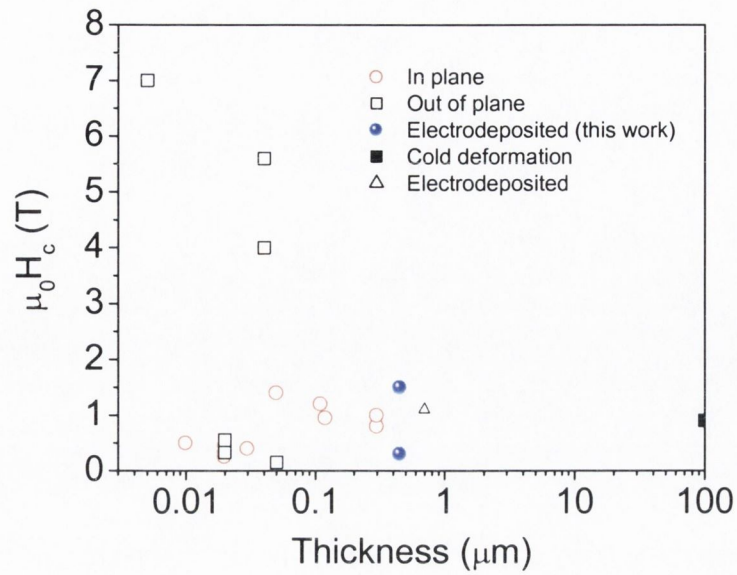


Figure 22. Coercivity dependence on the thickness of equiatomic FePt. Data taken from the current literature including the present thesis. Open circles, open squares, black circles and black squares stand for in plane and out of plane coercivity of sputtered samples, isotropic electrodeposited samples and isotropic bulk samples, respectively.

1.4.1.2 Co-Pt

Many of the recent studies of CoPt alloys are devoted to the preparation of recording media. In contrast to FePt alloys, there are many studies of electrodeposition of CoPt alloys. As Co is the only magnetic element to exhibit uniaxial anisotropy due to its stable hcp structure at room-temperature, it is largely used for media recording. The vacuum techniques for the preparation of CoPt films include sputtering^{37, 30, 38, 39, 40} and electron-beam evaporation⁴¹ (e-beam). Additionally, arc-melting⁴² was used for the preparation of the bulk alloys. Electrodeposition has also been exploited for the preparation of CoPt /Co-rich-Pt as multilayers^{43, 44, 45, 46, 47, 48}, alloys^{49, 50, 51, 52, 53, 54, 55, 56, 57, 58, 59} and Co-rich alloys excluding Pt^{60, 61, 62, 63, 64, 65, 66}.

The effect of additives on the ordering temperature of sputtered CoPt was studied for Sn, Ag, Pb, Sb and Bi additives. In 2001, Kitakami et al. studied the formation temperature of ordered CoPt with the addition of Ag, Sn, Pb, Sb and Bi. According to the authors, with the exception of Ag, all these low-melting point elements segregate to the surface of the film lowering the crystallization temperature of CoPt. Addition of Ag to the granular film is effective in reducing the ordering temperature, while there is no effect on continuous films. The mechanism proposed is the increase in diffusivity of Co-Pt due to an excess of defects caused by the low melting point elements, which segregate to the surface of the film during annealing. They concluded that Sn is the most effective additive to reduce the ordering temperature. A coercivity of 0.6 T was obtained in 40 nm thick films containing 4.3 at. % Sn after annealing at temperatures as low as 450 °C.

In 2001, Keitoku et al. prepared Co-Cr-Pt alloys by sputtering and found coercivities up to 0.5 T for media applications. The composition of the alloy studied was Co-Cr-Pt with 13-18 at. % Cr, 12-22 at. % Pt and the films were sputtered onto heated substrates ($T_s = 400-450\text{ }^{\circ}\text{C}$). Films with composition Co-Cr₁₅-Pt_{14.7} and a thickness of 30 nm developed out of plane coercivity of 0.558 T after annealing at 400 °C.

Several authors have studied the electrodeposition of multilayers. In contrast to sputtered films the authors did not post-anneal the samples. There are reports of two electrochemical techniques for the preparation of multilayers. One makes use of a dual bath. In this case the electrode is transferred to each bath that contains either Co or Pt ions. The other technique consists of using a single bath and by changing the applied potential (pulse-plating) to deposit a Pt or Co-rich alloy. In 1996, Jyoko et al. prepared Co/Pt multilayers on Pt (111) with each layer as thin as 5 nm by electrochemical plating from separate baths, however no magnetic properties were studied. Also in 1996, Georgescu et al. electrodeposited Co/Pt multilayers with layer thicknesses ranging from 0.8 to 15 nm from a single electrochemical bath using the pulse the plating technique.

In 1997, Hayashi et al. prepared electrodeposited Co/Pt multilayers on Cu substrates from two electrochemical baths. Films as thick as 100 nm were magnetically soft with 0.025 T coercivity.

In 2000, Georgescu et al. prepared Co/Pt multilayers on either Pt or Pt (50 nm)/Cu substrate by electrodeposition with a layer thickness of about 1 nm. The authors claimed to deposit films containing the ordered $L1_0$ phase or ordered CoPt_3 . However, only a very small coercivity (15 mT) was measured for the 100 nm thick film, contradicting the claims of an $L1_0$ phase.

In 2000 and 2001, Jyoko et al.^{47, 48} electrodeposited Co/Pt and CoNi/Pt multilayers and alloys onto Cu from two separate baths. In plane coercivities of up to 0.15 T were obtained for CoNi/Pt multilayers with a total thickness of 150 nm. The authors suggested that the increase of coercivity is associated with the pinning of the domain wall in the grain boundary due to the presence of non-magnetic or weakly magnetic Pt.

A remarkable progress has been made in the improvement of coercivity of electrodeposited Co rich alloys containing about 20 at. % Pt. One of the first electrodeposited films to show considerable high coercivity (0.25 T) was prepared by Bozzini et al. Historically, all the publications related to the electrodeposition of Co-Pt alloys which present reasonable coercivity are linked to the same group of researchers in Italy: Bozzini, Zangari, Callegaro⁵¹ and Franz who are all close collaborators of Cavallotti and more recently Zana who is a former student of Zangari.

In 1993, Bozzini et al. electrodeposited Co-Pt and Co-Pt-P onto Cu substrates from novel electrochemical bath with thicknesses up to 0.3 μm . Thin films (30 nm) containing Pt (17-20 at. %) and P developed 0.2605 T in plane coercivity.

In 1995, Callegaro et al. studied the magnetic interaction in CoPtP electrodeposited films. For very thin films the authors found out of plane coercivity of about 0.5 T. The addition of P accounted for the change of magnetic interaction from exchange to magnetostatic. Additionally, the authors explained that the decoupling between grains is associated with the formation of non-magnetic material around the grain boundary (P) leading to the reduction of exchange among grains. The P rich grain boundaries act as pinning sites for the domain wall, causing discontinuous jumps by incoherent irreversible rotation of the single-domain grain, which enhances the coercivity. In CoPt samples,

instead, reduced number of pinning sites and exchange coupling favour domain expansion by avalanche processes which also account for the loop squareness.

In 1996, Zangari et al. also electrodeposited CoPtP (P 0.5 to 5 at. %) from the same bath earlier introduced by Callegaro. The authors suggested that the absorption or incorporation of oxides and hydroxides may also play a role in the magnetic interaction besides the co-deposition of P.

In 1998, Cavallotti et al. electrodeposited CoPt and CoPtP aiming to identify the magnetic phases. The Curie temperature was found to be above 1000 K ($> 727^{\circ}\text{C}$) which can be compared to the Curie temperature of hcp Co (1390 K)⁶⁷. Co was found to be the main phase which was also confirmed by X-ray diffraction pattern. Additionally the authors studied the dependence of the coercivity on film thickness. The out of plane coercivity was about 0.4 T for a 0.1 μm thick film and quickly dropped to 0.25 T for a 4 μm thick film, where the film composition was $\text{Co}_{80}\text{Pt}_{19}\text{P}$.

In 2002 and 2004, Zana et al.^{55, 57} electrodeposited 1 μm thick $\text{Co}_{80}\text{Pt}_{20}\text{P}$ films onto Cu (111) substrate with coercivities as high as 0.61 T out of plane.

Also in 2004, Fujita et al. have electrodeposited and annealed thin films of nearly equiatomic CoPt on ITO substrates to obtain coercivities as high as 1.1 T for the isotropic CoPt tetragonal phase.

1.4.1.2.1 Co-rich alloys including elements other than Pt

The electrodeposition of ferromagnetic Co-rich based alloys excluding CoPt has been carried out for well over 30 years. In 1970, Luborsky et al. studied the effect of additives from the groups VA and VIB. (Cr, Mo, W, P, As, Sb, Bi) on the magnetic properties of

electrodeposited Co. The authors found that coercivities of up to 0.1 T can be achieved and stated that the ability of the additional element to enhance coercivity is directly related to the segregation of the element in the grain boundary of the Co.

The addition of P has also been recently studied by other authors and considerable progress has been made. In 1996, Fenineche et al. prepared CoNi and CoNiP on Cu substrates and studied the magnetic properties of the films but only a modest 0.05 T coercivity was obtained.

In 2000, Myung et al. compared a series of Co-rich alloys. They claimed that $\text{Co}_{41}\text{Pt}_{58}\text{P}$ on brass substrates have coercivities of 0.262 T (//) and 0.292 T ($\perp$). In 2002, Park et al. from the same group as Myung electrodeposited CoNiP and characterized the magnetic properties. They showed coercivities up to 0.2 T out of plane and 0.1 T in plane, associated with to the formation of hcp cobalt. They found that the addition of P to CoNi deposits favours the formation of hcp Co with texture [002] confirmed by X-ray diffraction pattern.

In 2004, Ji et al. electrodeposited Co-Pb into porous membranes and after annealing at 700 °C for 30 min obtained coercivities as high as 0.25 T.

1.4.1.2.2 Overview of the magnetic properties of Co based alloys

Fig. 23 shows the dependence of coercivity on film thickness for electrodeposited Co based samples without any annealing. The data includes all Co/Pt multilayers, CoPt, CoPtP and Co-rich alloys. It is notable that there are no films thicker than 20 μm and in this range the coercivity does not exceed 0.3 T. A complete list of references and related magnetic properties are listed in table 1.

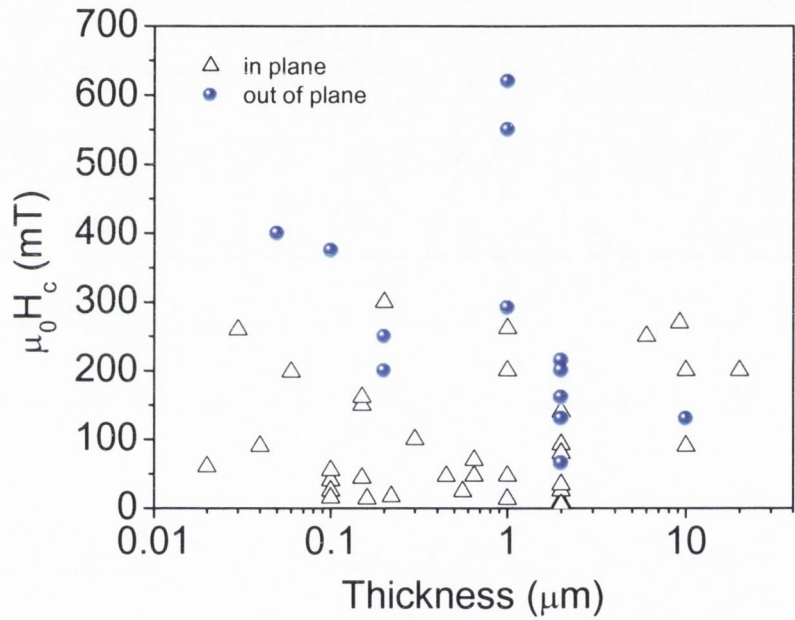


Figure 23. Room-temperature coercivity in as-electrodeposited Co-based alloys vs. thickness.

Table 1. Magnetic properties of electrodeposited (Ec), sputtered (Sp), e-beam evaporated (E-b) and arc-melted (Arc) CoPt alloys. All sputtered, e-beam evaporated and arc-melted samples were either prepared on heated substrates or with post-deposition annealing. Symbols “*”, “//”, “⊥” stand for electrodeposited samples which were post-annealed, in plane and out of plane coercivity, respectively.

Process code	Electrodeposited Alloy	Alloying element (at. %)	$\mu_0 H_c$ (mT), [thickness (μm)]	M_s (T); M_r (T)	S	References
Ec	CoNi	20-40 Ni	30-50	1.4-1.6	0.7-0.8	Bondar ⁶⁸
Ec	CoNi	20-40 Ni	10 (//), [2]	1.4-1.6	0.6-0.775	Myung
Ec	CoP	4.3 P	70, [0.65]	1.61	-	Luborsky
Ec	CoP	7.3 P	47[0.65], 32[1.0]	1.0	0.72	Fisher ⁶⁹
Ec	CoP (electroless)	9.1 P	90[0.04]	-	-	Mirzamaani ⁷⁰
Ec	CoP	3.7 - 7.3 P	140 (//), 130 (⊥), [2.0]	1.5-1.6	0.2-0.5 (//), 0.1-0.3 (⊥)	Myung
Ec	CoNiP	10-20 Ni, 3.7 - 7.3 P	70-80	0.6	0.5-0.6	Bondar
Ec	CoNiP	-	102	-	-	Luborsky
Ec	CoNiP (electroless)	-	250 (⊥) [0.2]	-		Itakura ⁷¹
Ec	CoNiP	18-37 Ni, 2-6 P	92.6 (//), 215 (⊥), [2]	1.2-1.4	0.2-0.45(//), 0.1-0.3 (⊥)	Myung
Ec	CoMnP	1 Mn, 9 P	80	1-1.1	0.7-0.8	Bondar
Ec	CoMnP	< 5 P, < 1 Mn	92 (//), 161 (⊥) [0.2]	-	-	Horkans ⁷²

Ec	CoMnP	< 1 Mn, 4-7 P	80 (/), 200 ($\perp$), (2)	1.4-1.5	0.1-0.3 (/), 0.1-0.2 ($\perp$)	Myung
Ec	CoNiMnP	10 Ni, 10 P, 0.5 Mn	90 (/), 130 ($\perp$), [10-45]	1.3	0.23	Liakopoulos ⁷³
Ec	CoNiMnP	12.8 Ni, < 1 Mn	200 ($\perp$) (0.2)	-	-	Horkans
Ec	CoAs	6.5 As	13.5[1.0]	1.38	-	Luborsky
Ec	CoSb	12 Sb	24 (0.56)	1.16	-	Luborsky
Ec	CoBi	50 Bi	17[0.22]	0.52		Luborsky
Ec	CoW	2-6 W	35-50	1	0.5-0.6	Bondar
Ec	CoW	4-20 W	40 (/)[0.10]	1.0-1.5	0.2-0.5	Myung
Ec	Co ₃ W/CoW	12-18 W	25 (/)[2.0]	1.2-1.3	0.2-0.5	Myung
Ec	CoMo	15 Mo	46.5[0.45]	1.05	-	Luborsky
Ec	CoCr	22 Cr	14[0.16]	1.02		Luborsky
Ec	CoPt	20-30 Pt	20-100	-	0.2-0.8	Zangari
Ec	CoPtP	30 Pt, 2 P	262 (/), 292 ($\perp$)[1.0]	1.07	0.4-0.6 (/), 0.3-0.4 ($\perp$)	Myung
Ec	CoPtP	23.4 Pt, 0.5 P	400[0.05], 200[10]	-	-	Cavallotti
Ec	Co/Cu	4.5-48 Cu	34 (/), 65 ($\perp$), [2]	0.7-1.3	0.6-0.7 (/), 0.1-0.2 ($\perp$)	Myung
Sp	(CoPt)C (30 vol. %)	50 Pt and 30 vol. % C	1200[0.1]	0.78	-	Yu
Sp	(CoPt) _{1-x} Sb		> 600[0.04]		-	Kitakami ⁷⁴
Sp	Co (16.7 nm)/CoPt (25)//Si		200[0.025]		-	Crew

Sp	CoCrPt	15 Cr, 14.7 Pt	558 (⊥) [0.030]	0.63	-	Keitoku
Sp	CoCrPt	14.2 Cr, 20 Pt	441 (⊥) [0.030]	0.50	-	Keitoku
Sp	CoPt//Si		> 700 [0.010]		-	Zeng
E-b	CoPt	60 Pt	100[0.100]		-	Pouloupoulos
arc	CoPt		508[400]	0.795	0.75	Xiao
Ec	Co/Pt//Cu	-	25[0.100]	-	-	Hayashi
Ec	Co/Pt	-	15[< 0.100]	-	-	Georgescu
Ec	CoNiPt	10 Ni, 30 Pt	150[0.150]	-	-	Jyoko ^{47, 48}
Ec	CoPt	30 Pt	44[0.150]	-	-	Jyoko ^{47, 48}
Ec	CoPt	30 Pt	100[0.300]	-	-	Bozzini
Ec	CoPtP	17-20 Pt	260 (//) [0.030]	0.42; 0.30	-	Bozzini
Ec	CoPtP	17-20 Pt	198 (//) [0.060]	0.78; 0.54	-	Bozzini
Ec	CoPtP	17-20 Pt	161 (//) [0.150]	2.23; 1.42	-	Bozzini
Ec	CoPd	92 Pd	5[2]	-	-	Zangari
Ec	CoPtP	20 Pt+P	375[0.100- 0.500]	-	-	Callegaro

Ec	CoPt	20 Pt	55[0.100-0.500]	-	-	Callegaro
Ec	Co ₇₉ PtP	20 Pt, 0.5-5 P	550 (⊥) [<0.10]	-	-	Zangari
Ec	CoPtP	19 Pt, 0.5-5 P	200[20]		-	Cavallotti
Ec	CoPtP	19 Pt, 0.5-5 P	300[0.200]	1.08-1.15	-	Zana
Ec	CoPt	35 Pt	250[6]	1.10-1.25	-	Mallet
Ec	CoPtP	-	620[1]	0.98-1.05	0.9-1.0	Zana
Ec	CoPtW (P)	85.2 Co, 12.6 Pt, 2.2 W	270 [9.2]	-; 0.5 T	-	Franz
Ec	CoPt (*)	57 Pt	1100[0.3]	-	-	Fujita
Ec	CoPb (*)	52 Pb	[250]20	-	-	Ji
Ec	CoNiP	20 Ni	200[1]	-	-	Park

1.4.1.3 Co-Pd

When compared to CoPt, there are fewer studies undertaken on the preparation and characterization of CoPd. CoPd alloys do not have a tetragonal phase and thereby the magnetic properties of these alloys are limited to those of Co itself. Investigators prepared CoPd by sputtering^{75, 76, 77, 78, 79} e-beam evaporation^{80, 81} and electrodeposition⁸².

In 1992, Maeno et al. prepared Co-Pd/Pd multilayers on glass substrates by sputtering. They found coercivities up to 0.25 T and magnetization of 0.15 T for 20 nm thick Co-Pd multilayers. No annealing was carried out.

In 1993, Yamane et al. prepared Co-Pd multilayers on either glass or Si substrates by sputtering and annealed the samples at 300 °C in air to obtain coercivities up to 0.2 T. The formation of Co-O during the atmospheric annealing is believed to serve as pinning centers which lead to an increase in the coercivity. Annealing in vacuum did not result in any coercivity. The effect of atmospheric annealing is evident with the formation of Co_3O_4 . As the temperature is raised to 500 °C the Co in the films is almost totally consumed by oxidation resulting in the decrease of coercivity and magnetization.

In 1992, Kim et al. prepared ultrathin (< 10 nm) Co/Pd multilayers on silicon consisting of a few atomic layers of Co by sputtering on substrate temperature from 30-80 °C. The authors measured coercivities of up to 0.4723 T in as-deposited multilayers.

In 2001, Roy et al. prepared Co/Pd multilayers on Ta and ITO substrates by sputtering. Films deposited on ITO show coercivities of up to 0.68 T. The authors explained that as the films were annealed the low melting ITO allows the grain segregation, thereby favouring coercivity.

In 2002, Kawaji et al. prepared Co/Pd multilayers by sputtering onto Pd/Si seed layers deposited on glass. Films with a 10 nm Pd seed layer showed coercivities as high as 0.78 T, with the structure $[\text{Co}_{0.2\text{nm}}/\text{Pd}_{0.8\text{nm}}]_{10}/[\text{Pd} (10 \text{ nm})/\text{Si} (100 \text{ nm})]$. The authors explained that the switching mechanism in the films as coherent rotation which accounts for the high coercivity.

In 2001, Kudo et al. electrodeposited Co (0.4 nm)/Pd (1 nm) multilayers on Cu substrates from a dual bath and characterized the magnetic properties of the films. The authors obtained coercivities of 0.08 T for structures as thick as 50 nm. The coercivity diminishes as the thickness increases.

1.4.1.4 Fe-Pd

Equiatomic FePd alloys are included in the uniaxial $L1_0$ (tetragonal) alloy family. The investigation of these alloys has probably been overshadowed by the achievements obtained with FePt alloys. Several techniques for the preparation of FePd films have been investigated including sputtering^{83, 84} e-beam evaporation⁸⁵ and electrodeposition^{86, 87}. On the other hand the bulk materials have been prepared by melt-spinning⁸⁸, floating zone⁸⁹ and cold deformation⁹⁰. Bulk samples only give small coercivities of 0.1 T.

In 1998, Okumura et al. prepared nanocrystalline $Fe_{50}Pd_{50}$ by sputtering and ball milling. After annealing 0.1 to 0.5 μm thick samples in vacuum at 575 °C for 160 hours the alloys developed coercivities ranging from 0.2 to 0.25 T.

In 2003, Sato et al. prepared $Fe_{58}Pd_{42}/NaCl$ (001) nanoparticles by e-beam evaporation onto heated substrates maintained at 773 K and 873 K. Coercivities of up to 0.35 T were obtained from samples as thick as 10 nm with perpendicular anisotropy.

There are only a few reports of electrodeposition of FePd films. Two similar baths were reported by Chow and Bryden. Chow prepared alloys with composition 61 at. % Pd-39 at. % Fe from a bath containing 4.43 g/L $PdCl_2$, 10.15 g/L of $Fe_2(SO_4)_3$, 25.42 g/L of sulfosalicylic acid and 19.8 g/L of $(NH_4)_2SO_4$. After annealing the electrodeposited films on Cu substrates at 500 °C the authors observed the formation of a disordered FePd and $CuPd_3$ phase. Bryden's bath contained 0.1 M $PdCl_2$, 0.02-0.1 M $FeSO_4 \cdot 7H_2O$, 0.04-0.2 M sulfosalicylic acid and 0.3 M ammonium sulphate. The composition of the films was Fe_xPd_{1-x} ($x = 7$ to 40 at %). Despite the fact that a suitable electrochemical bath already exists no studies of the magnetic properties of the electrodeposited alloys were carried out.

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Chapter 2

2 Experimental methods

2.1 Scanning microscopy imaging

The transmission and scanning electron microscopes are the most used microscopes for studying nanostructures these days. Important accessories have been introduced to these microscopes allowing composition characterization and device patterning (focussed ion beam) as well as the common imaging features. This work makes use of the scanning electron microscope for the purpose of imaging and composition analysis. The ultimate resolution of any microscope is related to the wavelength of the beam used to probe the sample. For example, blue light, which has a wavelength of 350 nm, sets the resolution limit of the optical microscope. Typically, a commercial optical microscope can show clear images with resolution of 1 μm . The wavelength of electrons can be controlled by their energy, $E = hc/\lambda$ hence the wavelength can easily reach values as small as 5 nm with a 50 keV beam typically used in high resolution scanning electron microscopes (SEM). Usually the ultimate resolution of the SEM is limited by the interaction of the beam with the sample rather than the wavelength of the electron beam itself.

The interaction between the incident electronic beam and a sample results in elastic and inelastic scattering of the initial beam. Most of the initial energy of the beam is transformed into heat in the sample and the remaining energy is used up in the generation of backscattered primary electrons, secondary electrons, Auger electrons, photons and X-rays.

Backscattered primary electrons mostly result from elastic scattering and as the backscattering depends weakly on the atomic number of the specimen it accounts for

some contrast related to the sample chemical composition. Also, as the backscattered signal may come from beneath the surface, the topography signal is weaker than that for secondary electrons. Secondary electrons usually have energy below 50 eV and are generated by inelastic scattering of the primary electronic beam. As most of the secondary electrons are generated in the surface of the sample they are used for the topographic imaging of the sample. Edges and rough areas tend to generate more intense signals than flat surfaces creating good contrast. Secondary electrons also may give a resolution of the order of 5 nm in high vacuum microscopes using a 50 keV beam.

Low energy photons are emitted when electronic transitions within the atoms occur. When vacancies are created by the collisions between the primary beam and the electronic core, electronic transitions occur to fill the lower energy levels, generating photons. This low energy photon emission is known as luminescence and carries information about material boundaries and defects in the structure.

X-ray emission occurs as a consequence of high energy electronic transition. As the X-ray is generated from specific transitions in the atom they carry information about the electronic structure of the atom, which serves as a fingerprint to identify the composition of the sample. The use of X-rays to characterize chemical composition is known as energy dispersive X-ray spectroscopy (EDS).

The use of the scanning electron microscope (SEM) requires the sample to be conductive. In this work all the samples are metallic and the substrates conductive. Here, the SEM measurements provided chemical and topographic analysis and were carried out in the Center for Microscopic Analysis (CMA) in Trinity College.

2.2 SQUID magnetometer

The superconducting quantum interference device (SQUID) makes use of Josephson junctions to detect small magnetic flux. The magnetic field goes through a superconducting ring producing a flux. Due to the high sensitivity of SQUIDs, magnetic fields as small as a few nT can be measured. The SQUID magnetometer makes use of a SQUID to measure magnetic moment. A magnetized sample produces a non-uniform field in its surroundings, which is then converted into flux and detected using the SQUID. The SQUID magnetometer currently in use in the laboratory has a signal to noise ratio which allows nominal measurements down to $10^{-11} \text{ J T}^{-1}$ (10^{-8} emu). Highly, accurate measurements are typically obtained in the 10^{-9} J T^{-1} (10^{-6} emu) scale. The maximum field that can be applied using this SQUID magnetometer is 5 T.

The SQUID magnetometer is applied in medicine, for example to measure brain activity. The electrical current produced by the neurons generates a magnetic field which can be detected using a SQUID array.

2.3 Sputtering and evaporation

For electrodeposition purposes, metallic films were prepared as electrodes on insulating or poorly conducting material using sputtering and evaporation techniques. There are two types of sputtering systems: direct current (DC) sputtering and radio frequency (RF) sputtering. Ions are accelerated and collide with a target, which can be either a single element or an alloy, and as a result of the collision atoms are ejected from the target in different directions. Most of the collisions between the ions and the target result in heat and only a small fraction of the collisions result in sputtering. RF sputtering is used where the target is an insulating or weak conductor. As the sputtering process is caused by a mechanical collision it does not depend on the melting point of the target element(s), so the composition of the films prepared by sputtering is very close to that of the target alloy.

Films can also be prepared by evaporation, which depends strongly on the melting point of the element used. The material to be evaporated is placed in a tungsten alloy boat. An electrical current is passed through the boat and heats it up, melting and then evaporating the material. The evaporated material is then collected onto a substrate. A huge amount of heat is dissipated to the surroundings compared to the small amount which converts the molten metal into the vapour phase. As this technique is strongly dependent on the melting point of the material, a smaller number of alloys can be deposited as compared to sputtering.

A small commercial DC sputtering machine was used to prepare electrodes of Pt and Ag. Evaporation was used to prepare Ag electrodes on the back of alumina membranes.

2.4 X-ray diffraction

X-ray diffraction spectroscopy is an important tool for the characterization of the crystalline structures within a sample. Constructive diffraction occurs when the X-ray wavelength is a multiple of the interatomic distances within the structure, thus the interatomic distances can be directly probed and related to the crystal lattices depending on the structure as illustrated in Fig. 24. A condition for the occurrence of X-ray diffraction is that the wavelength should be comparable to the lattice parameter. The wavelength of Cu radiation ($K\alpha = 0.154056 \text{ nm}$) is used here.

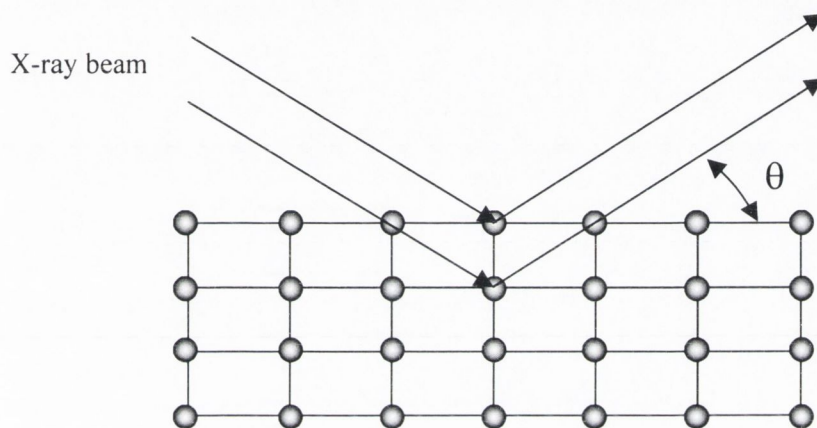


Figure 24. Principle of X-ray diffraction spectroscopy; Bragg scattering.

The Bragg condition expresses the relationship between the interatomic spacing, d , and the diffraction angle, θ , measured from the lattice plane. Bragg reflection can only occurs for wavelengths of order $2d$ or less:

$$2d \sin\theta = n\lambda$$

where n is the diffraction order. In an X-ray diffraction experiment, the intensity of a diffracted monochromatic beam of X-rays is measured against the angle θ . Once the X-ray diffraction pattern is measured it is then compared to a standard in order to identify

the phases present in the sample. We carried out the X-ray diffraction experiments for this work in a Philips X-Pert Pro X-ray machine which is held in the SFI Trinity nanoscience laboratory.

2.5 The electrochemical cell

A standard three-electrode electrochemical cell was used for all the electrochemical experiments in this work. A schematic diagram of such a cell is shown in Fig. 25. The working electrode and solution define an interface under investigation and may act either as cathode or an anode depending on the applied overpotential. The choice of electrode material for a particular application depends on a number of factors determined by electrochemical and chemical requirements. From an electrochemical point of view, an electrode should not react chemically with the solvent or the supporting electrolyte within the potential range of the experiment. Inert metals such as platinum, silver and gold are commonly used in electrochemical experiments. In electrochemistry the electrode should conduct electrons, therefore it is not possible to electrodeposit on insulating materials.

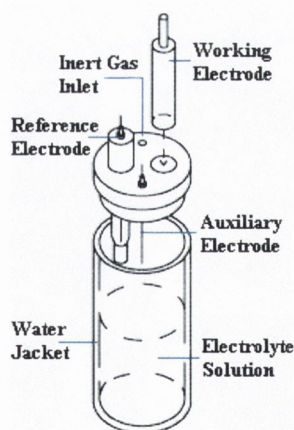


Figure 25. Illustration of a three-electrode electrochemical cell.

The reference electrode provides a constant potential against which the potential of the working electrode may be measured. In this work, the reference electrode was silver/silver chloride in a solution containing a high concentration of chloride ions. The entire solution is encased in glass and contact with the bulk solution is made through a porous Vycor frit. Two different electrodes were used during the course of this work; Ag/AgCl (saturated KCl) and Ag/AgCl (3M KCl). Both exhibited good stability in the potential range employed. The standard reduction potential of Ag/AgCl electrode relative to the standard hydrogen electrode (SHE) is 0.220 V¹.

The counter or auxiliary electrode is used to close the electrical circuit in the solution, thus passing current through the cell. 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. Counter electrodes used in this work were made of platinum.

A water jacket is used to set the temperature of the electrochemical bath. When water is used as the heating fluid the temperature can be controlled from 0 to 98 °C. An inert gas is used to reduce the oxygen concentration in the solution when the solution is vulnerable to oxidation.

There are two basic types of electrodeposition experiments: potentiostatic and galvanostatic. Potentiostatic experiments are carried out by keeping the potential difference between the working electrode and the reference electrode constant. An external source varies the potential between the working and counter electrodes in order to match the required potential difference between the reference and working electrodes. Consequently, the current in cell varies freely. Galvanostatic experiments are carried out by keeping a constant current between the working and counter electrodes, and the potential difference between reference and working electrodes is free to vary. While the

use of a reference of electrode is useful in galvanostatic experiments, it is not necessary. However it is required for potentiostatic experiments.

2.6 Shadow masking

Shadow masking is one of the simplest patterning techniques. It is used in combination with one of the deposition techniques (sputtering or evaporation) to produce certain patterns. The shadow mask is an obstacle put between the source of material and the substrate. It covers the substrate from the depositing material in certain regions depending on the shadow mask shape. They are easy to construct, but their dimensions are limited by mechanical precision, which is typically under the millimetric scale. For example, for the preparation of a metallic stripe a 100 μm slit shadow mask can be used, as illustrated in Fig. 26.

When small patterns are required one should look for other techniques such as UV lithography (down to 0.5 μm), focussed ion beam (FIB) lithography (down to 50 nm) and focussed electron beam milling (nanometer scale). In this work, a shadow mask was built using wires to deposit metallic stripes.

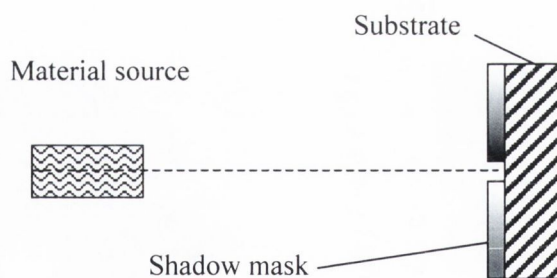


Figure 26. Schematic diagram showing the use of a shadow mask. The shadow mask protects the substrate allowing material to be deposited only in certain areas.

2.7 The magnetic profiler

We have made some adaptations to a commercial x-y-z positioning system to enable the measurement of static magnetic fields around small permanent magnets. We call the system the magnetic profiler. A typical rotor and its magnetic profile using the magnetic profiler are illustrated in Fig. 27. The magnetic profiler consists of a Hall probe and x-y-z positioning system interfaced with a computer allowing the measurement of the z-component of the magnetic field for flat surfaces, illustrated in Fig. 28. The Hall probe is integrated in a circuit which generates an electrical signal proportional to the magnetic field and can be positioned near the sample surface. The geometry of the Hall probe is such that the Hall sensor is about 250 μm away from the surface. The positioning system is based on stepper motors which can set coordinates with a precision greater than 10 μm . The magnetic profiler measures the magnetic field line by line as shown schematically in Fig. 28 (top).

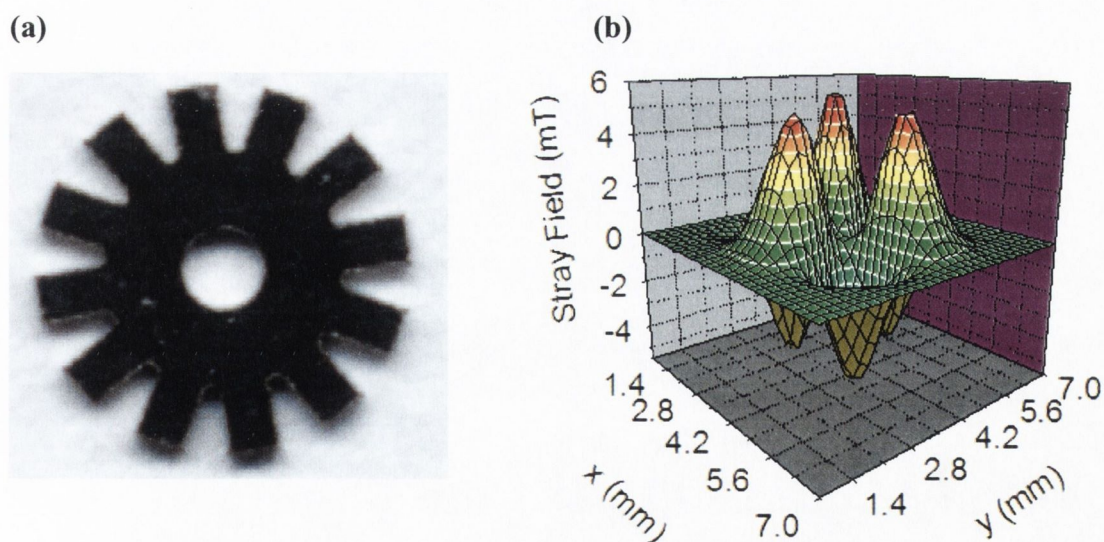


Figure 27. A CoPt rotor cut into 12 poles and magnetized with 6 poles (a) and its magnetic profile (b). The magnetic stray field is measured in the z-direction.

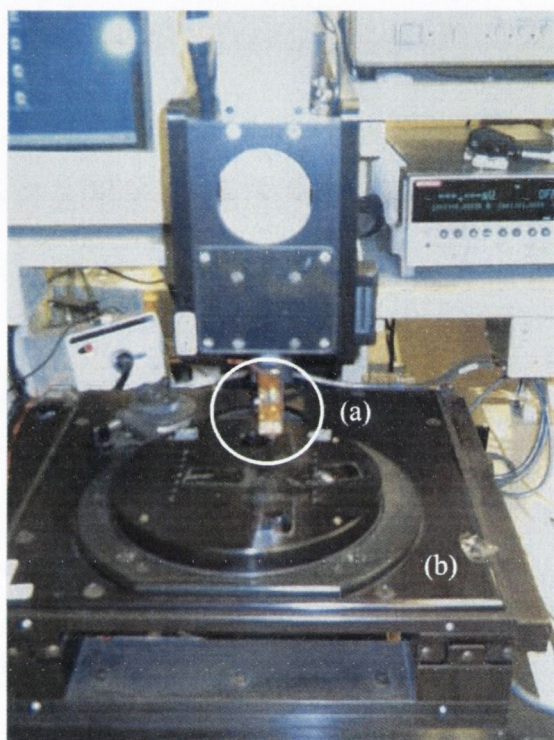
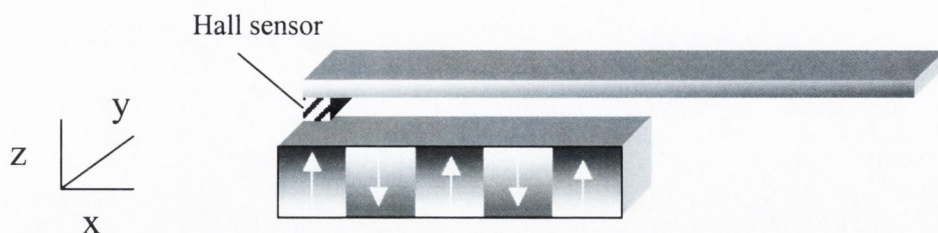


Figure 28. Above, a simplified diagram showing a magnetized sample and the Hall probe mapping the surface. Below, the magnetic profiler consisting of (a) a Hall probe and (b) the positioning stage.

The procedure to use the magnetic profiler is as follows. The sample is assembled on the stage [Fig. 28(b)]. The programs used to profile the magnets were developed and

implemented by P. Stamenov and they are self-explained. The Hall sensor attached to the z-axis [Fig. 28(a)] is positioned over the sample using the program called "Position.vi". Once the initial position for profiling is reached, which depends on the needs, the data is collected using the program called "XYScanner.vi". The number of step in the direction x (n_x) and y (n_y) and the size of each step are set through this program and the data is saved as matrix of dimension $n_x \times n_y$ into a ASCII file where each element represents the intensity of the stray field measured in the z direction.

¹ R.C. Weast, Handbook of Chemistry and Physics, The Chemical Rubber Co., Cleveland, 1972, D-111

Chapter 3

3 Electrodeposition of $L1_0$ and hexagonal magnetic alloys

3.1 Electrodeposited FePt thin films

The face-centred tetragonal FePt phase, known as the $L1_0$ phase, is of interest for permanent magnet applications due to its excellent intrinsic magnetic properties ($\mu_0 M_s = 1.43$ T, $K_1 = 6.6$ MJ m^{-3}) and corrosion resistance¹. Numerous studies have been carried out to develop hard magnet films of this material due to potential applications in high-density recording media and microelectromechanical (MEMS) systems². Most of these studies have used sputtering, vapor deposition or laser ablation. Thin continuous film samples typically show coercivities between 1-2 T^{3,4,5,6,7,8}, while bulk samples typically show coercivity values of 0.5 T⁹. Only recently Huang et al. electrodeposited nanowires of FePt in a porous anodized aluminium disc from a single bath¹⁰.

Here we present the preparation conditions of continuous FePt films by electrodeposition from a single sulphate bath and we also present their structural and magnetic characterization. Films were electrodeposited on Ag and Cu substrates and the effect of the annealing atmosphere on the magnetic properties was also investigated.

3.1.1 Electrochemical bath

FePt films were electrodeposited onto polycrystalline Cu or Ag substrates from a single sulphate bath containing 1 mM H_2PtCl_6 , 0.1 and 1 M Na_2SO_4 and 0.1 M FeSO_4 . The solution pH was adjusted to 2.9 by adding a small amount of either sulphuric acid or hydrochloric acid. The counter electrode was a 50 mm long Pt wire and the reference electrode was Ag/AgCl saturated with KCl. All potentials are quoted with respect to this reference electrode.

Solutions were prepared from 100 mL of deionized water. Ag and Cu substrate working electrodes were cut out from 99.8 % pure Ag and 99.9 % pure copper foils into 5 mm x 5 mm squares. These substrates were coated on one side with varnish and connected to a 1 mm diameter copper wire. Just before electrodeposition, the substrates were dipped into a 10 vol. % H_2SO_4 solution to remove any impurities on the surface and then dipped into deionized water. Fresh solutions were vigorously stirred in an open atmosphere at room-temperature and the deposition took place immediately after inserting the substrate into the bath. The deposition was controlled using an EG&G model 263A potentiostat. The film thickness was evaluated using an atomic force microscopy Nanoscope 3 (AFM) in contact mode.

Electrodeposition of FePt from a sulphate bath was carried out using two baths with different concentrations of the supporting electrolyte (Na_2SO_4). Films were smooth when electrodeposited at potentials ranging from -0.65 V to -1.4 V. We also found that hydrogen evolution starts at potentials as small as -0.7 V and the formation rate increases as the potential becomes more negative. We also observed that the films stick very well to Cu and

Ag substrates when the total charge per square unit is smaller than 9.6 C cm^{-2} . For higher charge densities the films lose their metallic look and start to peel off from the substrate. Smoother and shinier films were obtained from the solution containing $0.1 \text{ M Na}_2\text{SO}_4$.

Films electrodeposited at -0.9 V with a total charge of 2.4 C showed a thickness value of $0.45 \text{ }\mu\text{m}$ when plated over an area of 0.25 cm^2 . This gives a rate of $0.75 \text{ }\mu\text{m C}^{-1}\text{cm}^{-2}$ that was verified between 0.6 and 2.4 C as can be seen in Fig. 29.

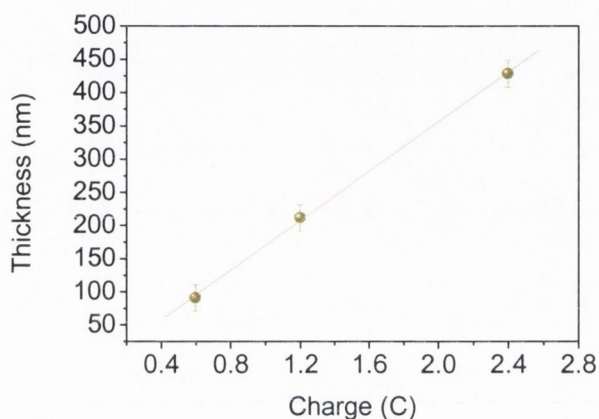


Figure 29. Thickness as a function of the total charge for samples deposited on 0.25 cm^2 Cu substrates. Measurements were carried out in the AFM.

3.1.2 Film composition

Composition of the samples was determined by energy dispersive X-ray spectroscopy (EDS) and morphology was examined using a scanning electron microscope (SEM) in the same unit. Composition dependence on the potential and concentration of the supporting electrolyte was studied. The supporting electrolyte was 0.1 and $1 \text{ M Na}_2\text{SO}_4$. The potential

was varied from -0.65 V to -1.4 V vs. Ag/AgCl as shown in Fig. 30. The content of Fe in the films increases as the potential becomes more negative. The range in which the composition is controlled by the potential corresponds to the kinetically controlled region of Fe (less noble metal) and the mass transport limited region for Pt (more noble metal). At potentials greater than -0.60 vs. Ag/AgCl (-0.38 vs. SHE) the deposition of the alloys could not take place, which can be explained in terms of the standard reduction potential of Fe (-0.409 vs. SHE).

The effect of the concentration of Na_2SO_4 is also illustrated in Fig. 30. As the Na_2SO_4 concentration increases the potential needed to obtain equiatomic FePt diminishes. This is associated with the increase of the polarization, the bulk resistance diminished as the supporting electrolyte concentration increased.

Fig. 31 shows the initial development of cracks in samples annealed at 400 °C for 20 min. It is likely that these cracks are due to internal stress in the films which may come from gases absorbed during the deposition such as N_2 and O_2 and the precipitation of metal hydroxides. As the hydrogen evolves, the pH near the electrode surface increases and hydroxides may precipitate. Upon annealing, the hydroxides may decompose generating the cracks observed in the film.

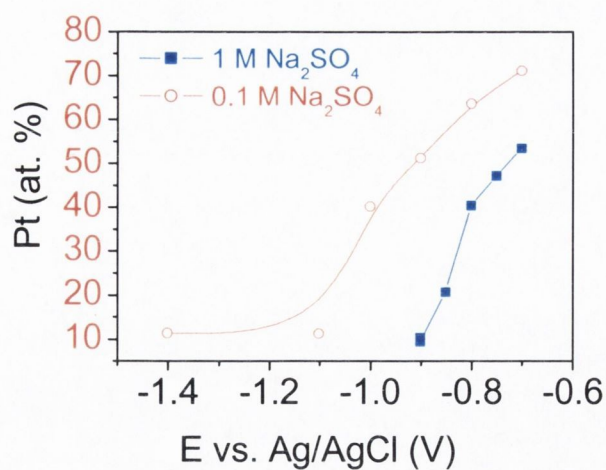


Figure 30. Film composition dependence on the potential and supporting electrolyte concentration (Na_2SO_4). The greater the amount of supporting electrolyte the higher is the potential to obtain the equiatomic FePt alloy.

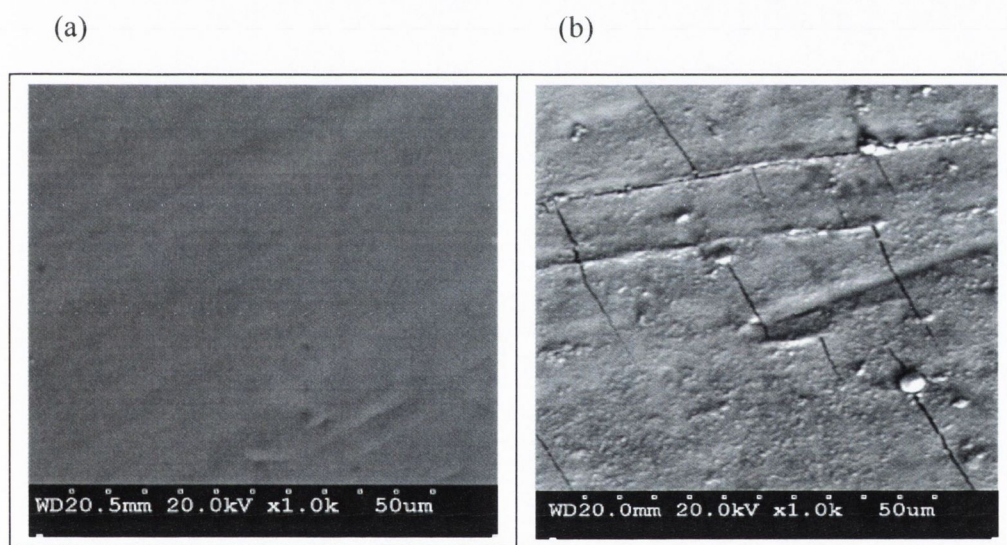


Figure 31. SEM pictures of an FePt sample before (a) and after (b) annealing at 400 °C for 20 min. Cracks develop on the sub-millimeter scale.

3.1.3 Structure of vacuum annealed FePt films

The structure of vacuum (10^{-6} Torr) annealed FePt films electrodeposited onto Cu was investigated by X-ray diffraction (XRD) with Cu K_{α} radiation and an angular (2θ) 0.02° step. The nearly equiatomic films were annealed at 400 and 500 $^{\circ}\text{C}$. The diffraction pattern of the as-deposited films at -0.9 V showed only a broad hump which is associated with a nanocrystalline disordered FePt structure. Annealed films developed a combination of the ordered tetragonal $L1_0$ FePt phase with a minor amount of Fe_3O_4 as shown in Fig. 32. The optimized annealing time that leads to the greater amount of $L1_0$ FePt in the annealed samples at 400 $^{\circ}\text{C}$ is 20 min, and at 500 $^{\circ}\text{C}$ it is 10 min. Samples subjected to long annealing times (60 min) showed severe cracking that partially or totally caused the film to peel off the substrate.

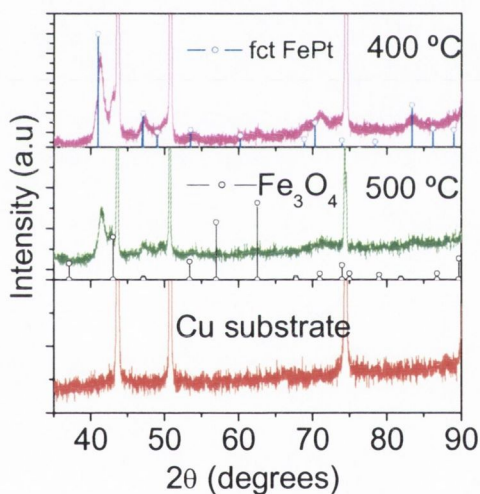


Figure 32. X-ray diffraction patterns of FePt films annealed at 400 $^{\circ}\text{C}$ and 500 $^{\circ}\text{C}$ and the Cu substrate. The nearly equiatomic films were electrodeposited at -0.9 V vs. Ag/AgCl.

Both films annealed at higher temperatures and for long periods tend to peel off the substrate.

3.1.4 Structure of H₂-annealed FePt films

Equiatomic FePt films electrodeposited onto Ag substrates were annealed in a H₂ atmosphere. The effect of the annealing temperature and annealing time on the structure of the films was investigated ranging from 500 °C to 900 °C and a period of up to 2 hours.

The samples were placed in a quartz tube inserted inside a furnace with a constant H₂ flow and annealing was carried out as follows: the furnace was heated up to the annealing temperature at a constant rate (40 °C min⁻¹), the annealing was then carried out and finally the furnace was cooled down to room-temperature at the same rate (40 °C min⁻¹).

The X-ray diffraction patterns of samples annealed at different temperatures is shown in Fig. 33. As-deposited films show a broad diffraction bump which is characteristic of a nanocrystalline structure. This diffraction pattern matches the cubic disordered FePt pattern. There was little structural change between the samples annealed at 500 °C and the as-deposited films. At 650 °C, the formation of the tetragonal FePt starts to happen, the grain size increases making the peaks sharper and the peaks which correspond to the tetragonal phase appear. At 800 °C and 900 °C, there is further growth in the grain size and peaks become even more distinct.

The annealing time was varied from 30 to 120 min, as shown in Fig. 34, while the temperature was kept at 800 °C. The formation of the tetragonal phase happens at the earlier stage of the annealing process at 800 °C. Significant grain growth is already present in samples annealed for 30 min. As the annealing is increased to 60 min and 120 min no further grain growth is observed. The effect of the annealing time is similar to the annealing temperature, at longer annealing times and higher temperatures the tetragonal FePt phase is formed.

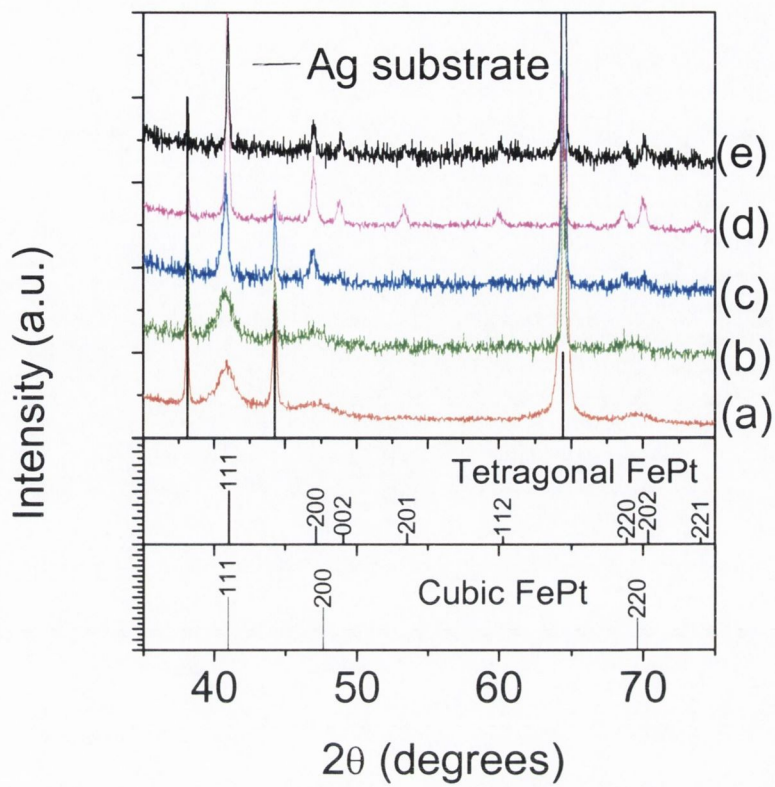


Figure 33. X-ray diffraction patterns of FePt films (a) as-deposited and annealed at (b) 500 °C, (c) 650 °C, (d) 800 °C and (e) 900 °C for 2 hours. Below, the X-ray pattern for the ordered tetragonal and disordered cubic FePt phases.

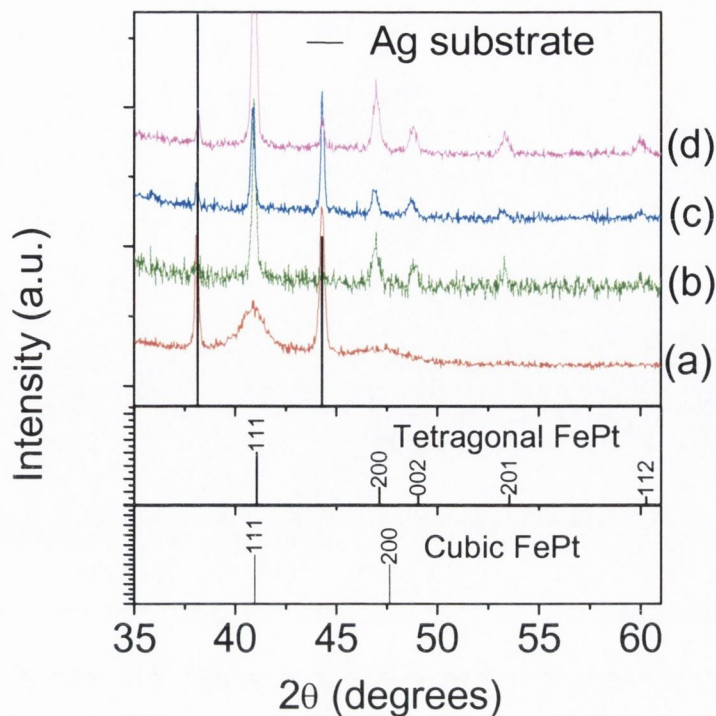


Figure 34. X-ray diffraction patterns of FePt electrodeposited films (a) as-deposited and annealed at 800 °C for (b) 30 min, (c) 60 min and (d) 120 min. Below, the X-ray pattern for the ordered tetragonal and disordered cubic FePt phases.

3.1.5 Magnetic properties of FePt films

The magnetic properties of the FePt electrodeposited films were investigated using the 5 T SQUID magnetometer. As-deposited films were all magnetically soft with coercivities smaller than 5 mT. The magnetic properties dependence on the annealing atmosphere (vacuum and H₂), annealing temperature and annealing time was investigated.

The vacuum post-annealing magnetic properties of nearly equiatomic FePt films

electrodeposited on Cu and Ag substrates are shown in Fig. 35a and 35b, respectively. For Cu substrates, the samples annealed at 500 °C exhibit coercivity of 0.2 T and the shape of the magnetization curve suggests the presence of a soft magnetic phase. The shape and coercivity (0.3 T) were improved for samples annealed at 400 °C. Much higher coercivities (0.92 T) were obtained for samples electrodeposited on Ag substrates (Fig. 35b). The ratio of remanence saturation magnetization σ_r/σ_s calculated for this sample is about 0.65 for the Cu substrate and 0.9 for the Ag substrate. All the samples are magnetically isotropic. The estimated saturation magnetization (J_s) of 0.70-0.9 T was based on the film thickness and sample area.

Room-temperature magnetization measurements of FePt electrodeposited on Ag substrates after annealing in a H_2 atmosphere at different temperatures are shown in Fig. 36. The initial curve is characteristic of a combined nucleation and pinning type magnet. As the coercivity increases the contribution of nucleation to the reversal switching mechanism increases. All samples are magnetically isotropic indicating that the films are polycrystalline.

The dependence of the coercivity on the annealing time and temperature is shown in Fig. 37. Coercivity quickly increases and reaches a 1.4 T limit as the annealing time reaches 20 min. Samples annealed at low temperature (500 °C for 2 hours) show the same coercivity of as-deposited samples. Coercivity only starts to develop at temperatures higher than 500 °C, then it sharply increases and saturates at temperatures above 800 °C.

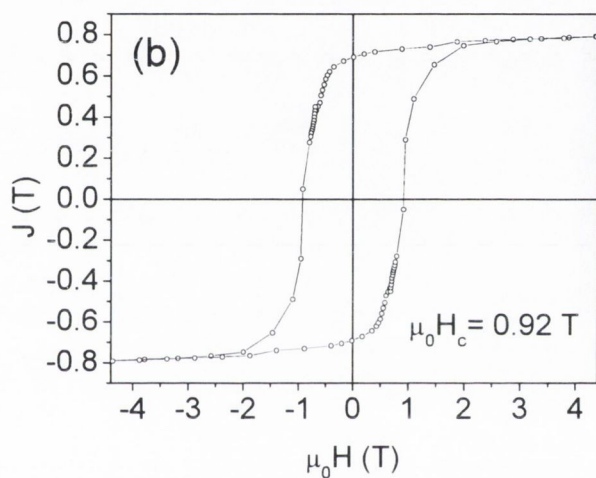
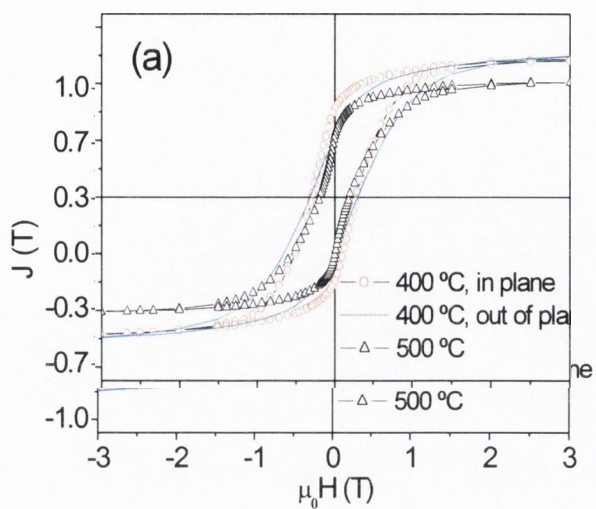


Figure 35. Room-temperature hysteresis loops of FePt films (a) electrodeposited onto Cu substrates and annealed at 400 °C and 500 °C and (b) electrodeposited onto Ag substrates and annealed at 500 °C.

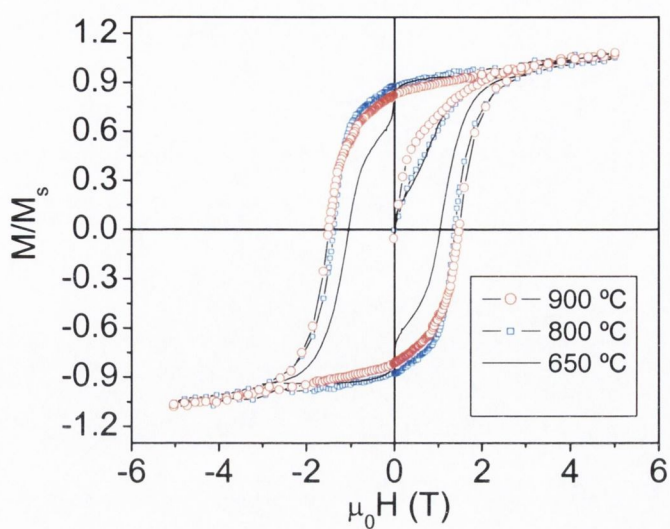


Figure 36. Room-temperature magnetization measurement of samples annealed at 650 °C, 800 °C and 900 °C for 2 hours.

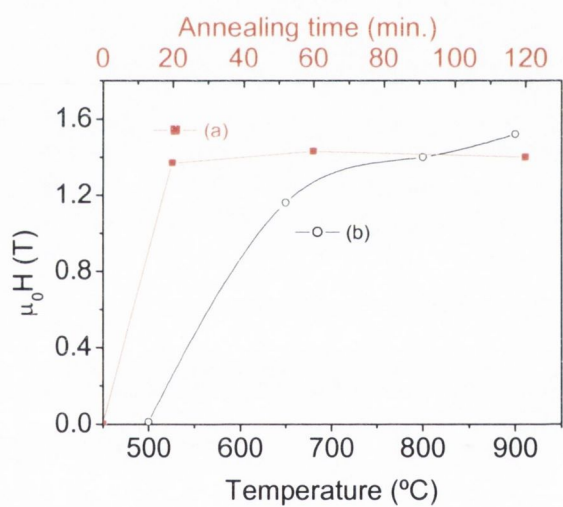


Figure 37. Coercivity dependence on the (a) annealing time and (b) temperature.

3.1.6 Discussion

In the electrochemical bath studied, platinum is electrodeposited from a complex ion PtCl_6^{2-} in two consecutive steps, onto the working electrode (Cu or Ag substrate):



The standard reduction potentials for the reactions (1) and (2) are 0.52 V and 0.54 V vs. Ag/AgCl reference electrode¹¹. As Pt is more noble than Cu, we observed that the Pt displaces Cu and Pt deposition occurs even without applying any potential to the electrochemical cell. The standard potential for Fe^{2+} reduction is -0.629V vs. Ag/AgCl. The range in which the electrodeposition of the FePt alloy occurs is such that the deposition rate of Fe is governed mainly by reaction kinetics and Pt by mass transport. By measuring the thickness of the film in an AFM and taking account of the integrated charge we estimate the current efficiency. Values of about 5 % at -0.7 V and 23 % at -1.1 V were found.

Pt content in the films was found to vary almost linearly around -0.9 V as shown in Fig. 30. Films were shiny and homogeneous. The diffraction pattern of the as-deposited films at -0.9 V showed only a broad hump corresponding to a nanocrystalline structure. After annealing in vacuum the films electrodeposited on Cu substrates developed a combination of ordered L1_0 FePt phase with a minor amounts of Fe_3O_4 , as shown in Fig. 32. The optimized annealing time that leads to greater amounts of L1_0 FePt in the annealed samples at 400 °C is 20 min, and at 500 °C it is 10 min. Samples subjected to long annealing times (60 min) showed severe cracking that partially or totally peeled the film from the substrate. On the other hand, for samples electrodeposited on Ag substrates and annealed in vacuum, the major phase is the tetragonal FePt phase.

The choice of Cu or Ag substrate cannot be driven by electrochemical requirements only, the fact that further annealing is required puts some constraints on this choice. In addition to the electrochemical requirements, the ideal substrate should not form any alloys with the elements constituting the film (Fe or Pt) during annealing and if possible should enhance the magnetic properties. Ag substrates match the electrochemical needs and as it does not have any common phase with any of the elements, it seems to be the most suitable substrate.

The shape and smaller coercivities found in vacuum annealed samples electrodeposited on Cu are associated with the presence of iron oxide in the films which is supported by the X-ray diffraction results. Additionally, the fact that annealing at lower temperature (400 °C) improves the coercivity can be associated with the smaller amount of iron oxide in the films. Additionally, the higher coercivity obtained for vacuum annealed samples deposited on Ag substrates can be explained by the absence of a common phase between Fe/Pt and Ag. Cu is known to form a tetragonal phase with Pt which is not magnetic.

Samples annealed in H₂ atmosphere showed greater coercivity than those annealed in vacuum. Coercivities as high as 1.5 T were obtained. The shape of the initial magnetization curve shown in Fig. 36 is characteristic of a nucleation-controlled permanent magnet. The samples annealed at 650 °C show a small contribution from a soft magnetic phase in the magnetization curve. This soft magnetic behaviour indicates that there is a contribution from the soft cubic FePt phase to the magnetization also accounting for the smaller coercivity (~1 T). The coercivity dependence on the annealing time and annealing temperature can be understood in terms of the conversion from the disordered phase into the ordered phase. For short annealing times and lower temperatures the conversion is far from complete, accounting for the smaller coercivities. As the annealing time and

temperature are increased the conversion approaches completion and the coercivity reaches its maximum value (1.5 T). The saturation magnetization of 0.70 – 0.9 T is in agreement with values (0.5 – 1.25 T) reported in the literature for films^{12,13,14}.

From the magnetic results it can be concluded that the annealing atmosphere plays an important role in the formation of the hard magnetic phase. Despite the good vacuum quality used for the annealing (10^{-6} bar), we found the formation of iron oxide. It is not clear whether the main source of oxygen is the vacuum related, the electrodeposition process or both. However, it is clear that films annealed in H_2 atmosphere show better results than those annealed in vacuum. H_2 is often used as a reducing agent in chemical synthesis¹⁵. It is possible that during annealing H_2 may have reduced oxides to H_2O and removed it from the films, however further studies are needed to clarify this matter.

The high coercivity (1.5 T) measured can be compared to current values found in the literature as shown in Fig. 38. The coercivity values were extracted from the references listed in table 1, chapter 1 section 1.4.1.1. Our data set a coercivity record for films with sub-micron thickness. Other reports of good coercivity (1 T) (2004) in electrodeposited FePt films were published after we first introduced our electrochemical bath (2003)¹⁶.

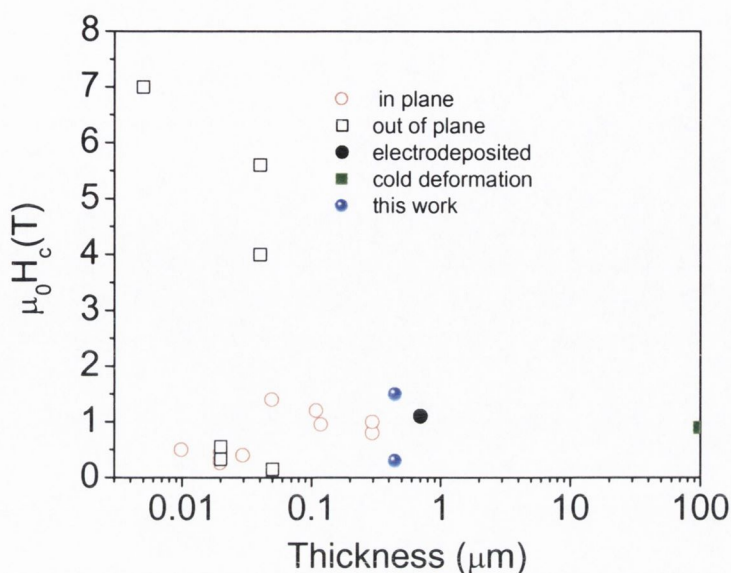


Figure 38. Coercivity dependence on the thickness of equiatomic FePt. Data is taken from the current literature and includes data from the present thesis (violet circles). Open circles, open squares, black circles and green square stand for the in and out of plane coercivity of sputtered samples, isotropic electrodeposited samples and isotropic bulk samples, respectively.

3.1.7 Conclusions

A novel bath for electrodepositing FePt films was developed and films were electrodeposited on copper and silver substrates with thickness of up to 0.45 μm. The magnetic and structural properties of the films were measured. Coercivities as high as 1.5 T were obtained in films after annealing in H₂ atmosphere. Films are shiny and smooth.

Morphology was found to be affected by the annealing process. This method using a novel bath, when compared to vapor deposition methods, opens an alternative route for the production of FePt films. Unfortunately, the requirement of annealing limits the application of FePt films in MEMS technology. This material and process can easily be incorporated into media recording technology.

3.2 Electrodeposition of FePd films

In this study FePd alloys were electrodeposited on three different substrates; silver, copper, a silver seed layer on silicon and an alumina membrane with 200 nm pore size, silver coated on one side.

The bath composition is listed in table 2. During the deposition the bath was kept at 40 °C in open atmosphere. Mechanical stirring was used. Bath pH was adjusted to 8.5 by adding small amount of NaOH. Sulfosalicylic acid was used as a complexant in order to increase the solubility of Fe at pH 8.5. NH_4SO_4 is used as a supporting electrolyte for the electrochemical bath. The bath temperature improves the solubility of Pd and increases the deposition rate.

After deposition films were annealed at temperatures above 400 °C in H_2 atmosphere. Film composition and morphology were investigated by X-ray diffraction and scanning electron microscopy. Magnetic properties were determined at room-temperature in a 5 T SQUID magnetometer.

Table 2. Electrochemical bath for the electrodeposition of FePd.

Chemical bath	Concentration (g/L)	Concentration (M)
Bath name	FePd#1	
PdCl ₂	4.43	0.017
Fe ₂ (SO ₄) ₃ .7H ₂ O	10.15	0.014
Sulfosalicylic acid.5H ₂ O	25.42	0.1
(NH ₄) ₂ SO ₄	19.8	0.15
NH ₄ OH	pH 8-8.5	
Temperature	40 °C	
Stirring	290 rpm	
Potential range	-0.7/-1.3 V vs. Ag/AgCl	
Current density	5 –20 mA cm ⁻²	
Counter electrode	Pd	

3.2.1 Morphology of FePd deposits

Electrodeposited FePd films and nanowires are shown in Fig. 39. Films were electrodeposited at -1.3 V [Fig. 39(a), (b)] and -0.95 V [Fig. 39(c)] vs. Ag/AgCl. More negative potentials (-1.3 V) tend to form rough deposits which have a spherical shape. At higher potential (-0.95 V) the deposit is smoother with small grains. Smooth, shiny deposits were obtained for a total charge of 2.4 C with a thickness of 1.5 μm .

The deposition into the membrane template is shown in Fig. 39d. The membrane template was dissolved in a concentrated solution of NaOH at 60 °C. The length of the wires ranges from 9-12 μm which were electrodeposited at -0.9 V vs. Ag/AgCl potential.

Electrodeposition into porous membranes eliminates the spherical growth because each pore works as a center of growth and does not interfere with the neighbouring pore. Additionally, thicker structures can be deposited using membrane templates.

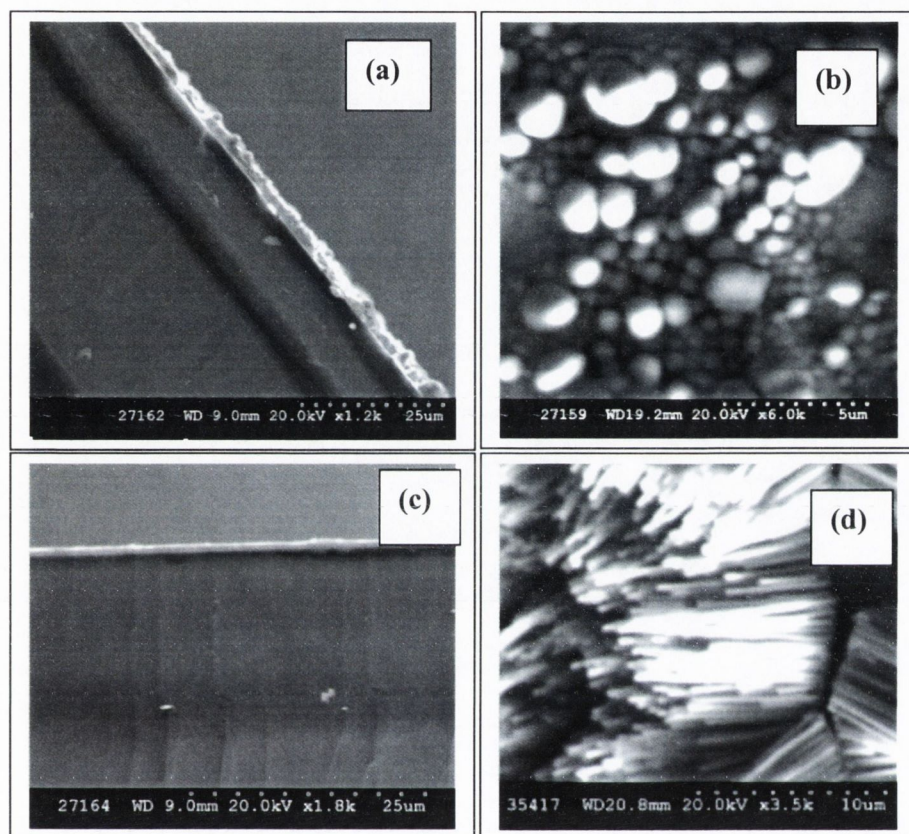


Figure 39. Morphology dependence on plating potential and electrodeposition into membrane templates. Deposits on Ag//Si substrates at (a) and (b) -1.3 V, (c) -0.95 V and (d) into a membrane template.

3.2.2 Composition of the films

Energy dispersive X-ray spectroscopy (EDS) was used to characterize the composition of the deposits. Typical EDS spectra of FePd films electrodeposited onto Cu and Ag substrates are shown in Fig. 40. These two spectra show that no impurity metals or compounds are incorporated in the deposit during the electrodeposition. The Ag, Si and Cu peaks correspond to the substrates.

Changing the bath potential from -0.9 V to -1.3 V vs. Ag/AgCl varied the composition of the films. As in the electrodeposition of FePt, the content of Fe in the films increases as the potential becomes more negative (Fig. 41). The range in which the composition is controlled by the potential corresponds to the kinetic controlled region of Fe (less noble metal) and mass transport limited region for Pd (more noble metal).

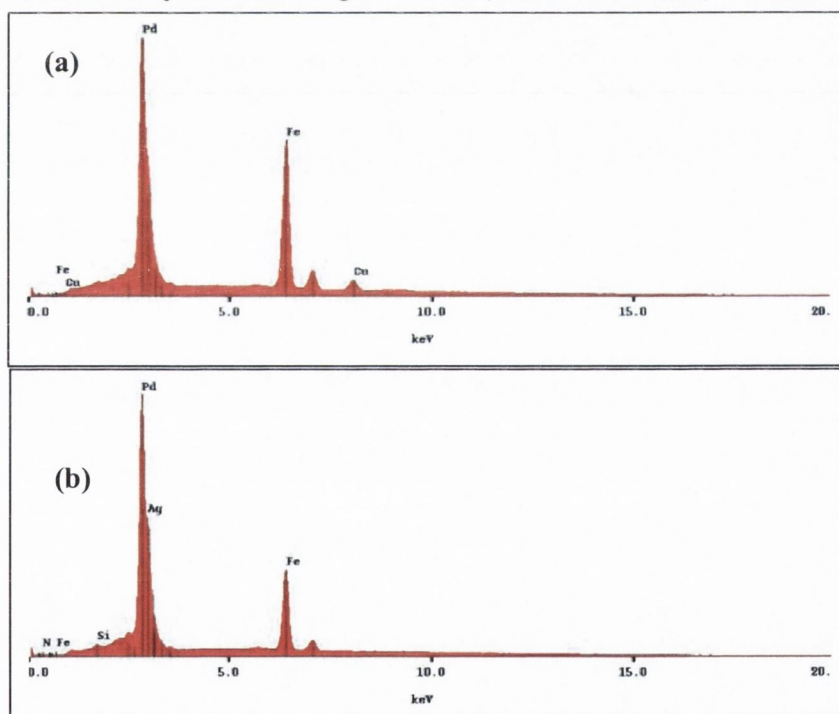


Figure 40. EDS spectrum of FePd electrodeposited on (a) Cu and (b) Ag/Si substrates. No metal impurities are observed in the spectra.

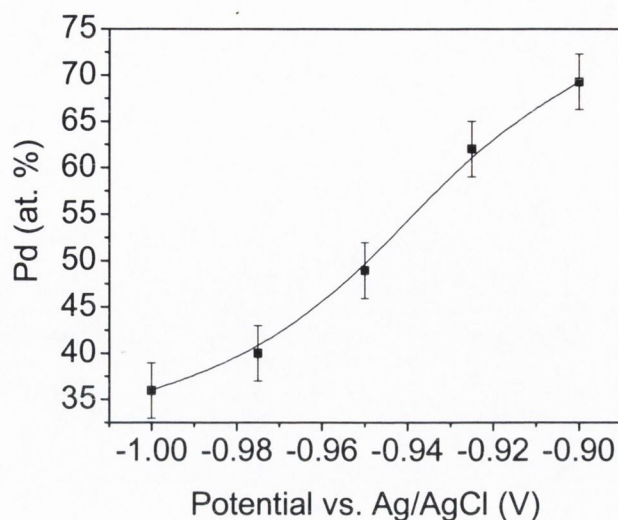


Figure 41. Dependence of composition on the deposition potential of FePd films.

The electrodeposition of Fe-Pd alloys occurs in a broad range of potentials starting from about -0.7 V vs. Ag/AgCl. At this low potential the alloy is Pd rich. The potential modulated region goes from -0.7 to -1.3 V, beyond that we have the mass transport limited region for both Pd and Fe. Despite the fact that FePd can be electrodeposited in a wide range of potentials, the region of useful deposits is very narrow ranging from -0.9 to -1.0 V. Films electrodeposited in this region are shiny and stick very well to the substrate. At lower potentials the deposits are spongy and powder-like and at high potential the films are very rough.

3.2.3 X-ray diffraction

Films electrodeposited onto Ag substrates and in 200 nm membrane templates were annealed in H₂ atmosphere and the structure of the deposits was studied as a function of the deposition potential, annealing time and temperature. Films electrodeposited on Cu substrates were not annealed due to the possible formation of a Cu-Pd alloy.

The effect of annealing on the structure of samples electroplated at different potentials is shown in Fig. 42. At 500 °C no significant effect on the structure can be observed. The structure resembles the structure of the as-deposited films, which is the disordered FePd phase. Additionally, annealing for times as long as 3 hours has no effect on the structure, as shown in Fig. 43. On the other hand when the films were annealed at 800 °C, the tetragonal FePd phase was formed (Fig. 44).

The effect of annealing temperature on the structure of electrodeposited FePd in the membrane templates is shown in Fig. 45. The tetragonal FePd phase is formed at temperatures as high as 700 °C and 800 °C, while as-deposited samples only show a disordered FePd nanocrystalline structure.

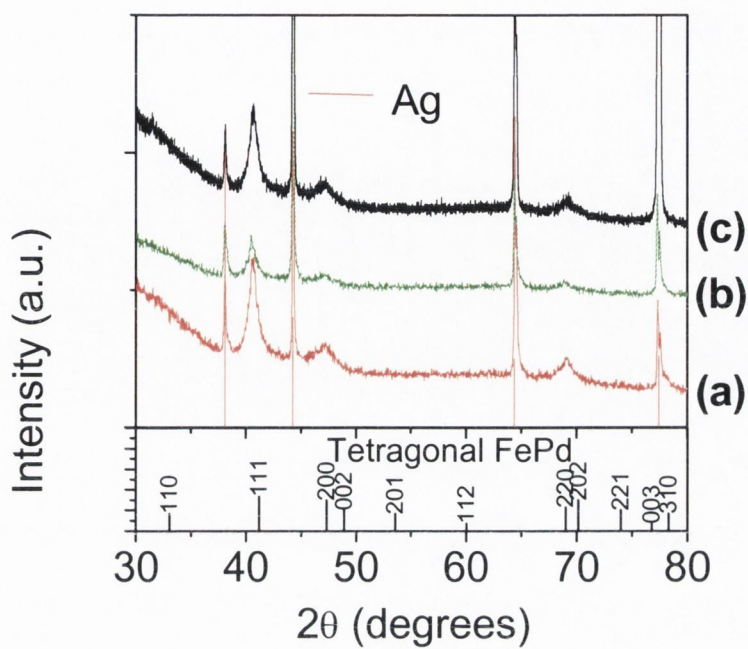


Figure 42. X-ray diffraction pattern of electrodeposited FePd on Ag substrates annealed at 500 °C as a function of the plating potential (a) -0.925 V, (b) -0.950 V and (c) -0.975 V vs. Ag/AgCl. Also shown is the diffraction pattern of the tetragonal FePd phase.

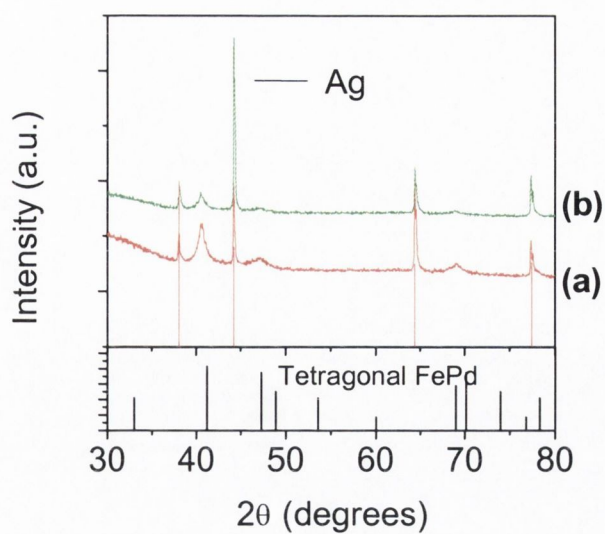


Figure 43. X-ray diffraction pattern showing the effect of annealing time on the structure of electrodeposited FePd films on Ag substrates. The films were annealed at 500°C for (a) 30 min and (b) 180 min.

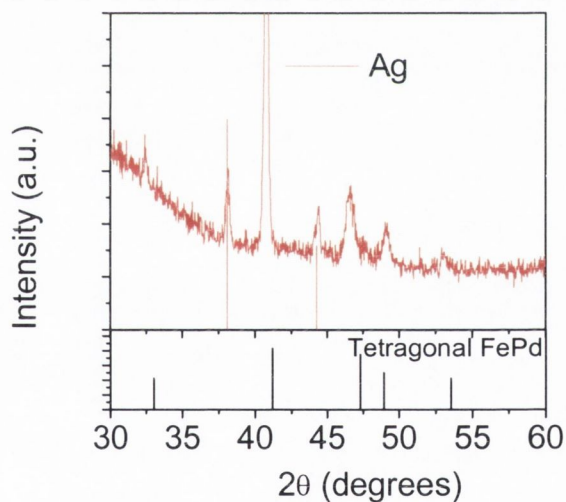


Figure 44. X-ray diffraction pattern of FePd films annealed in H_2 atmosphere at 800°C for 2 hours. Also shown is the diffraction pattern of the tetragonal FePd phase.

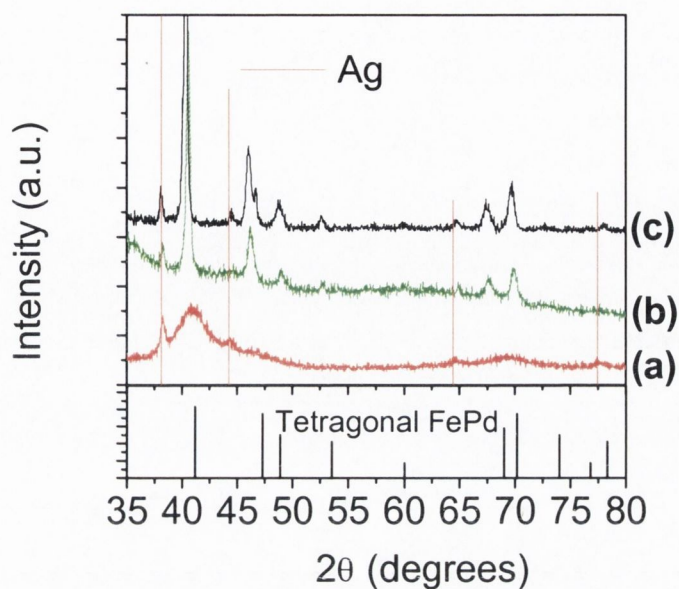


Figure 45. X-ray diffraction pattern of FePd electrodeposited into membrane templates. (a) As-deposited and annealed at (b) 700 °C and (c) 800 °C in H₂ atmosphere. Also shown, the diffraction pattern of the tetragonal FePd phase.

3.2.4 Magnetic measurements

The magnetic properties of electrodeposited FePd alloys were studied using a 5 T SQUID magnetometer. All as-deposited FePd samples showed soft magnetic behaviour which is associated with a disordered FePd nanocrystalline structure. Coercivity was developed after annealing. The in plane room-temperature magnetization curve of a FePd film annealed at 700 °C in H₂ atmosphere is shown in Fig. 46. Coercivity of 150 mT was measured. Smaller coercivity was found in FePd electrodeposited into a membrane

template (85 mT) as shown in Fig. 47. The initial magnetization curve is characteristic of a pinning-controlled magnet. Saturation magnetization values of 1.2-1.4 T were estimated based on sample volume. For the deposits in the membrane template, with a filling factor of 50 vol. %, the saturation magnetization, J_s , was estimated to be between 0.6-0.7 T.

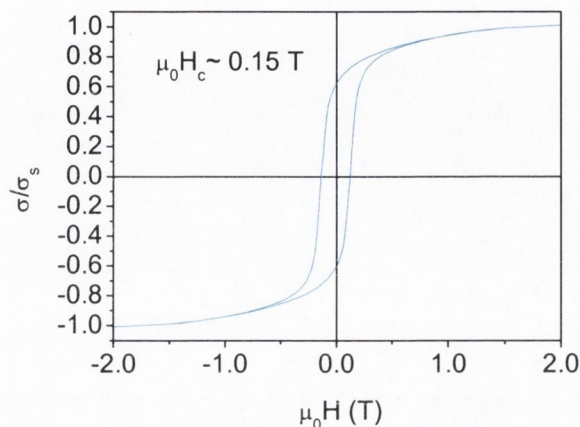


Figure 46. Room-temperature magnetization measurement of FePd electrodeposited on a Ag substrate after annealing at 700 °C for 2 hours in a H_2 atmosphere.

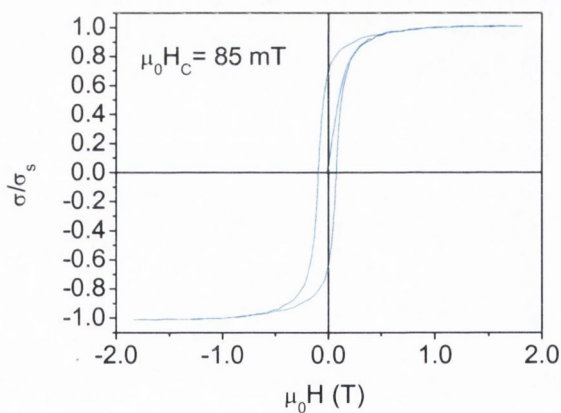


Figure 47. In plane room-temperature magnetization of FePd electrodeposited in a 200 nm membrane template after annealing at 700 °C for 2 hours in a H_2 atmosphere.

The dependence of coercivity on the annealing temperature was studied for samples electrodeposited into the membrane template as shown in Fig. 48. Coercivity starts to develop only at temperatures higher than 600 °C, then at about 700 °C it reaches a maximum value and remains almost constant from 700 °C to 900 °C.

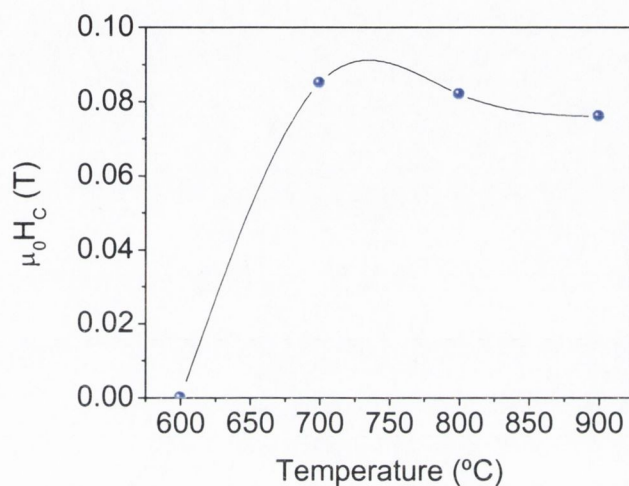


Figure 48. In plane room-temperature coercivity measurements of FePd electrodeposited in membrane templates vs. annealing temperature. Annealing was carried out in a H_2 atmosphere for 2 hours.

3.2.5 Discussion

As Pd is more noble than Fe it starts to plate at a higher potential and as the potential becomes more negative then Fe also starts to plate. However an undesirable reaction also takes place just after Fe starts to plate, hydrogen evolution ($2 H_2O + 2 e^- \rightarrow H_2 + 2 OH^-$). This reaction drains most of the current required in the electrochemical process, reducing the current efficiency considerably. It also may block nucleation sites due to adhesion of

bubbles to the substrate surface and increases the pH near the electrode. We have used strong stirring to remove the bubbles from the surface of the electrode. Additionally, metals less noble than Pd tend to be displaced. Therefore if an Ag substrate is left in a solution containing Pd ions after some time a Pd film is formed on top of the Ag substrate. This happens according to the reaction $2 \text{Ag} + \text{Pd}^{2+} \rightarrow \text{Pd} + 2 \text{Ag}^{1+}$.

Only samples annealed at temperatures higher than 600 °C developed coercivity. This is associated with the fact that above 600 °C the tetragonal FePd phase is formed. The dependence of coercivity on the annealing temperature can be associated with the following sequence of events: at lower temperatures the sample mostly consists of the disordered FePd phase while at temperatures as high as 700 °C the disordered phase is converted to the tetragonal phase increasing the magnetic anisotropy which enhances the coercivity. In addition, above 700 °C the sample is mostly composed of the ordered tetragonal phase and little change in the anisotropy can be observed, consequently the coercivity reaches its maximum. Therefore, the shape of the coercivity dependence on the annealing temperature is characteristic of the transformation from the disordered to ordered phase.

The different coercivities found in films and deposits in the membranes are likely to be associated with sample composition. Deviations from the equiatomic FePd have a direct effect on the intrinsic magnetic properties. The range of compositions that lead to the formation of the FePd tetragonal phase is very narrow 50-60.5 at. % Pd. This idea is supported by the fact that there is some mismatch between the peak positions of the experimental and standard X-ray diffraction patterns for the tetragonal phase. The mismatch can be understood as a deviation from the equiatomic tetragonal FePd phase.

This is the first report of the magnetic properties of electrodeposited FePd films and deposits in membrane templates. The coercivities obtained (0.15 T) are smaller than those

(0.35 T) obtained by e-beam evaporation¹⁷ and comparable to coercivities obtained in bulk samples (0.1 T)¹⁸. Sato et al. prepared samples with large coercivity on heated substrates with 10 nm nominal thickness, representing the largest coercivity values reported in the literature. The difference between our results and the report by Sato can be explained in terms of the structure. Sato et al. obtained oriented nanoparticles dispersed on the substrate with the c-axis perpendicular to the plane of the deposit. In our case the deposit is compact with random distribution of the c-axis orientation, which is known to reduce the coercivity. Additionally, the reversal mechanism in our deposits is of the pinning type which usually shows smaller coercivity than the nucleation type for decoupled particles.

The values of saturation magnetization 1.2-1.4 T are in line with values reported in the literature (1.5 T). The saturation magnetization depends on the composition and the degree of order in the alloy. The highest values in equiatomic FePd are obtained in fully ordered FePd.

The use of membrane templates into the deposition of FePd shows an important advantage over the deposition of films. It allows the plating of thicker structures without the problems of cracking and peeling often in films. The thickness of the deposits in the membranes can well be over 50 μm , whereas for the bath used, films are 5 μm or thinner.

3.3 Electrodeposition of equiatomic CoPt

This section describes the electrodeposition of equiatomic CoPt alloys on Ag substrates and membrane templates. We have studied the electrodeposition of CoPt from two different electrochemical baths, (a) the chloride and (b) the ammino-complex baths. The magnetic properties of the films were investigated. We systematically studied the morphology, composition and the structure in order to understand the origin of coercivity in the films. Three chloride bath compositions were investigated.

Two annealing processes were tested: vacuum annealing and annealing in a H₂ atmosphere. The effect of these two annealing processes on the structure of the films was compared by X-ray diffraction pattern.

3.3.1 Films electrodeposited from chloride baths

CoPt films were potentiostatically electrodeposited on polycrystalline Cu and Ag substrates from a single bath as shown in table 3. The solution pH was adjusted to 3 by adding a small amount of hydrochloric acid (HCl). A Pt wire of 0.25 mm diameter and 70 mm length was used as a counter electrode and Ag/AgCl saturated with KCl as the reference electrode. All potentials are quoted with respect to this reference electrode. Solutions were prepared from 100 mL of deionized water. Cu and Ag substrates were used as working electrodes and cut out from 99.9 % pure Cu foil 0.5 mm thick and from 50 μ m thick 99 % pure Ag foil into 5 mm x 5 mm squares. These substrates were varnished on one side and connected to a copper wire 1 mm of diameter. Just before electrodeposition, the substrates were dipped into a 10 % H₂SO₄ solution to remove any contamination on the surface and then dipped into deionized water. Deposition was carried out from fresh

solutions which were either vigorously stirred or stagnant in an open atmosphere at room-temperature. The deposition was controlled using an EG&G model 263A potentiostat.

The deposition of Pt may occur on Cu substrates even in the absence of an applied potential. Pt can displace Cu according to the following reaction: $\text{PtCl}_6^{2-} + 2 \text{Cu} \rightarrow \text{Pt} + 6 \text{Cl}^- + 2 \text{Cu}^{2+}$.

Table 3. Chemicals for the electrodeposition of CoPt.

Bath name	CoPt#0	CoPt#1	CoPt#2
Chemical	Concentration (M)		
CoCl_2	0.1	0.2	0.25
H_2PtCl_6	0.005	0.005	0.005
Na_2SO_4	0.1	0.1	0.1

The electrodeposition of CoPt from chloride was carried out using three baths with different Co^{2+} concentrations as shown in table 3. Na_2SO_4 is used as a supporting electrolyte with the purpose of increasing the solution conductivity, thereby reducing the effect of the gradient of the electrical field in the solution. This is important for having smooth deposits. Neither Na^+ nor SO_4^{2-} are oxidized or reduced in the electrodeposition.

Films were found to be smooth when electrodeposited at potentials ranging from -0.65 V to -1.3 V. We found that hydrogen evolution starts at potentials as small as -0.7 V and increases as the potential becomes more negative. We also observed that the films stick very well to Cu and Ag substrates when the total charge per square unit is smaller than 40 C cm^{-2} corresponding to a thickness of 2 to 3 μm . For higher charge densities the films lose their metallic look and start to peel off from the substrate.

In order to measure thickness, CoPt films were electrodeposited on silicon substrates coated with 50 nm of Cu and examined by electron microscopy. A typical cross-section of a CoPt film is shown in Fig. 49.

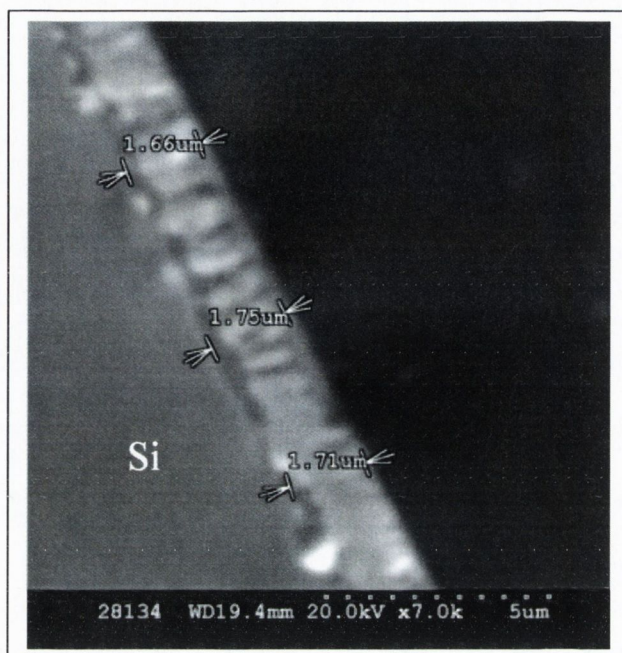


Figure 49. Micrograph of CoPt showing the film thickness. On the left is the silicon substrate.

The morphology of a typical CoPt film is shown in Fig. 50. CoPt films grew smoothly only at the beginning of the electrodeposition. As the films grew thicker the roughness increased, Fig. 50(a). Additionally, when films became a few microns thick they started to develop cracks on the sub-millimetric scale, Fig. 50(b) and subsequently the films peeled off the substrate.

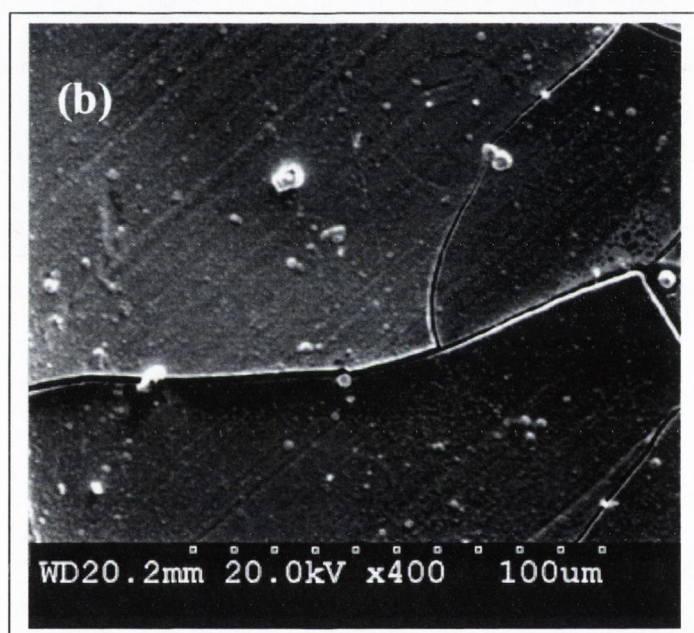
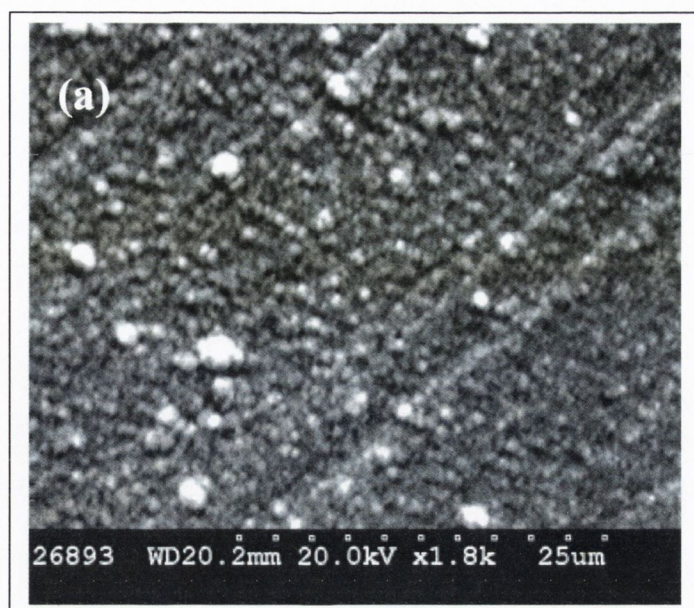


Figure 50. SEM pictures showing the surface of the films after electrodepositing at (a) - 0.7 V with 2.4 C of charge and (b) the development of cracks after passing more than 15 C of charge.

The effect of the overpotential on the morphology of the films was also investigated, as shown in Fig. 51. At more negative potentials the deposits form clusters and a spherical growth takes place [Fig. 51(b)]. At higher potentials the thickness of the deposits is more uniform [Fig. 51(a)].

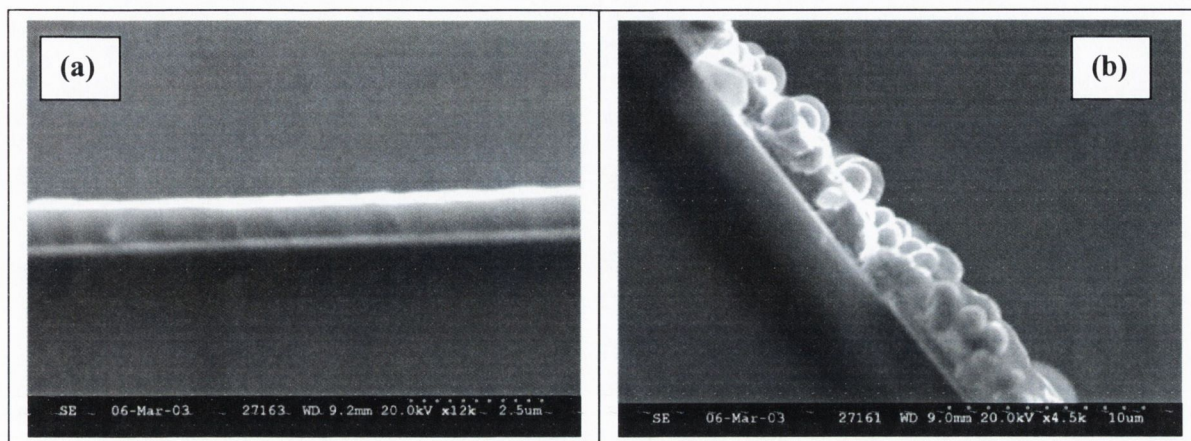


Figure 51. Morphology of electrodeposited CoPt dependence on the potential. Films were electrodeposited at (a) -0.8 V and (b) -1.3 V vs. Ag/AgCl.

3.3.1.1 Composition of the films

The dependence of the film composition on bath temperature, overpotential, CoCl_2 concentration and stirring conditions in the bath was studied. Film composition was measured by EDS. The bath temperature was found not to affect the film composition in the range from 20-60 °C. We also found that the film compositions are almost constant in the range of potentials studied (-0.7 V to -1.3 V) as shown in Fig. 52. Here the films were potentiostatically electrodeposited from the bath containing 0.1 M CoCl_2 with strong mechanical stirring. The deposition was stopped when the charge reached 10 C.

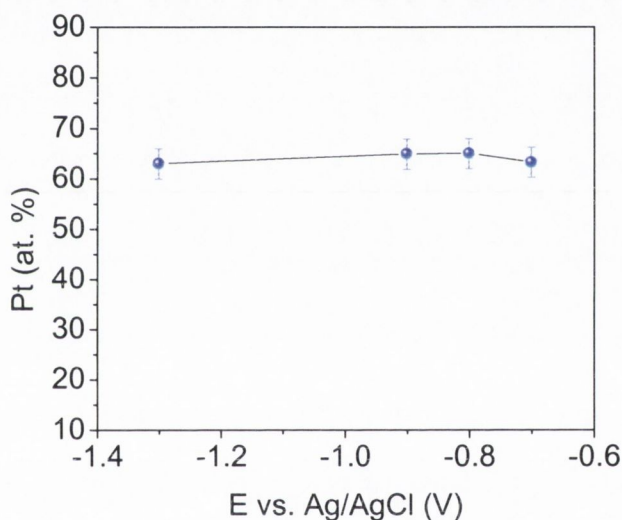


Figure 52. Composition dependence on the overpotential of films electrodeposited from a bath containing 0.1 M CoCl_2 (CoPt#0). The bath was mechanically stirred during the electrodeposition.

The composition dependence on the CoCl_2 concentration is shown Fig. 53. The films were electrodeposited from the three different baths (table 3). Vigorous mechanical stirring

was used during the electrodeposition. Since the PtCl_6^{2-} concentration was kept constant in the bath, the increase of CoCl_2 leads to an increase in the amount of Co in the films. It is worth to noticing that to obtain equiatomic CoPt one should use CoCl_2 at around 0.24 M, if -0.7 V is the depositing potential.

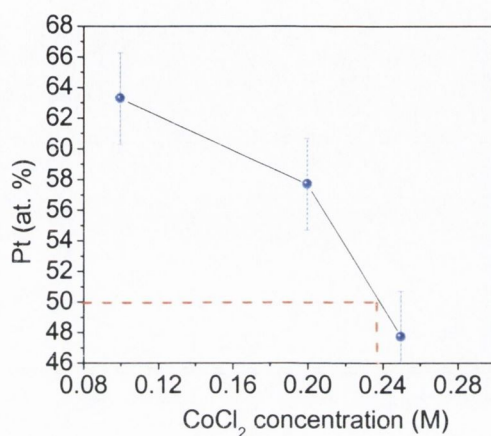


Figure 53. Pt content dependence on the CoCl_2 concentration in the electrochemical bath. Films were electrodeposited at -0.7 V vs. Ag/AgCl reference electrode with vigorous mechanical stirring.

In the absence of stirring the Co content of the films was found to be in the range of 80 to 89 at. % for baths containing 0.1 M and 0.25 M of CoCl_2 . Additionally, the composition of films electrodeposited from stagnant solutions was not as uniform as those electrodeposited from stirred baths.

3.3.1.2 Structure of as-deposited films

The crystalline structure was investigated by X-ray diffraction (XRD) with CuK_α radiation. The X-ray patterns of as-deposited films electrodeposited at -0.7 V vs. Ag/AgCl

on Ag substrates are shown in Fig. 54. The spectrum was corrected for 2θ misalignments by matching the diffraction pattern of the cubic silver substrate. Films are nanocrystalline with the most intense peak around 41° which is in between the (111) diffraction peaks pattern of the CoPt_3 and CoPt phases. As the CoCl_2 concentration in the bath increases the position of the peak around 41° moves towards the CoPt phase. The width of the peaks indicates that the deposited films are composed of nanocrystalline grains, therefore it is not possible to distinguish between the cubic and tetragonal phases. Also the appearance of other reflections in the spectrum suggests that the films are polycrystalline.

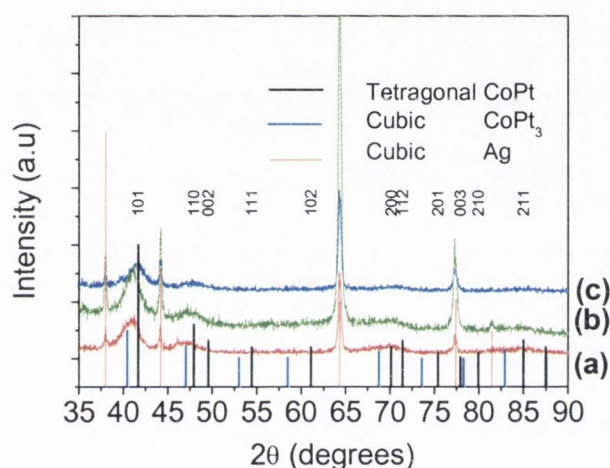


Figure 54. X-ray diffraction patterns of as-deposited CoPt films electrodeposited from baths with different CoCl_2 concentration (a) 0.1 M, (b) 0.2 M and (c) 0.25 M.

3.3.1.3 Structure of vacuum annealed CoPt samples

Vacuum annealing was carried out using a tubular furnace, a quartz tube and a vacuum system: samples were left in the vacuum for at least 24 hours before the annealing process took place to obtain a pressure of 1×10^{-6} bar. The annealing process was carried out as

follows. The furnace was first heated to the annealing temperature, the quartz tube was then inserted into the furnace for the required time. After annealing the quartz tube was removed from the furnace and allowed to cool to room-temperature under vacuum.

The effect of the annealing time on the structure of the films is shown in Fig. 55, Fig. 56 and Fig. 57 for samples individually annealed and electrodeposited at -0.725 V, -0.700 V and -0.650 V vs. Ag/AgCl, respectively. Little change is observed in the width of the diffraction pattern peaks as the annealing time is increased to 10 min. However, sharper peaks are found when the annealing time increases to 20 min which indicates that the films are more crystalline after longer annealing times (Fig. 55d). In addition, as the annealing time increases, the cubic CoPt phase becomes more evident. For samples electrodeposited at -0.725 V the X-ray patterns show that the main phase present is the cubic CoPt after annealing for 20 min. Samples electrodeposited at -0.700 V and -0.650 V show diffraction patterns which also match the cubic phase at higher angles and a strong peak near 41° which does not match either CoPt or CoPt₃. These two facts together suggest that cubic CoPt or CoPt₃ is the main phase present and there is a lattice distortion which shifts the (111) peak from the cubic CoPt or the CoPt₃ standard pattern as shown in Fig. 56 and 57. Additionally, as the plating potential goes from -0.725 V to -0.650 V the (111) reflection shifts towards the CoPt₃ phase.

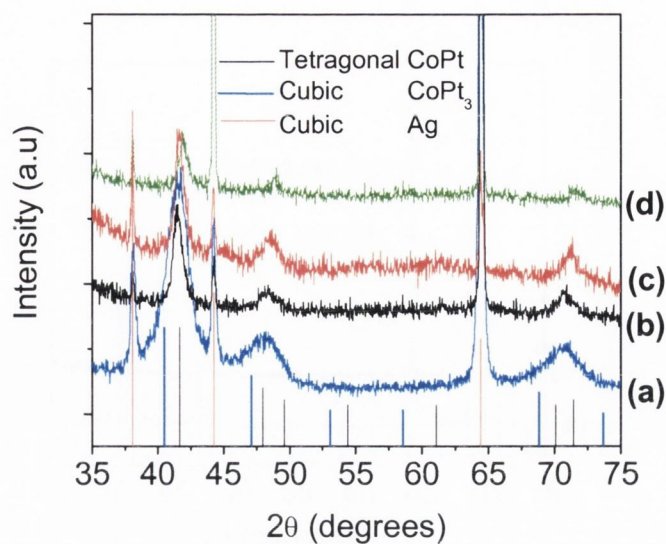


Figure 55. X-ray diffraction patterns of nearly equiatomic CoPt films (a) as-deposited and annealed at 660 °C for (b) 5, (c) 10 and (d) 21 min. Films were electrodeposited at - 0.725 V vs. Ag/AgCl.

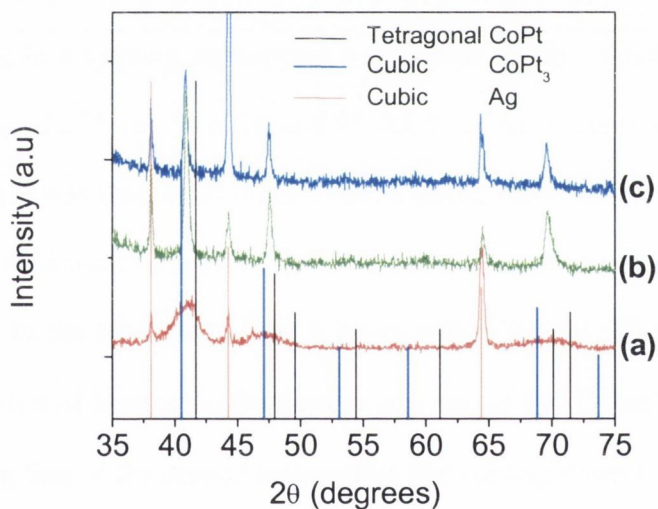


Figure 56. X-ray diffraction patterns of nearly equiatomic CoPt films (a) as-deposited and annealed at 660 °C for (b) 21 and (c) 40 min. Films were electrodeposited at -0.700 V vs. Ag/AgCl.

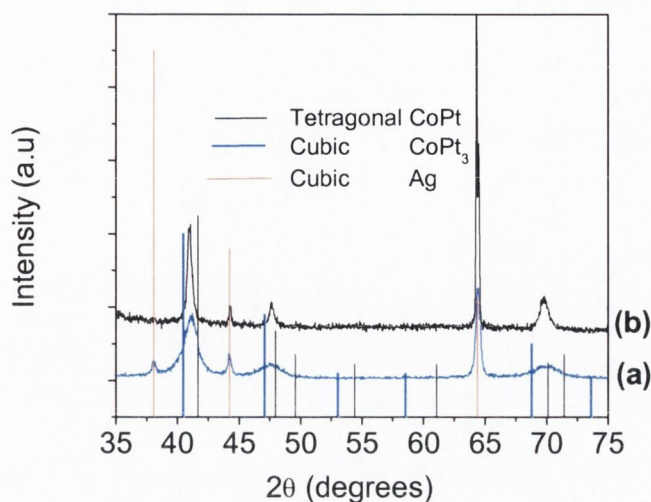


Figure 57. X-ray diffraction patterns of nearly equiatomic CoPt films annealed at 660 °C for (a) 20 and (b) 40 min. Films were electrodeposited at -0.65 V vs. Ag/AgCl.

3.3.1.4 Structure of CoPt films annealed in a H₂ atmosphere

Annealing in a forming atmosphere was carried out in a tubular furnace. The forming gas is composed of 5 vol. % of H₂ and 95 vol. % of Ar. A constant flow rate of 0.6 mL s⁻¹ of forming gas was used at all times. Here, a quartz tube was used which allows the H₂ to flow during the annealing process. Before the annealing process took place, the forming gas was flushed in the tube for at least 8 hours with a 0.6 mL s⁻¹ flow rate. The annealing process consists of heating up the furnace at a rate of 80 °C min⁻¹, leaving the sample for the annealing time at the desired temperature and cooling down to room-temperature at the same heating rate.

The X-ray patterns of films electrodeposited at different overpotentials and annealed at 800 °C for 2 hours is shown in Fig. 58. Films were electrodeposited from the bath containing 0.1 M CoCl₂. As can be seen in the diffraction pattern, all of the films show

sharp peaks due to the long annealing time. At -0.650 V and -0.675 V the patterns correspond to a mixture of cubic CoPt and CoPt₃. On the other hand, samples electrodeposited at -0.725 V show the formation of the tetragonal CoPt phase which can be identified with the appearance of the (002) peak near 49.583 ° and the (112) peak near 71.419 °.

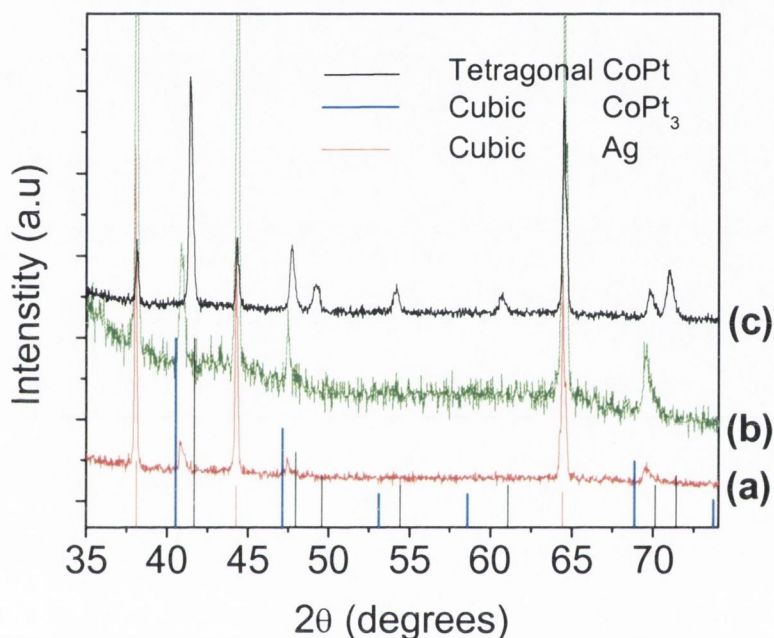


Figure 58. X-ray patterns of nearly equiatomic CoPt films annealed at 800 °C for 2 hours in a H₂ atmosphere. Films were electrodeposited at (a) -0.650 V, (b) -0.675 V and (c) -0.725 V.

Films electrodeposited from baths containing 0.2 and 0.25 M of CoCl₂ were also annealed at 800 °C for 2 hours as shown in Fig. 59. All films were electrodeposited at -0.725 V and after removal from the furnace they had a metallic look. All the films showed the L1₀ CoPt structure. The diffractions pattern for the films electrodeposited from the bath

containing 0.25 M CoCl_2 looks noisier because the measurements were carried out only for 4 hours where usually they are carried out for 8 hours.

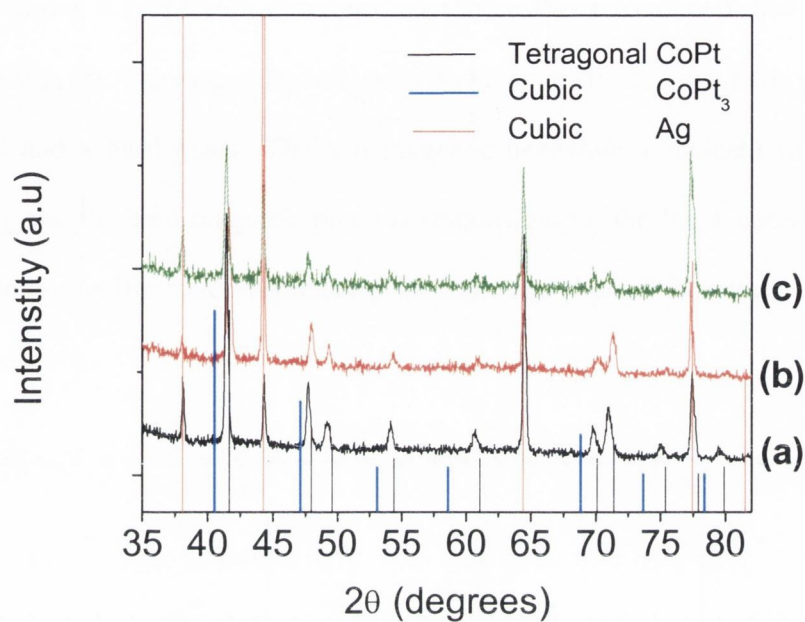


Figure 59. X-ray diffraction patterns of CoPt films annealed at 800 °C for 2 hours.

Films were electrodeposited from electrochemical baths containing (a) 0.1 M, (b) 0.2 M and (c) 0.25 M of CoCl_2 at -0.725 V vs. Ag/AgCl.

3.3.1.5 Magnetic measurements

All as-deposited samples were magnetically soft. Vacuum annealed samples from the bath containing 0.1 M CoCl_2 developed coercivity after annealing at 660 °C for 20 min as shown in Fig. 60. The magnetization curve is characteristic of a magnetic system composed of a soft and a hard phase. The soft magnetic behaviour is evident from the low field switching and the hard magnetic phase is responsible for the 0.4 T coercivity in this film. Additionally, the films are magnetically isotropic and showed the same in plane and out of plane coercivity.

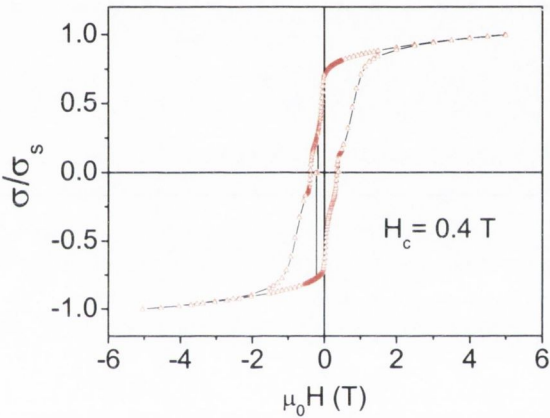


Figure 60. Room-temperature magnetization measurement of a CoPt film annealed at 660 °C for 20 min in vacuum. The films were electrodeposited from the bath containing 0.1 M CoCl_2 .

The effect of the plating potential on the coercivity of films is illustrated in table 4.

Table 4. Coercivity of films annealed in vacuum and H_2 atmosphere.

Bath#	Potential (V vs. Ag/AgCl)	Annealing conditions (°C x min)	Coercivity for samples vacuum annealed (T)	Phases for vacuum annealed samples	Coercivity for samples H_2 annealed (T)	Phases for H_2 annealed samples
CoPt#0	-0.675	660 x 20	0.1	CoPt ₃ + cubic CoPt	-	-
CoPt#0	-0.700	660 x 20	0.4	Cubic CoPt	-	-
CoPt#0	-0.725	660 x 20		CoPt ₃ + cubic CoPt	-	
CoPt#0	-0.750	660 x 20		CoPt ₃ + cubic CoPt		
CoPt#0	-0.675	660 x 20				
CoPt#0	-0.725	660 x 20				
CoPt#0	-0.750	660 x 20				
CoPt#1	-0.725	660 x 20	0.6	Cubic CoPt	-	-
CoPt#2	-0.725	660 x 20	0.6	Cubic CoPt	-	-
CoPt#0	-0.700	800 x 120			0.63	Tetragonal CoPt
CoPt#1	-0.725	800 x 120	-	-	1.0	Tetragonal CoPt
CoPt#2	-0.725	800 x 120	-	-	1.0	Tetragonal CoPt

Samples electrodeposited from baths containing 0.2 M (Fig. 61) and 0.25 M of CoCl_2 also developed coercivity after annealing at 660 °C for 20 min. Films electrodeposited from these two baths showed coercivities of around 0.6 T.

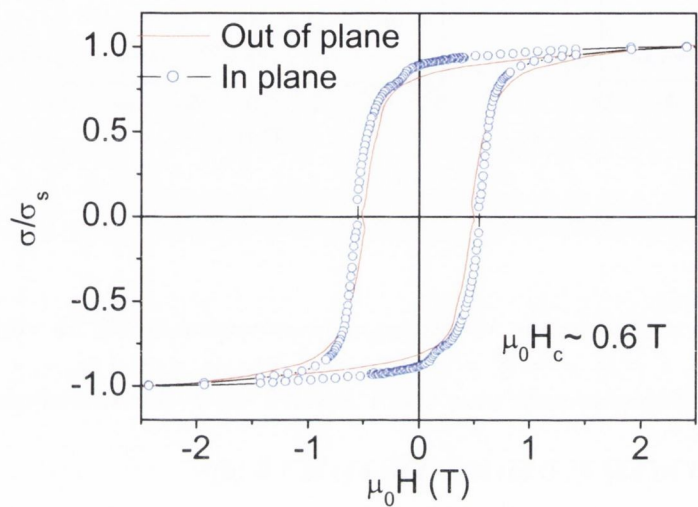


Figure 61. Room-temperature magnetization of films electrodeposited from the bath containing 0.2 M of CoCl_2 and annealed at 660 °C for 20 min in vacuum.

In contrast to vacuum annealing, films annealed in a H_2 atmosphere at temperatures up to 800 °C look metallic. Room-temperature magnetization measurements of CoPt films annealed at 800 °C for 2 hours are shown in Fig. 62. The dominant reversal magnetization process in these films is nucleation as can be identified by the behaviour of the initial magnetization curve.

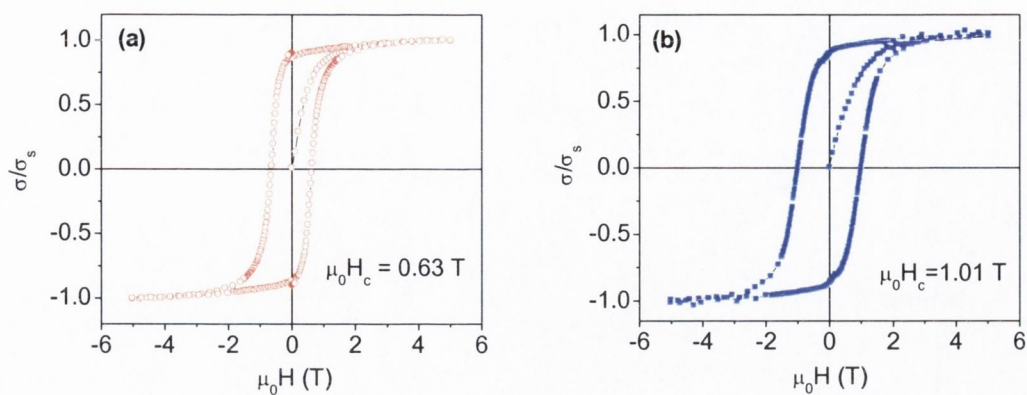


Figure 62. Room-temperature magnetization measurements of CoPt films annealed in H_2 atmosphere at 800 °C for 2 hours. Films were electrodeposited from the bath containing (a) 0.1 M of CoCl_2 and (b) 0.25 M CoCl_2 .

The estimated saturation magnetizations of the films, based on thickness, are about 0.85 - 0.95 T.

3.3.2 Electrodeposition of CoPt from the ammino-complex bath

3.3.2.1 Film electrodeposition

Electrodeposition of nearly equiatomic CoPt was carried out from baths described in table 5. Electrodeposition was carried out from stagnant solutions, at room-temperature. Films were galvanostatically electrodeposited with current densities ranging from 10-50 mA cm⁻². The solution pH was adjusted to 5 by adding either small amounts of HCl or 3 M solution NH₄OH. Di-ammonium hydrogen citrate is used as a supporting electrolyte and is not reduced during the electrodeposition. The reference electrode and counter electrodes were Ag/AgCl and a 50 mm long Pt wire, respectively. Films were electrodeposited on Ag and Cu electrodes cut as described in section 3.3.1.1 for a chloride bath. The effect of agitation was not studied for the ammino-complex baths. Electrodeposited films are smooth and show cracks at the early stages of the electrodeposition.

Table 5. Bath composition for the electrodeposition of CoPt from ammino-complex.

Chemical name	Chemical formula	Concentration (M)
Pt p-salt	[Pt(NO ₂) ₂ (NH ₃) ₂]	0.01-0.35
Cobalt sulfamate	Co(NH ₂ SO ₃) ₂	0.10
Di-ammonium hydrogen citrate	(NH ₄) ₂ C ₆ H ₆ O ₇	0.10

The addition of NH₄OH was found to have an additional effect besides the solution pH adjustment, thereby we added different amounts of this chemical and corrected the pH by adding HCl. The effect is related to stress changes in the films evident from the micrographs showed in Fig. 63. Small amounts of NH₄OH result in a higher density of cracks. For comparison, a combination of NaOH and HCl did not result in any change in the density of cracks.

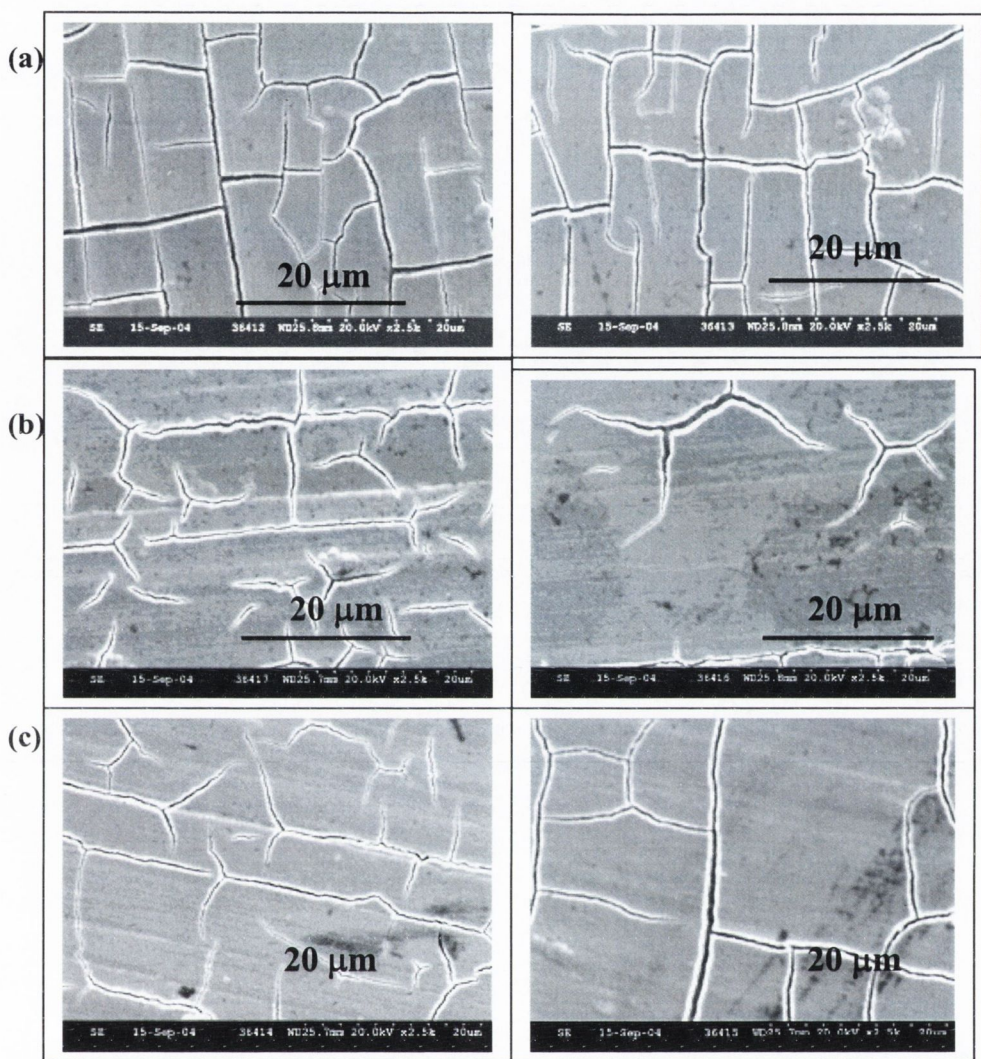


Figure 63. Films electrodeposited from baths containing (a) 0.03 M, (b) 0.06 M and (c) 0.180 M of NH_4OH . Side by side are micrographs of the same film in different areas. Films were electrodeposited at -5 mA for 25 min.

3.3.2.1.1 Composition of the films

The composition of the films was found to be independent of the current density in a wide range of values (30-50 mA cm⁻²). The film composition was more effectively changed by the bath composition than the current density which is illustrated in Fig. 64. Here composition was measured using EDS and the films were electrodeposited on Ag substrates using a current density $j = 48 \text{ mA cm}^{-2}$.

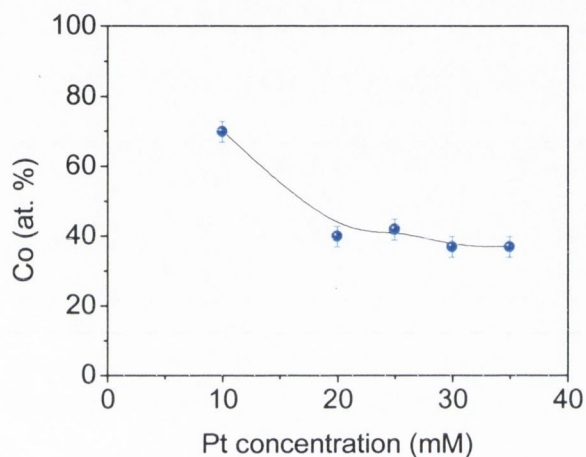


Figure 64. Co content in films vs. the concentration of $\text{Pt}(\text{NO}_2)_2(\text{NH}_3)_2$. Films were electrodeposited on Ag substrate using a current density of 48 mA cm^{-2} .

3.3.2.1.2 Structure of H_2 annealed films

Samples were annealed in a H_2 atmosphere and the effect of the annealing temperature and annealing time on the structure of the films was investigated. The annealing

temperature was varied from 500 °C to 900 °C. And the annealing time was varied from 20 min to 2 hours.

The effect of the annealing temperature on the structure of films electrodeposited on Ag substrates is shown in Fig. 65. Films were electrodeposited with $j = 48 \text{ mA cm}^{-2}$. Films annealed at 500 °C for 2 hours did not show any significant change in structure as compared to as-deposited films. As-deposited films show a nanocrystalline structures similar to that of films electrodeposited from chloride baths as shown in Fig. 54.

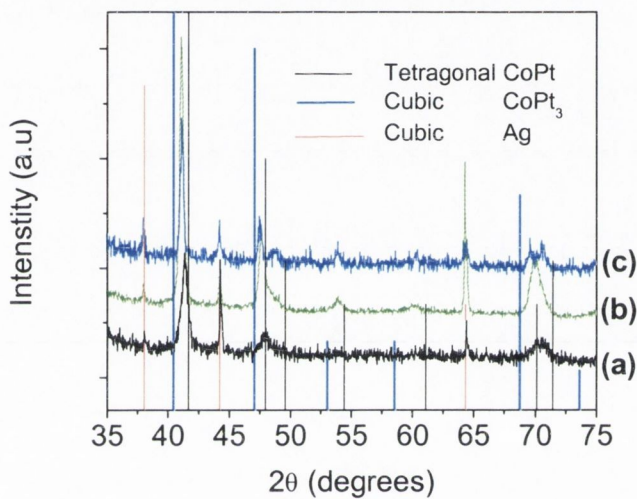


Figure 65. X-ray diffraction patterns of $\text{Co}_{45}\text{Pt}_{55}$ films electrodeposited from the ammino-complex baths and annealed at (a) 650 °C, (b) 800 °C and (c) 900 °C for 2 hours.

As can be seen from the X-ray diffraction patterns the formation of the L1_0 CoPt phase starts to happen at temperatures above 650 °C. At temperatures as low as 650 °C only the cubic CoPt phase is formed. At 800 °C, the disordered cubic phase starts to be converted into the L1_0 CoPt phase.

A comparison of samples annealed for 20 min and 2 hours is shown in Fig. 66. As the annealing time increases the grain size increases. Samples annealed for long times show the formation of $L1_0$ CoPt.

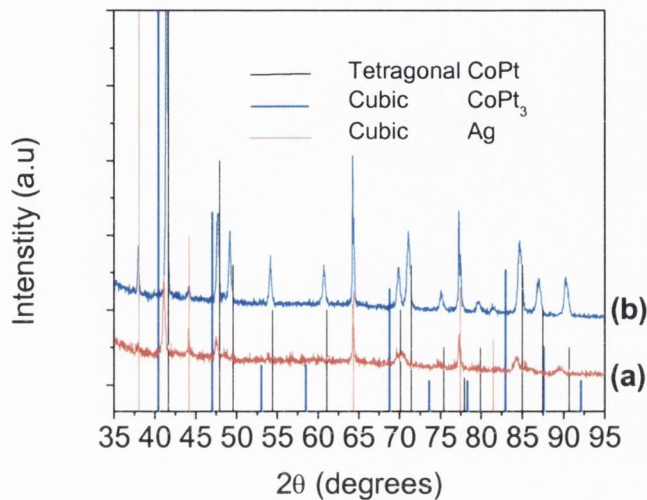


Figure 66. X-ray diffraction patterns of $Co_{45}Pt_{55}$ films annealed at 800 °C for (a) 20 min and (b) 2 hours.

The effect of composition on the structure of films is shown in Fig. 67. All the samples were annealed at 800 °C for 2 hours. Smaller amounts of Co favour the formation of cubic CoPt. There is a tetragonal distortion in these films as can be seen by the peak around 47 °. When the content of Co approaches the equiatomic value the $L1_0$ phase starts to form. On the other hand, when the concentration of Co in the films is much greater than 50 % the tetragonal symmetry is lost.

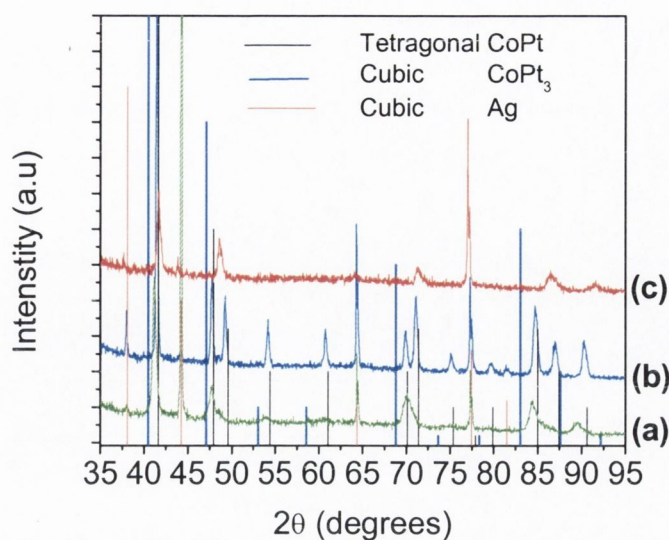


Figure 67. X-ray diffraction patterns of samples annealed at 800 °C for 2 hours containing (a) 34, (b) 39 and (c) 70 at. % Co.

3.3.2.1.3 Magnetic measurements

Film composition, annealing temperature and annealing time were varied and their effect on the coercivity of CoPt films was investigated. Measurements were carried out at room-temperature in the SQUID magnetometer. Fig. 68 shows a comparison between the in plane magnetizations of samples annealed at 800 °C for 20 min and 2 hours, the structure is shown in Fig. 66. Magnetization curves were corrected for the diamagnetic contribution coming from the Ag substrate. As can be seen the two annealing times lead to the same coercivity which is about 1 T. The initial magnetization shown for the sample annealed at 800 °C for 2 hours is characteristic of a pinning type magnet.

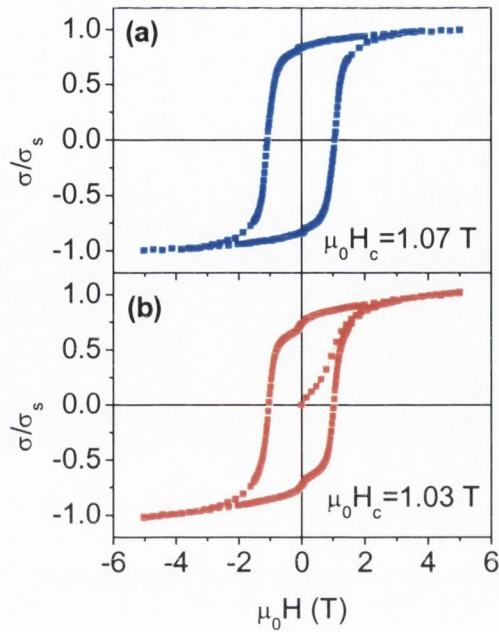


Figure 68. In plane room-temperature magnetization curves comparing samples annealed at 800 °C for (a) 20 min and (b) 2 hours.

Adjusting the annealing temperature can control the coercivity. Coercivity sharply increases between 600 °C and 800 °C, beyond this point the coercivity reaches a maximum of 1.07 T as shown in Fig. 69. Also, there is a range of compositions in which samples show coercivity as shown in Fig. 70. Maximum coercivity is obtained for compositions with 40-47 at. % Co. The saturation magnetization of the films of 0.85 - 0.95 T was estimated using the volume of the samples. All films are magnetically isotropic and as-deposited films are magnetically soft.

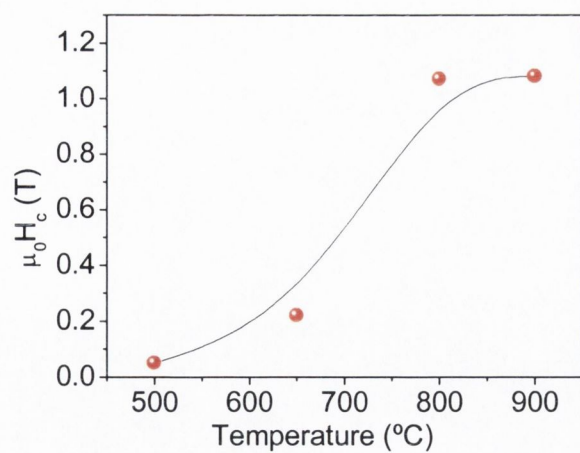


Figure 69. Coercivity dependence on the annealing temperature for samples annealed in a H_2 atmosphere.

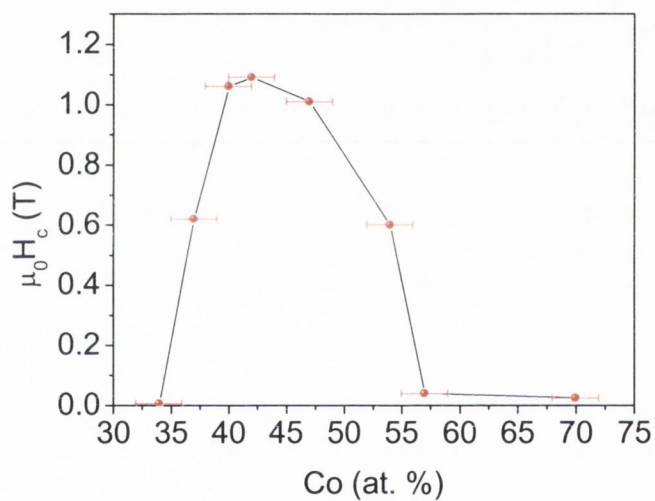


Figure 70. Coercivity dependence on the Co content for films annealed in a H_2 atmosphere.

3.3.2.2 Electrodeposition in membrane templates

There are a few important aspects that have to be taken into consideration when electrodepositing into porous membranes. If the length of the porous membrane is comparable to the diffusion layer thickness, which is typically 100 μm , the effect of stirring the bath is less effective than in the case of plating on flat surfaces. Therefore, due to inefficient stirring, the composition of the alloy electrodeposited into membranes may differ from that of electrodeposited films. We have chosen a bath that does not require any stirring in order to carry out the deposition into the membrane. Another important feature about electrodeposition into membranes is that the pH of the bath should be kept within the range 4-9. If the pH is out of these limits the membrane simply dissolves.

Electrodeposition in membrane templates was carried out using commercial alumina membranes with 100 nm and 200 nm pore size from Whatman. The pores constitute about 50 % of the membrane volume. Membrane thickness is 66 μm . A back electrode of 100-200 nm of Pt or Ag was produced by sputtering and evaporation, and the pores were filled with nearly equiatomic CoPt from the bath shown in table 5. The pH of the solution was adjusted to 5 by adding NaOH and the electrodeposition was carried out at room-temperature in an open atmosphere. No stirring is used during the deposition and the potential was varied in the range -2.5 to -5.0 V with current densities ranging from 10-50 mA cm^{-2} . Samples were annealed in vacuum at 10^{-6} bar or in hydrogen. First a furnace was heated up to the desired temperature, and then the sample in a quartz tube under vacuum was pushed into the furnace and after annealing was quenched in water.

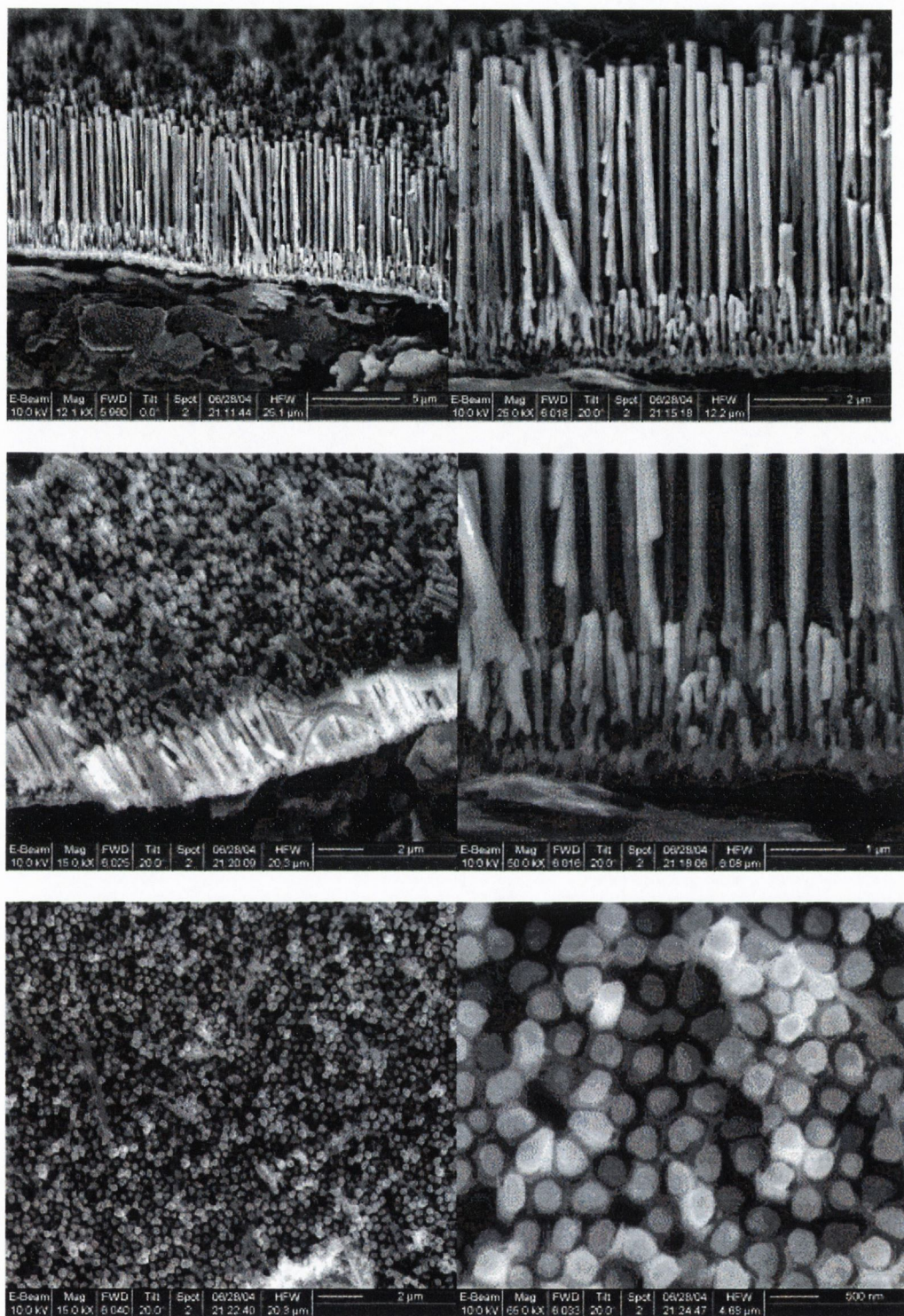


Figure 71. Micrographs showing CoPt electrodeposited into 200 nm membranes. The deposition was carried out at -30 mA cm^{-2} for 4 hours.

When necessary, the membrane was removed using 3 M NaOH solution. Fig. 71 illustrates the electrodeposition of CoPt in membrane templates and the partial removal of the membrane.

When thick deposits are required it is convenient to look for a bath which leads to a reasonable deposition rate. Usually the least soluble salt present in the electrochemical bath limits the maximum deposition rate, which in our case is the Pt p-salt. A bath containing a high concentration (35 mM) of dinitrodiammine platinum $[\text{Pt}(\text{NO}_2)_2(\text{NH}_3)_3]$ provided a deposition rate which is about $6\text{--}8\ \mu\text{m hr}^{-1}$. Fig. 72 shows a CoPt deposit which was carried out for 4 hours.

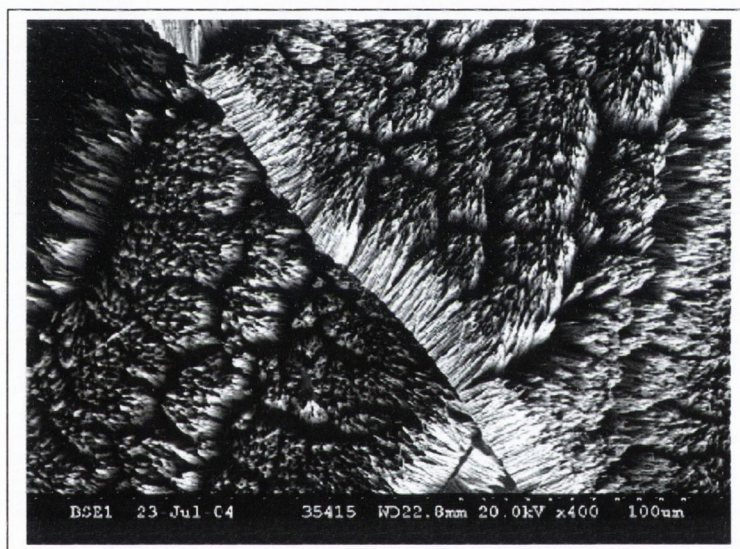


Figure 72. Micrograph of CoPt electrodeposited from a bath containing 35 mM of Pt p-salt after the removal of the membrane template.

The use of the same current densities ($10\text{--}50\ \text{mA cm}^{-2}$) as used for the electrodeposition of films leads to the same composition when plating in the membrane templates. The tuning in composition was made by using different bath compositions as earlier described. All the

characterizations refer to samples prepared from the bath containing 20 mM Pt p-salt in 200 nm porous membranes unless otherwise stated.

3.3.2.2.1 Structure of vacuum annealed deposits

The vacuum annealing was carried out as described in section 3.3.1.3. We investigated the effect of annealing time and temperature on the structure of electrodeposited CoPt in the membrane templates. Annealing time was varied from 5 min to 2 hours and the annealing temperature from 450 °C to 700 °C.

For the annealing times investigated the temperature was kept at 700 °C. Fig. 73 shows the changes in the structure with annealing time. The structure of the deposits annealed for only 5 min is very similar to the as-deposited. The diffraction pattern shows a slight sharpening of the peaks. The main phase present is the CoPt disordered phase. When annealed for 30 min, the diffraction pattern shows a clear transformation from the disordered to the ordered phase, evident from the appearance of the peak at 33 ° corresponding to the (110) peak of the $L1_0$ phase and splitting of peaks around 47 and 70 °. On the other hand, when the annealing time is about 2 hours the splitting of the tetragonal phase seems to be less pronounced.

The formation of the $L1_0$ phase as the temperature is increased is only evident when samples are annealed at 700 °C as shown in Fig. 74. As the temperature is raised the peaks in the pattern become sharper. Temperatures as low as 450 °C are not sufficient to induce significant structural changes in the deposits.

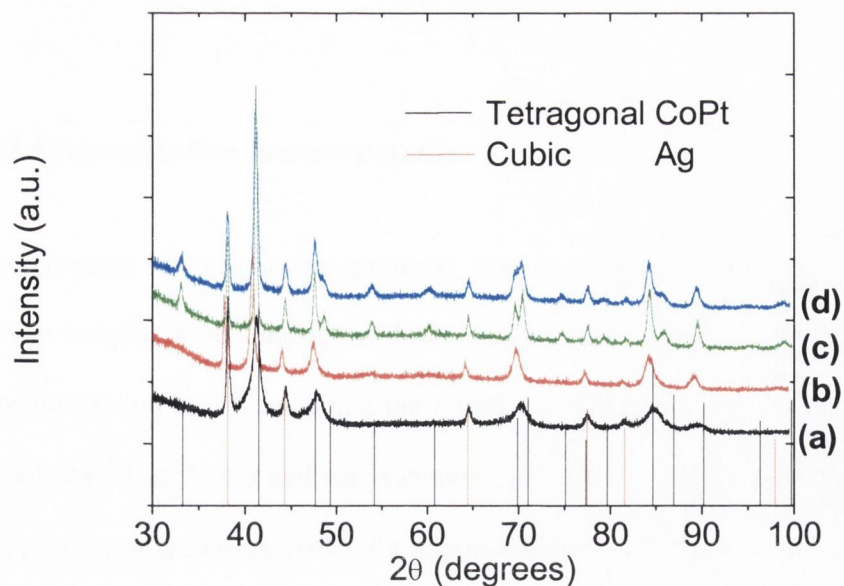


Figure 73. Evolution of the X-ray patterns of CoPt electrodeposited in membrane templates with annealing time. Samples are (a) as-deposited and annealed at 700 °C for (b) 5 min, (c) 30 min and (d) 2 hours.

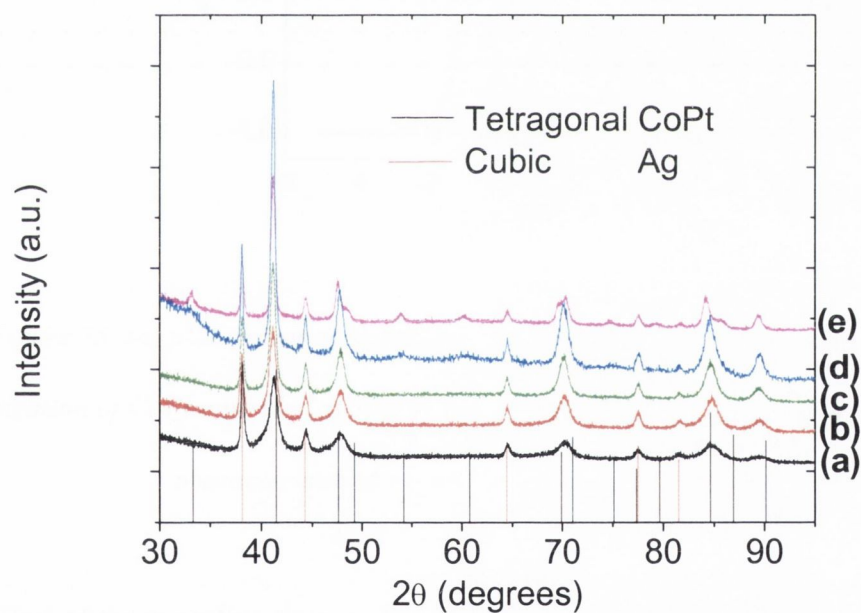


Figure 74. Evolution of the X-ray patterns of CoPt electrodeposited in membrane templates with annealing temperature. Samples are (a) as-deposited and annealed at (b) 450 °C, (c) 550 °C, (d) 650 °C and (e) 700 °C for 30 min.

3.3.2.2.2 Magnetization measurements

All as-deposited samples are magnetically soft, showing coercivities smaller than 0.01 T. Therefore samples were annealed with the membrane template to develop coercivity. A typical magnetization curve, including the initial magnetization, is shown in Fig. 75. The sample contains 53 at. % Co and was vacuum annealed at 700 °C for 30 min. The initial magnetization curve is characteristic of a pinning-controlled magnet. The squareness of the loop, 0.93, suggests the existence of a strong exchange interaction among the grains.

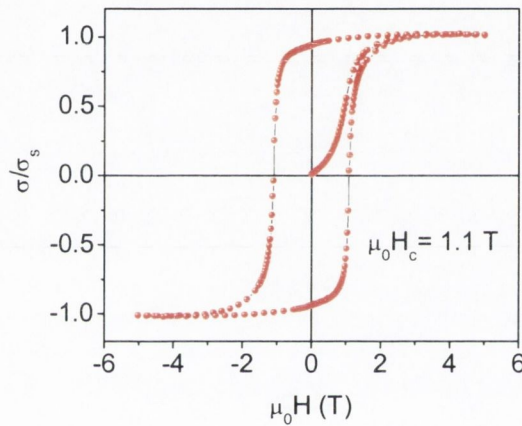


Figure 75. In- plane room-temperature magnetization curve showing the initial magnetization of CoPt annealed at 700 °C for 30 min. The initial magnetization curve is characteristic of a pinning-controlled magnet.

The effect of the annealing time on the in plane and out of plane magnetic properties of the deposits is shown in Fig. 76 and 77, respectively. All values of magnetization were estimated taking into account the volume of the sample, the filling factor of the membrane (~ 0.5) and the density of equiatomic tetragonal CoPt (15957 kg m^{-3}). The shape of all

magnetization measurements is characteristic of a single magnetic phase, none of the samples showed a shoulder like shape. A direct comparison between Fig. 76 and Fig. 77 for the same annealing times shows that the films are all magnetically isotropic. In isotropic magnets the distribution of the c-axis is random, resulting in the same coercivity in plane and out of plane.

Fig. 78 shows the dependence of the coercivity on the annealing time for samples annealed at 700 °C. Annealing for shorter times, such as 10 min, results in modest coercivity amounting to 0.5 T. As the annealing time is increased, so is the coercivity, which reaches its maximum at 30 min and remains almost constant for longer annealing periods. The shape of the curve suggests that after 30 min of annealing the structure of the deposits does not change significantly.

The dependence of the coercivity on the annealing temperature is shown in Fig. 79. The structural changes in the deposits only start to have an effect on the coercivity at 550 °C. Coercivity sharply increases between 600 °C (0.4 T) and 700 °C (1.1 T) and then starts to decrease above 750 °C. Somewhat higher coercivity, up to 1.3 T, is obtained by annealing in hydrogen at 700 °C for 30 min.

In plane room-temperature recoil curves were measured for comparison in samples annealed at 650 °C and 700 °C, as shown in Fig. 80. First the sample is brought to magnetic saturation followed by a measurement of the remanence at zero field. Then, a series of reverse fields in the opposite direction to the remanence is applied. Once the minimum value of field is reached on the recoil curve the field is increased to zero and the recoil curve measured. The process is repeated cyclically for different points in the second quadrant. There is a larger contribution of reversible magnetization in samples annealed at 650 °C (Fig. 80a) than in samples annealed at 700 °C (Fig. 80b). This suggests that the

magnetization is the result of the contribution of a hard and soft phase. Samples annealed at 650 °C have a greater contribution from the soft phase to the magnetization than the samples annealed at 700 °C, and the two magnetic phases are exchange coupled. This behaviour is called the exchange spring.

Deposits were also made into a 100 nm membrane templates. The magnetic properties of the deposits into the 100 nm pores are similar to those deposited into the 200 nm pores membranes suggesting that in both magnetic structures are the same. Coercivities in annealed samples are about 1.0 T after annealing at 700 °C for 30 min.

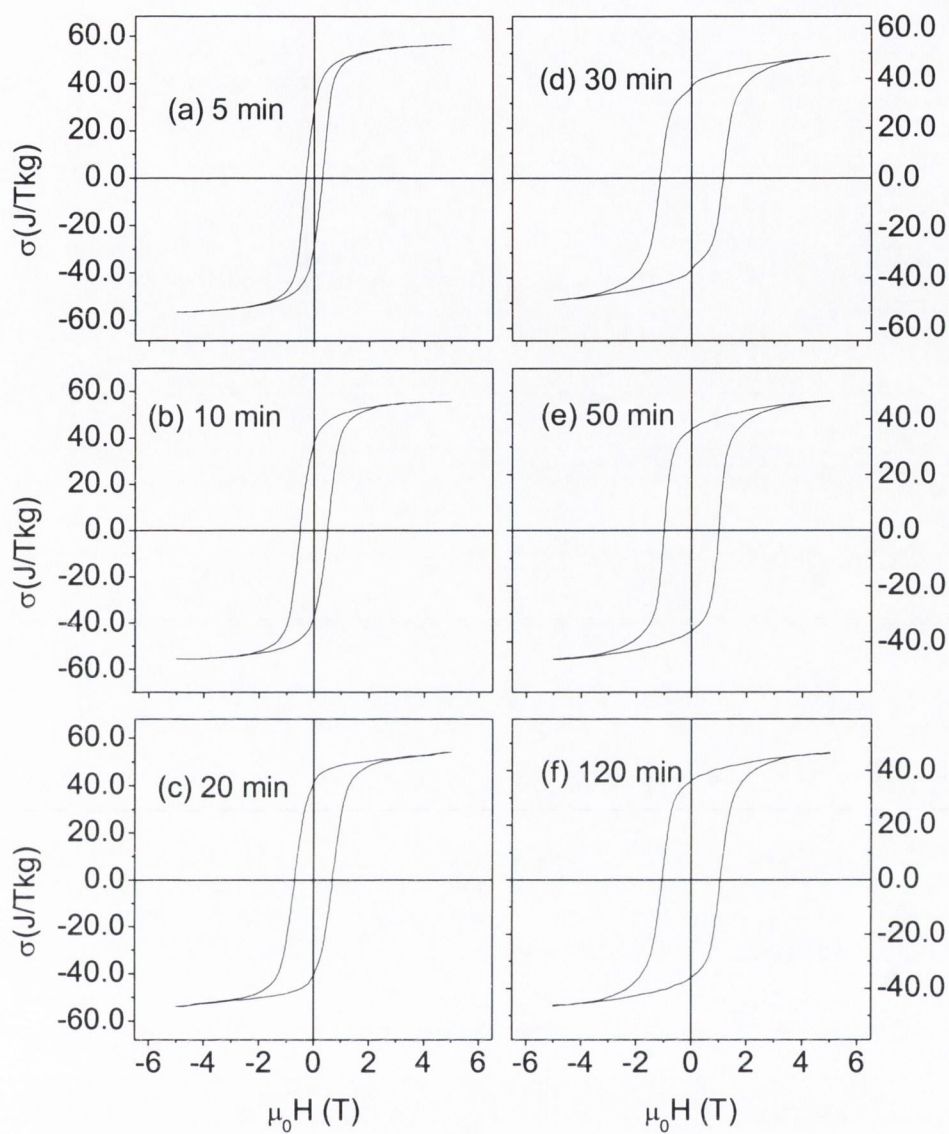


Figure 76. In plane room-temperature magnetic measurements showing the effect of annealing time for 8-10 μm samples annealed at 700 °C. Samples were annealed for (a) 5 min, (b) 10 min, (c) 20 min, (d) 30 min, (e) 50 min and (f) 120 min.

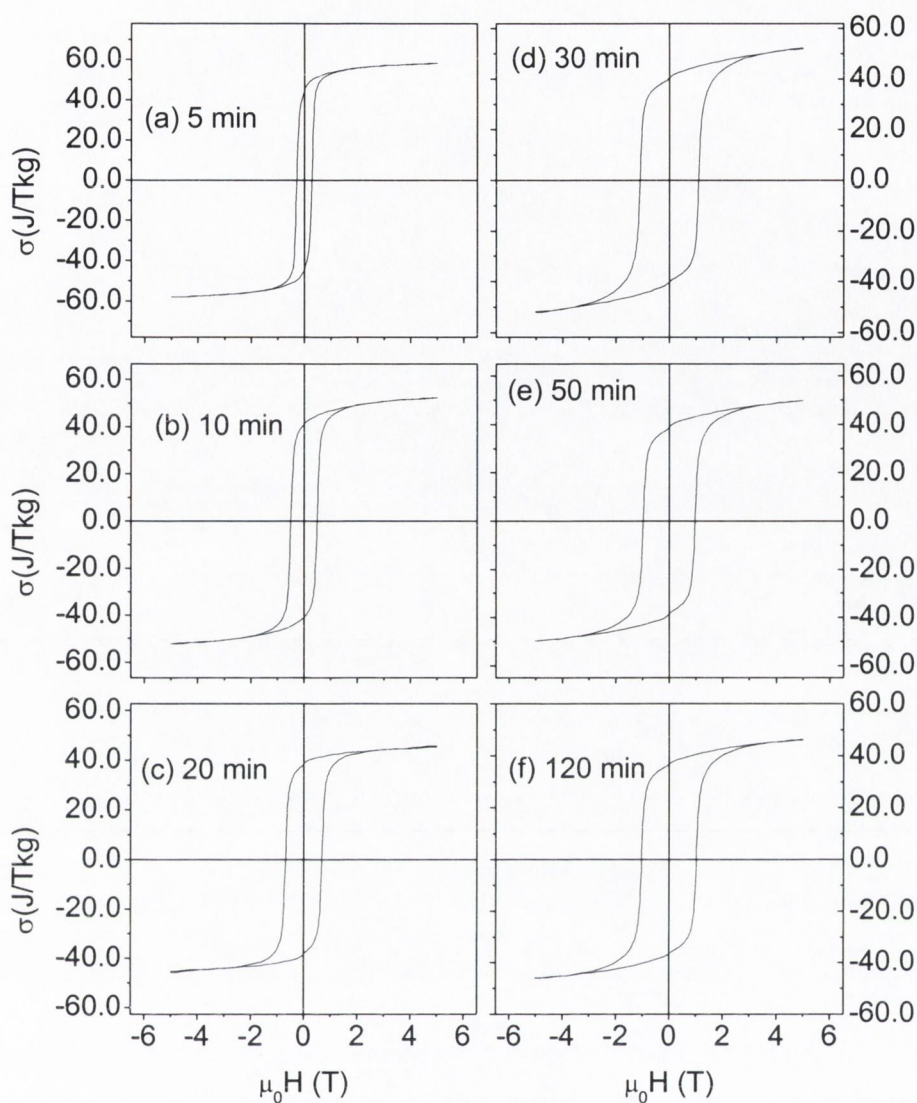


Figure 77. Out of plane room-temperature magnetic measurements showing the effect of annealing time for 8-10 μm samples annealed at 700 $^{\circ}\text{C}$. Samples were annealed for (a) 5 min, (b) 10 min, (c) 20 min, (d) 30 min, (e) 50 min and (f) 120 min.

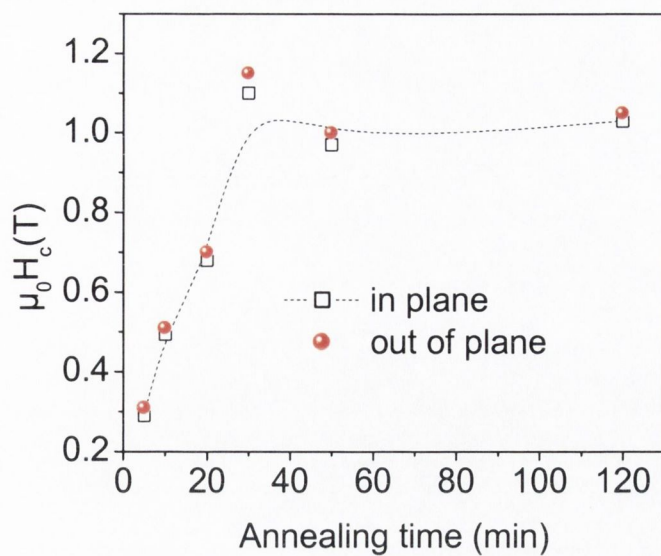


Figure 78. Coercivity dependence on the annealing time of deposits into 200 nm membranes. All samples were annealed at 700 °C.

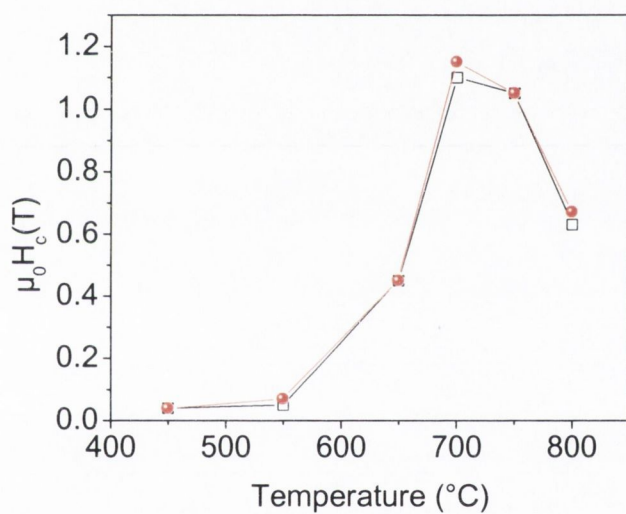


Figure 79. Coercivity dependence on the annealing temperature of deposits into 200 nm membranes. All samples were annealed for 30 min.

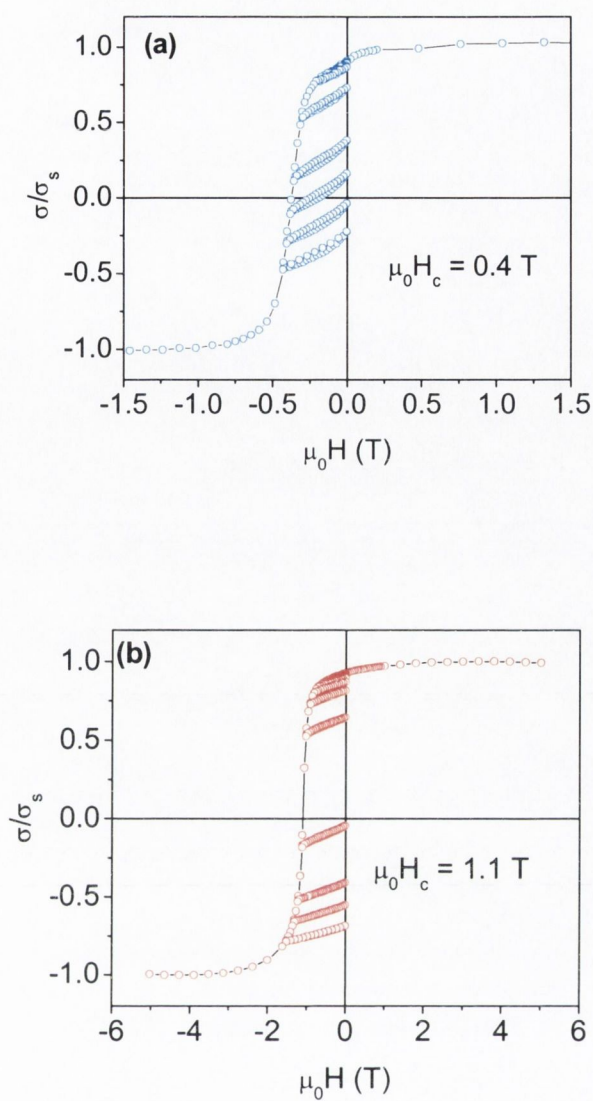


Figure 80. In-plane room-temperature recoil curve of the samples annealed at (a) 650 °C for 30 min and (b) 700 °C for 30 min.

3.3.3 Discussion

The electrodeposition from the chloride bath can be classified as normal co-deposition since the more noble elements (Pt) start to plate first as the potential becomes more negative. It is also clear that for potentials smaller than -0.7 V vs. Ag/AgCl both Co and Pt reduction are mass transport limited which can be seen in Fig. 52. In other words, changes in the potential in this range do not affect the composition of the film. The use of potentials more negative than -1.5 V faces an obstacle: hydrogen evolution. As the potential becomes more negative the pH of the solution near the electrode increases, which favours the precipitation of metal hydroxides and disrupts the film growth. Even at -0.7 V vs. Ag/AgCl there is already hydrogen evolution which is observed by the formation of bubbles on the surface of the electrode in stagnant solutions.

Another feature not shown in Fig. 52 appears in the X-ray diffraction pattern in Fig. 55, 56 and 57 corresponding to annealed deposits grown at potential of -0.725 V, -0.700 V and -0.650 V, respectively. These show that the structure depends on the plating potential going from the disordered cubic CoPt to the cubic CoPt₃ as the potential goes from -0.700 V to -0.650 V, suggesting that the composition of the films at higher potentials (>-0.650 V) is Pt rich. Therefore, at -0.650 V the deposition of Co is kinetically controlled. On the other hand, at about -0.7 V the deposition is already mass transport limited and the composition no longer depends on the plating potential. Samples electrodeposited at -0.725 V and annealed in H₂ atmosphere support this observation.

The composition of CoPt films was also controlled through bath composition, Fig. 53. The control of the composition of the films was done by controlling the partial current

density of Co. For depositions limited by mass transport, the composition of the alloy depends on the partial current according to the following equation:

$$A = I_{LA} / (I_{LA} + I_{LB}) \quad (1)$$

Where I_L , A and B are the limiting current and the species reduced at the electrode interface, respectively. I_L can be written according to the Nernst equation:

$$I_L = nFDC_0/\delta \quad (2)$$

Where n , F , D , C_0 , and δ are the number of electrons per atom, the Faraday constant, the diffusion constant, the bulk concentration of the species and the diffusion layer thickness, respectively.

Fig. 81 shows the experimental data than in the range of composition from 40 to 60 Pt at. %, the composition dependence on the CoCl_2 concentration is almost linear, thereby the composition of the films can be predicted once a calibration curve has been measured.

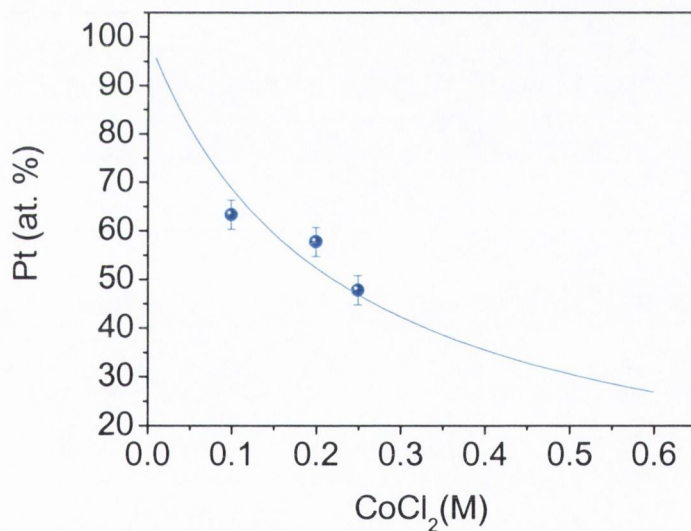


Figure 81. Pt composition dependence on the CoCl_2 concentration for films electrodeposited from chloride.

We noticed that the temperature of the bath affects the deposition rate but not the composition which we confirmed by plating a few films at different bath temperatures. The reason to have an independent composition is that the rise in the temperature increases the partial current by changing the diffusion constant according to equation (2), but the ratio of partial currents is independent of the temperature.

In the ammino-complex bath the effect of NH_4OH on the stress in the film is related to the fact that this chemical compound dissociates in water as NH_3 and OH^- . When $\text{Pt}(\text{NO}_2)_2(\text{NH}_3)_2$ is dissolved in solution it is likely that some of the NH_3 will be lost which is then balanced by the extra NH_3 coming from NH_4OH . Therefore a minimal stress is obtained from solutions containing $\text{Pt}(\text{NO}_2)_2(\text{NH}_3)_2$ with an excess of NH_3 .

The electrodeposition from an ammino-complex bath showed some important advantages over the chloride bath. The reduced stress in deposits from the ammino-complex baths allows the deposition of shiny and smooth films up to 20 μm thick compared to only a few microns thick from a chloride bath. The fact that the deposition using an ammino-complex bath can be carried out from a stagnant solution permits the deposition into porous membranes which only limits the thickness of the deposit by the thickness of the membrane.

For the chloride bath, the X-ray diffraction patterns shown in Fig. 54 reveal that all as-deposited films are nanocrystalline. Annealing is required to change the microstructure. Grain size was found to increase as samples were vacuum annealed and the films crystallised into cubic CoPt and CoPt_3 . The lattice parameter of the cubic CoPt is expected to be smaller than that of the tetragonal CoPt ($a = 3.803 \text{ \AA}$ and $c = 3.701 \text{ \AA}$). Films vacuum annealed at temperatures up to 660 $^\circ\text{C}$ only developed a crystalline structure rich in the

disordered CoPt phase Fig. 55, 56 and 57. On the other hand annealing in a H_2 atmosphere favoured the formation of the tetragonal CoPt phase shown in Fig. 58 and 59.

We observed that the coercivity of deposits is strongly correlated to the crystalline structure and does not depend on the bath chosen for the deposition. As-deposited films with nearly equiatomic composition are all magnetically soft. Comparable coercivities were found in films deposited from chloride and ammino-complex baths. The only requirements seem to be related to the formation of the tetragonal CoPt which requires the composition to be in the range 46 - 66 at. % Pt according to Fig. 70. This range of composition is in accordance with that in the CoPt phase diagram (Fig. 18) which leads to tetragonal phase (41-75 at. % Pt).

A common feature found in the X-ray data of all as-deposited films, which after annealing developed the tetragonal phase, is the appearance of a broad peak around 41.6° corresponding to (111) reflection of cubic CoPt. This can be considered as a landmark in the X-ray pattern. The coercivity dependence of films on the annealing time and temperature is related to changes in the crystalline structure of the films. The maximum values obtained are associated with the maximization of the amount of $L1_0$ CoPt in the deposits. At shorter annealing times crystallization is far from complete and the crystalline microstructure is mainly composed of disordered CoPt resulting in low coercivity. As temperature and annealing time increase the amount of the $L1_0$ phase increases resulting in higher coercivity. Finally, when the maximum conversion to $L1_0$ is obtained the coercivity reaches a maximum value.

The electrodeposition of CoPt into membranes compared to the electrodeposition of films allows the plating of thicker structures without the problem of peeling. On the other hand, as the membrane occupies space itself, and the final moment per unit volume is

smaller than that of films, resulting in a reduction of the total volume magnetization by the filling factor of the membrane, which is at least 50 % for 200 nm pore size with 50 nm spacing.

The behaviour of the recoil curves shown in Fig. 80 also supports the idea of a strong dependence of the magnetic properties on the crystalline structure of deposits. Data on samples annealed at 650 °C, Fig. 80(a), show larger reversible magnetization than those of samples annealed at 700 °C, Fig. 80(b). This is due to the fact that at 650 °C the transformation from the disordered to ordered $L1_0$ phase is far from complete. The soft disordered phase is stiffened by exchange coupling to the hard ordered phase – the exchange spring¹⁹. The exchange coupling prevents the shoulder-like behaviour in the magnetization curves. As the annealing temperature is raised to 700 °C most of the disordered phase is converted to the $L1_0$ phase and the recoil curves show a smaller reversible magnetization.

The features of the initial magnetization curves bring information about the switching mechanism of the deposits. In the case of samples electrodeposited from the chloride bath we observed that the initial curve is characteristic of nucleation-controlled magnet while for the deposits from the ammino-complex bath it is a pinning-controlled type. It is known that the switching mechanism depends on the microstructure of the deposits, however the X-ray results were not sufficient to identify the differences. A further study including transmission electron microscopy may bring more information to explain this behaviour.

We obtained the coercivity of 1.3 T which is the highest reported in the literature in the range of thicknesses studied (up to 60 μm). Typical values for sputtered CoPt films on silicon substrates are 0.7 T for a 10 nm thick²⁰ and drops to 0.6 T for 40 nm²¹. Bulk alloys as thick as 400 μm only have coercivities of 0.5 T²². Coercivity values comparable to the

values we obtained were only reported in diluted magnets where the exchange interaction between particles is reduced. In this case, 100 nm thick films composed of a mixture of equiatomic CoPt and C (30 vol. %) prepared by sputtering²³ showed 1.2 T coercivity after annealing at 750 °C. The saturation magnetization measured of about 0.85-0.95 T is in line with values reported for bulk raring from 0.8 T to 1 T.

In conclusion, the electrodeposition of equiatomic CoPt results only in the presence of the disordered CoPt phase, the ordered phase is only obtained after annealing. So far, there is not any available low temperature method or technique that allows the preparation of ordered $L1_0$ permanent magnets. If such a process should exist one may expect that this process should have a low energy state which corresponds to the ordered phase at low temperature (room-temperature). Only the disordered phase has been prepared at low deposition temperature, using vacuum techniques such as sputtering and vapour deposition.

3.4 Co rich Pt alloys

Co rich Pt alloys were electrodeposited from an electrochemical bath similar to that introduced by Bozzini et al²⁴. We electrodeposited $\text{Co}_{80}\text{Pt}_{20}(\text{P})$ on Cu, silver and alumina porous membranes and FeNi. We investigated the structure and the magnetic properties of the deposits using SEM, X-ray diffraction, EDS and SQUID magnetometer. The parameters varied were film composition, bath composition, bath temperature, current density and plating potential. We also investigated the correlation between coercivity and film structure.

3.4.1 Electrochemical bath

We prepared $\text{Co}_{80}\text{Pt}_{20}(\text{P})$ deposits by electrodeposition from a single bath and studied their structural and magnetic properties. The deposition was carried out on Cu, FeNi and membrane with 200 nm pore diameter. The electric contact of Ag or Au was made in the back of the membrane by vapour deposition. The bath composition is given in table 1. The pH of the bath was adjusted to 8 by adding small amounts of NaOH. The temperature of the bath was varied from 20 °C to 60 °C. The use of glycine ($\text{NH}_2\text{CH}_2\text{COOH}$) reduces the stress of the deposits. Di-ammonium hydrogen citrate $(\text{NH}_4)_2\text{C}_6\text{H}_6\text{O}_7$ is used as a supporting electrolyte. Cobalt sulfamate, diammineplatinum (II) nitrite ($[\text{Pt}(\text{NO}_2)_2(\text{NH}_3)_2]$) also known as Pt p-salt, and sodium hypophosphite were used as sources of Co, Pt and P respectively.

Films as thick as 50 μm , shown in Fig. 82a, were electrodeposited from a bath at 40 °C after passing a constant current density of 20-30 mA cm^{-2} for 9-10 hours. The deposition rate was found to be 5-6 $\mu\text{m h}^{-1}$. This optimum temperature was found to result in deposits that stick very well to all substrates studied. Also at this temperature, the insulating coating (varnish) used on one side of the electrodes is chemically stable. At temperatures above 45 °C the varnish start to melt and react with the solution. Additionally, the effect of increasing temperature was found to diminish H_2 inclusions in the deposits and therefore reducing the stress in the films.

Table 1. Optimised bath composition to electrodeposit $\text{Co}_{80}\text{Pt}_{20}(\text{P})$ films.

Starting reactants	Concentration (M)
$[\text{Pt}(\text{NO}_2)_2(\text{NH}_3)_2]$	0.01
$\text{Co}(\text{NH}_2\text{SO}_3)_2$	0.1
$(\text{NH}_4)_2\text{C}_6\text{H}_6\text{O}_7$	0.1
$\text{NH}_2\text{CH}_2\text{COOH}$	0.1-0.2
$\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$	0.1

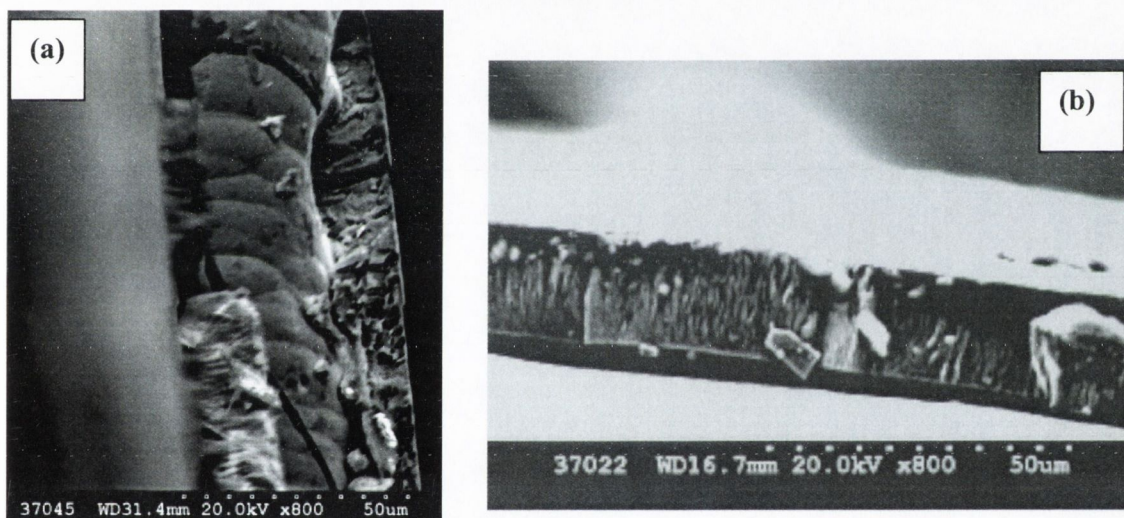


Figure 82. (a) Cross section of $\text{Co}_{80}\text{Pt}_{20}(\text{P})$ films electrodeposited for 9-10 hours showing the thickness of the deposit. (b) Cross section of CoPtP films showing that the thickness is uniform over large areas, the deposition was carried out for 210 min and the substrates are FeNi .

The electrodeposition into membrane templates was carried out with current densities ranging from 20-30 mA cm⁻², illustrated in Fig. 83. When higher current densities were used the membrane was found to break during the deposition. The membrane template was sometimes removed by using a solution containing 3 M NaOH at 60 °C. The back contact made of Au or Ag helps to keep the wire structure in place.

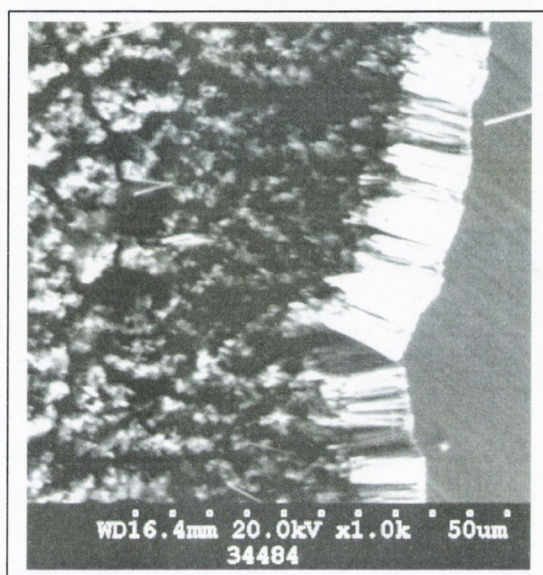


Figure 83. Co₈₀Pt₂₀(P) electrodeposited at 20-30 mA cm⁻² for 2 hours into alumina membrane template.

3.4.2 Deposit composition

The dependence of the deposit composition on Pt p-salt concentration ranging from 4 mM to 20 mM was investigated and the results are shown in Fig. 84. Films were electrodeposited on Cu substrates and the deposition took place from a bath at 40 °C using a constant current density from 20-30 mA cm⁻². At these current densities, the reaction rates of both Co and Pt are mass transport controlled. Therefore, changes in potential or current

density do not change the rate of reaction and do not affect the deposit composition. On the other hand, the cobalt content diminishes as the concentration of Pt p-salt increases. Current densities ranging from 20-50 mA cm⁻² were found to have little effect on the composition. The composition of the membrane deposits is the same as the films for the same range of current densities. The content of P in the films is about 3 at. % and was not affected by the changes in Pt concentration.

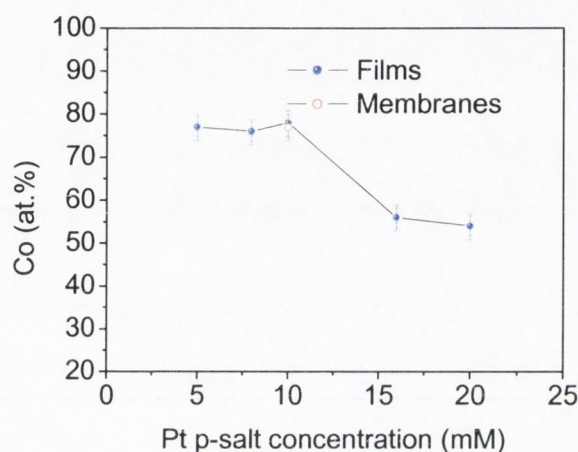


Figure 84. Co content (Co/(Pt+Co)) of the CoPt(P) deposits vs. Pt p-salt concentration.

3.4.3 Structure of the deposits

The structure of Co₈₀Pt₂₀(P) deposits was investigated using X-ray diffraction. The diffraction patterns of samples deposited at different potentials into membranes with Au back contacts are shown in Fig. 85. The structure does not depend on the potential or current density ranging from 18-30 mA cm⁻². The diffraction pattern is close to that of hexagonal Co. The shift of the peaks to the left suggests a change in the lattice parameter compared to the standard values ($a = 0.2503$ nm, $c = 0.406$ nm).

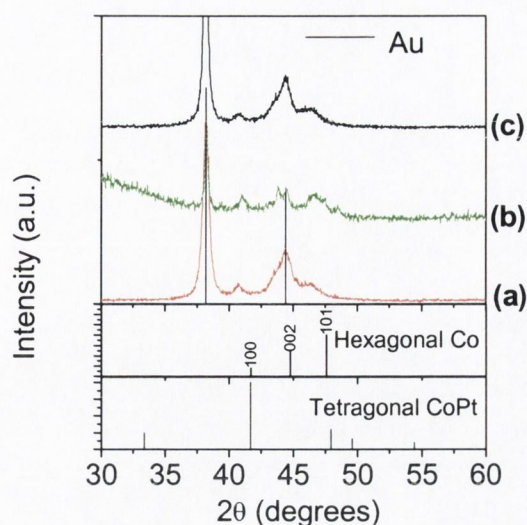


Figure 85. X-ray diffraction patterns of $\text{Co}_{80}\text{Pt}_{20}(\text{P})$ deposited into membrane templates at (a) -4 V (18 mA cm^{-2}), (b) -5 V (24 mA cm^{-2}) and (c) -6.5 V (30 mA cm^{-2}).

The effect of Pt p-salt concentration on the structure of $\text{CoPt}(\text{P})$ is shown in Fig. 86. At low Pt concentrations (5 and 8 mM) the main peak present is around 40.5° which matches Co_2P . As the concentration of Pt p-salt increases this peak shifts towards higher angles. Additionally, for the 10 mM bath, two other peaks appear at 44° and 47° . For higher concentrations of Pt only a very broad peak at around 41.8° can be seen. For samples electrodeposited from the bath containing 10 mM Pt p-salt, there is a peak near 44° which is very close to standard hexagonal Co and does not match the CoPt phase. It is likely that the alloy is formed by a combination of hexagonal Co and Co-Pt solid solutions rather than tetragonal CoPt. The formation of a solid solution of Co-Pt is supported by the phase diagram of CoPt (see section 1.4).

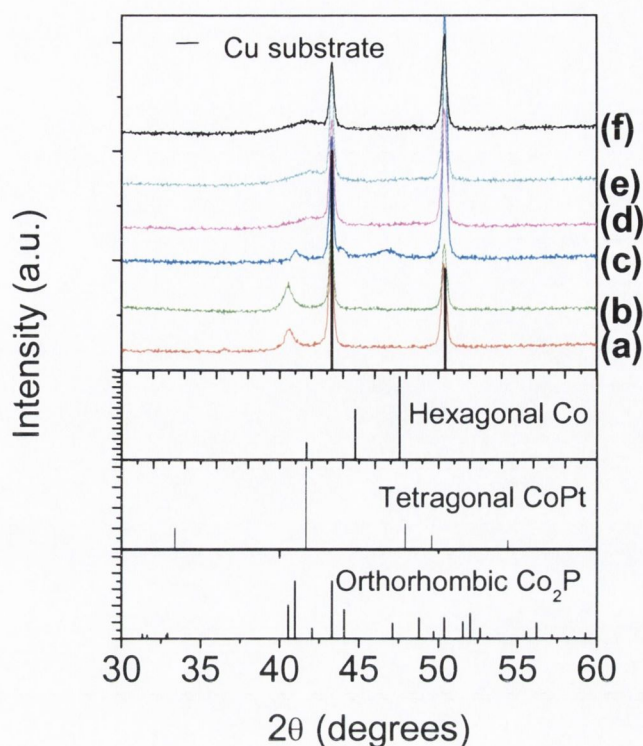


Figure 86. X-ray diffraction patterns of samples electrodeposited from CoPt(P) baths containing (a) 5, (b) 8, (c) 10, (d) 12, (e) 16 and (f) 20 mM of Pt p-salt. The phases that have the closest reflections to the experimental data are in the lower part of the picture.

The composition of the deposits is shown in Fig. 84.

3.4.4 Magnetic properties of electrodeposited $\text{Co}_{80}\text{Pt}_{20}(\text{P})$

The magnetic properties of thick films were studied using a 5 T SQUID magnetometer. Room-temperature magnetization measurements were carried out on 50 μm thick as-deposited $\text{Co}_{80}\text{Pt}_{20}(\text{P})$ films on Cu as shown in Fig. 87. The films were electrodeposited from the bath containing 10 mM of Pt p-salt at 40 °C. The initial magnetization curve is

characteristic of a pinning type magnet. Coercivity was found to be 0.35 T when measured out of plane of the films and 0.26 T in plane of the film. Saturation magnetization in the range of 1.1-1.3 T was measured out of plane of the films with squareness 0.9-0.95.

The coercivity dependence on the Pt concentration is shown in Fig. 88. Films were electrodeposited with a current density of 22 mA cm^{-2} and the maximum coercivity was obtained from baths containing 10 mM of Pt p-salt.

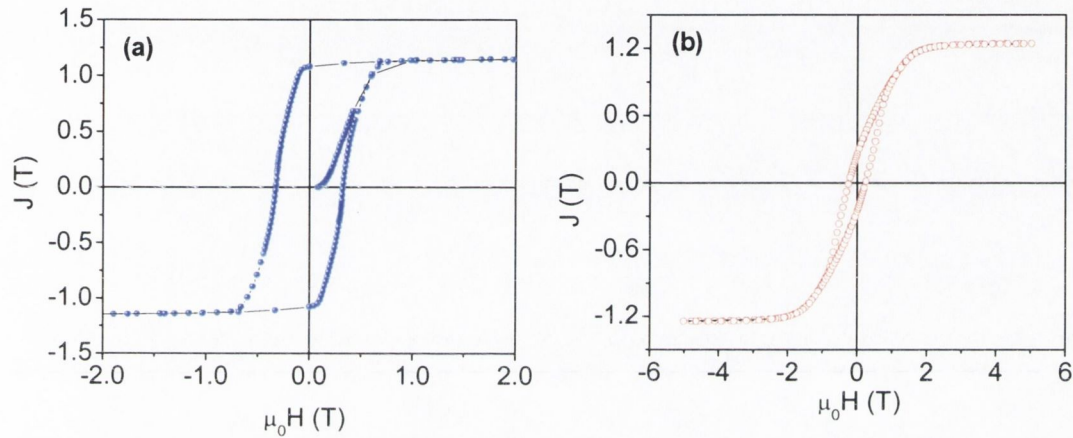


Figure 87. (a) Out of plane and (b) in plane room-temperature magnetization measurements of $\text{Co}_{80}\text{Pt}_{20}(\text{P})$ thick films electrodeposited at 40°C .

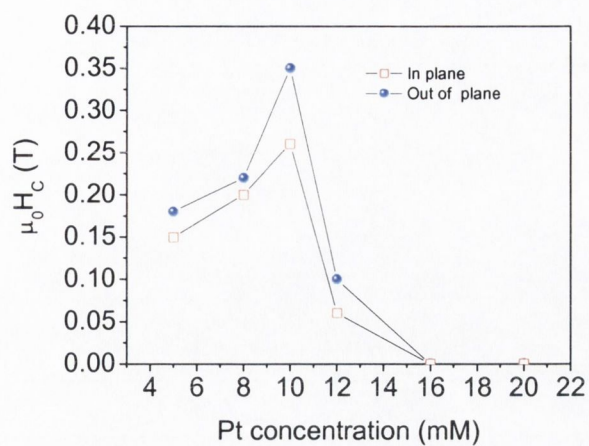


Figure 88. Room-temperature out of plane and in plane coercivity dependence on the Pt *p*-salt bath concentration. Films were electrodeposited at 22 mA cm^{-2} .

In plane recoil curves were measured for the sample showing the highest coercivity and is shown in Fig. 89. The recoil curve shows that there is a big reversible contribution to the magnetization at fields around the coercivity.

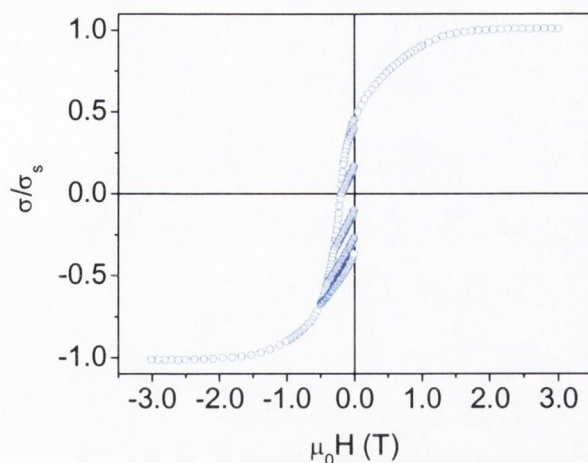


Figure 89. In plane room-temperature hysteresis loop measurement showing the recoil curve of $\text{Co}_{80}\text{Pt}_{20}(\text{P})$ on Cu substrate.

Room-temperature magnetic measurements of the deposits into membrane templates from the bath containing 10 mM of Pt p-salt at room-temperature were also carried out. Fig. 90 shows a typical room-temperature in plane and out of plane magnetization measurement of such a deposit. The corresponding SEM picture is shown in Fig. 83.

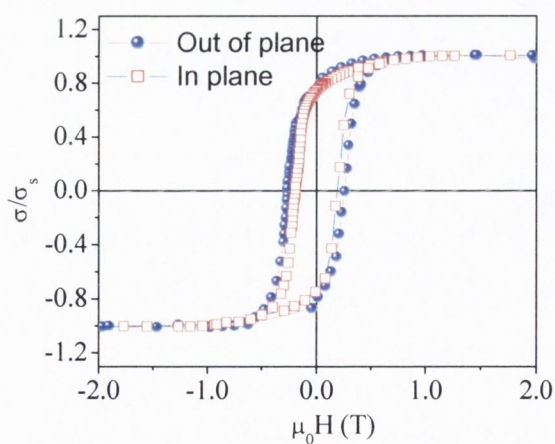


Figure 90. Room-temperature in plane and out of plane magnetization measurements of $\text{Co}_{80}\text{Pt}_{20}(\text{P})$ deposited into a membrane template. The in plane and out of plane coercivities are 0.18 T and 0.25 T respectively.

The dependence of the coercivity on the plating potential for the membrane deposits is shown in Fig. 91. The coercivity changes very little in the range of potential/current density studied which may be related to the fact that the composition does not change in this range.

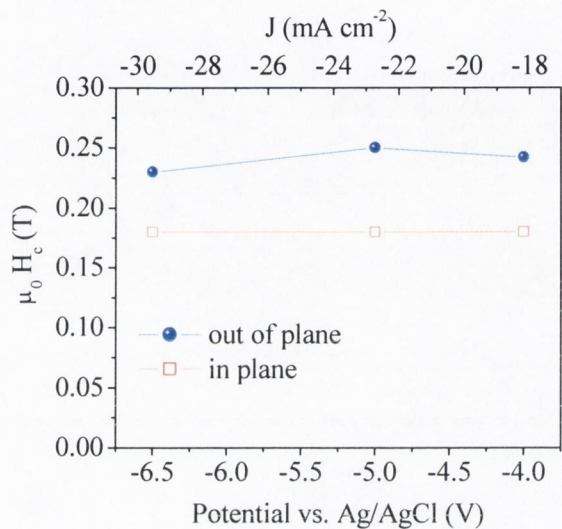


Figure 91. Dependence of coercivity on potential for $\text{Co}_{80}\text{Pt}_{20}(\text{P})$ deposits into porous alumina membranes.

3.4.5 Discussion

Cracks and peeling off from the substrate are some of the characteristics that can be directly related to film stress. The stress is associated with the incorporation of H_2 , N_2 gases and metal hydroxide during the deposition process. The effect of increasing temperature on the electrochemical bath is to reduce the concentration of H_2 near the electrode, higher bath temperatures diminish the solubility of the gases in solution and enhance diffusion.

Consequently the contribution of the incorporation of these gases is reduced and therefore the stress in the films. The optimum deposition temperature was found to be 40 °C. This takes into account the chemical stability of the coating polymers used on the electrodes.

The coercivity dependence on the composition of the deposit shows a maximum at around 10 mM of Pt p-salt in the bath (Fig. 88). Additionally, the X-ray diffraction patterns show that around this composition the main phase present in the deposits is hexagonal Co metal. When put together, these facts suggest that the coercivity observed in the deposits is linked to the presence of the hexagonal cobalt. The addition of phosphorus to Co₈₀Pt₂₀ helps to isolate the grains and to develop coercivity without annealing. These results are in line with the finding by Cavallotti et al.²⁵. Then, using the fact that coercivity is due to the hexagonal Co phase, and assuming the case limit where the exchange interaction between grains is negligible, one can calculate the maximum coercivity expected for Co deposits:

$$\mu_0 H_c < 2 K_1 / M_s$$

Taking $M_s = 163 \text{ J T kg}^{-1}$ and $K_1 = 0.53 \times 10^6 \text{ J m}^{-3}$ for Co, we obtain $\mu_0 H_c < 0.74 \text{ T}$, which sets the maximum coercivity expected for hexagonal Co metal. The condition of negligible exchange interaction can be met in films with isolated grains. Zana et al.²⁶ reported values as high as 0.6 T for such a system prepared by electrodeposition. For compact bulk samples with strong exchange coupling a smaller coercivity is expected. The values of coercivity we obtained for 50 μm thick films are in the range of coercivity values expected. In comparison to values in the literature they represent a remarkable improvement. A comparison between the in plane and out of plane magnetization curve [Fig. 87(a) and (b)] shows that the c-axis distribution is mainly perpendicular to the plane of the film. The existence of in plane coercivity indicates that a small fraction of the c-axis is also distributed in plane of the films, which accounts for the smaller out of plane

coercivity. Also, in the recoil curve shown in Fig. 89 there is a broad distribution of switching fields which is related to the fact that the return curves to zero are not completely reversible.

Additionally, a further improvement in the coercivity is expected for films showing stronger texture. The out of plane texture is more likely to be obtained than in plane. In terms of energy, one should expect the existence of two energetic states, in plane and out of plane. If the out of plane energy is the smallest the c-axis will be preferentially distributed around this direction, otherwise the c-axis will be in plane and in this situation any orientation of the c-axis in plane is as good as any other, resulting in a distribution of the c-axis in plane of the film. Consequently, one can expect the coercivity in plane to be smaller than the maximum value that can be obtained for out of plane coercivity. This is in line with our findings for coercivity shown in Fig. 88. We attempted to create a lower energy state by applying 1.5 T magnetic field parallel to the plane and perpendicular to the plane of the film during the deposition. However, no improvements in the texture of the film were observed.

The saturation magnetization of 1.1-1.3 T is consistent with the fact that the main phase in the deposits is hexagonal Co. Using a simple dilution law for 20 at. % Pt in Co and $M_s(\text{Co}) = 1.81 \text{ T}$, one can obtain magnetization of 1.42 T, showing a good agreement with the measured values. The remaining difference between the expected values and the dilution model can be explained in terms of the formation of a Co-P nanocrystalline phase in the grain boundary which is not ferromagnetic and therefore diminishes the total magnetization.

A comparison between our results and the current literature is shown in Fig. 92. Our results set a record for thick electrodeposited CoPt(P) alloys without the need for annealing.

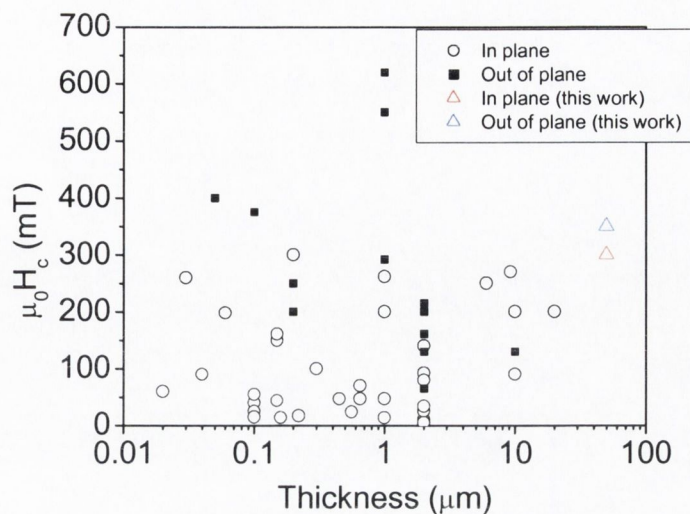


Figure 92. Values of coercivity vs. thickness found in the literature and including this thesis. The complete list of references used to construct this graph is shown in the introduction (section 1.4.1.2.1). The open and closed triangles represent our data.

3.4.6 Conclusion

We have successfully electrodeposited thick, coercive, CoPt(P) films without the need for annealing. Coercivities of up to 0.35 T were obtained with squareness 0.9-0.95. The saturation magnetization of the films ranges from 1.1-1.3 T which is in good agreement with the simple dilution model. The coercivity in the films can be explained in terms of rotation of domains in a nanocrystalline structure with weak exchange coupling.

We have demonstrated low temperature processing of permanent magnets. The films obtained have properties suitable for MEMS application and our methods and results are

currently being used in the preparation of MEMS devices by a partner company Swatch based in Switzerland.

3.5 Electrodeposited films from the application perspective

This work represents a systematic study of the electrodeposition of $L1_0$ and Co-rich [CoPt(P)] magnets where magnetic properties and thickness were pushed to their limits. As we learned through this work the magnetic properties of $L1_0$ FePt, FePd, CoPt and Co rich are strongly correlated to the microstructure of the deposits. The coercivity increases as the $L1_0$ phase content in the deposit increases. The range of composition to obtain the tetragonal phase is in accordance with the respective phase diagrams. The results are summarized in table 6.

The use of membranes for the electrodeposition leads to thick structures which are essential from the application perspective. While films are only a few microns thick, deposition into membranes is only limited by the template thickness.

The electrodeposition of $Co_{80}Pt_{20}(P)$ meets the requirement of low temperature processing and thickness of MEMS applications. The applications that will be directly affected by this are the micro-switch and the magnetic bias as well the micro/millimotor. The constraint in the motors application is the thickness rather than the processing temperature. In this view, the thick $L1_0$ electrodeposited CoPt may serve as an input. The magnetic properties of FePt are expected to be superior to those of CoPt, however further studies are necessary to obtain thick films. One area that may eventually incorporate our findings is the media recording industry since the required thickness is on the sub-micron

scale and annealing is not an issue. Also, FePd requires further studies to address its applications.

Table 6. Summary of results obtained for electrodeposited magnets.

Alloy	Composition	Saturation Magnetization (T)	Coercivity (T)	Thickness (μm)	Annealing temperature (°C)
FePt	50 at. % Pt	0.7-0.9	1.5	0.45	> 500
FePd	50 at. % Pd	1.2-1.4	0.15	12	> 500
CoPt	50 at. % Pt	0.85-0.95	1.2	60	> 500
CoPt(P)	20 at. % Pt	1.1-1.3	0.35	50	As-deposited

3.6 Bibliography

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Chapter 4

4 Application of permanent magnets in MEMS

There are few reports in the literature covering the construction and characterization of planar motors and their parts. The rotors reported were usually prepared by assembling magnetic parts cut out from sintered bulk^{1,2} or sputtered Nd-Fe-B³ magnets. The development of deformable magnetic mirrors for adaptive optics^{4,5} used in astronomy has been demonstrated using Nd-Fe-B permanent magnet pieces. Alternative techniques for the preparation of Nd-Fe-B are currently being tested including screen printing ($M_r = 0.5$ T)^{6,7}, high deposition rate sputtering ($M_r = 1.2 - 1.4$ T)⁸, tape casting ($M_r = 0.4$ T)⁹ and arc-plasma spraying ($M_r = 0.6$ T)¹⁰.

The motion of a motor is based on the magnetic force resulting from the interaction between a magnetic field gradient and a magnetic dipole. The component in a motor responsible for producing a magnetic field gradient is the rotor. Consequently for maximum energy density it is desirable to have the biggest value of the field gradient and the maximum force which depends on the geometry of the rotor (number of poles) and on the intrinsic properties of the material used. As the number of poles per unit area increases, the poles become smaller and the interaction between them becomes important, moreover, it becomes difficult to magnetically pattern the poles using the normal method of pulse magnetization. To address the patterning and characterization issue a few important tools and techniques can be exploited: the simple magnetizing tool based in an electromagnet, magnetic pulse magnetization and a magnetic profiler. Magnetic pulse magnetization was carried out by Swatch¹. We have developed a magnetizing tool and a magnetic profiler (see section 2.7) and demonstrated their use on the preparation of rotors

¹ M²EMS is an EU project in the ICT Program.

from commercial hard magnets. We characterized pulsed field magnetized rotors based on CoPt supplied by Swatch. Additionally, we have also developed a process which we term the dual coercivity technique based on the intrinsic properties of the permanent magnet.

We have studied the planar rotor which is magnetically patterned as shown in Fig. 93. An electromagnet based magnetizing tool can be built in such way that each sector [“A” or “B” directions (Fig. 93)] is magnetized individually, as we shall see in section 4.1. The magnetic pulse magnetization was done in a single step operation by building a magnetic flux guide combined with coils which delivers the appropriated flux to each pole.

The dual coercivity method consists of preparing the poles of the rotor from material with different intrinsic coercivities (see Fig. 94). For instance let us say that the sector “A” has a smaller coercivity (H_{cA}) than sector “B”, if an external magnetic field larger than H_{cB} is applied perpendicular to the rotor both sectors “A” and “B” will be magnetized in the same direction. Now if the field is reversed to a value between H_{cA} and H_{cB} then only the sector “A” will have the magnetization reversed. This leads to a magnetic pattern with neighbouring sectors having opposite magnetization.

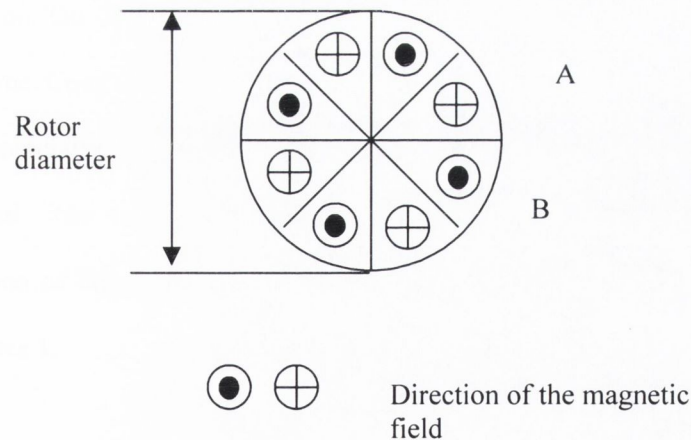


Figure 93. Typical magnetic configuration of a multipole planar rotor.

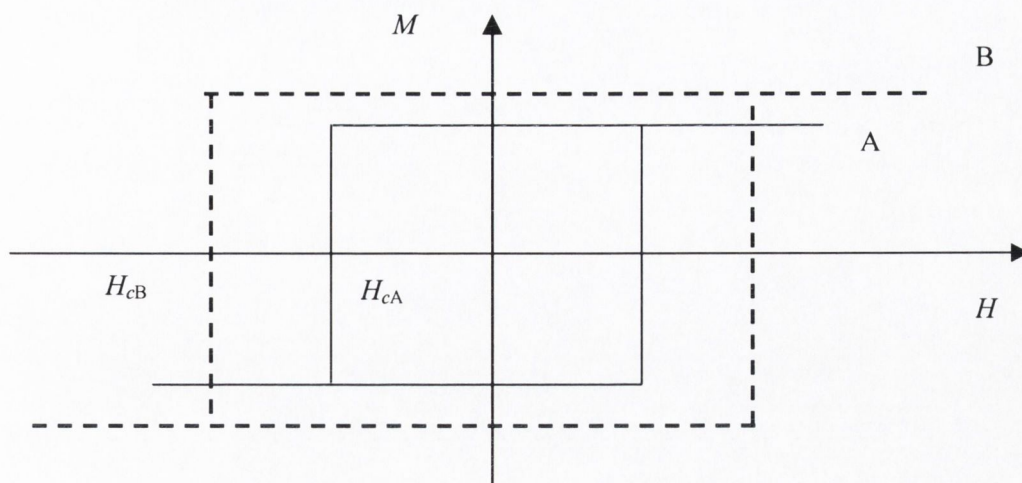


Figure 94. Hypothetical hysteresis loops for a feasible material that can be used in the rotor showed in Fig. 93.

Among the three devices described in the introduction, the bias magnet, the magnetic switch and the rotor, we concentrated on the rotors due to the close collaboration with Swatch, an industrial partner in the EU-funded M²EMS project. The material we incorporated in magnetic switch and the magnetic bias is CoPt(P) prepared by electrodeposition. On the other hand the thickness of the deposits for rotors is really a challenging issue. Commercial Nd-Fe-B and CoPt were used to solve the problem.

The dual coercivity method was tested by preparing a stripe structure using CoPt electrodeposited into membrane templates to demonstrate this technique. The electrodeposition of highly coercive CoPt was developed in our group as described in details in chapter 3.

4.1 Construction of the magnetizing tool

Here we describe the construction of the magnetizing tool which consists of specially shaped polar pieces mounted in an electromagnet. The design of the shaped polar piece, produced from soft iron, is shown Fig. 95. Before implementing this final design, we developed a 6 poles magnetizing tool which allows 3 poles to be magnetized at a time. However, due to the reduced dimension ($< 5\text{ mm}$) of the pole pieces we could not pursue this design. The final design of the pole-pieces was implemented in Physics Department workshop, Trinity College Dublin. The maximum magnetic stray field measured in a 3 mm air gap is 2 T. Usually, applying a magnetic field three times the coercivity is sufficient to magnetically saturate a sample, therefore our setup can be used for samples with coercivity of up to pieces about 0.7 T.

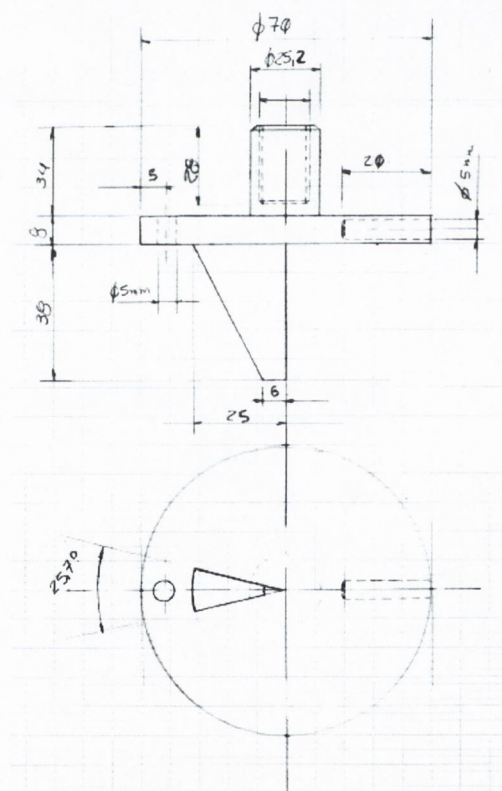


Figure 95. Polar piece design. Units are in mm unless otherwise stated.

Fig. 96 shows the fully assembled electromagnet tool. The magnetized tool can be operated continuously with the maximum applied field of 2 T.

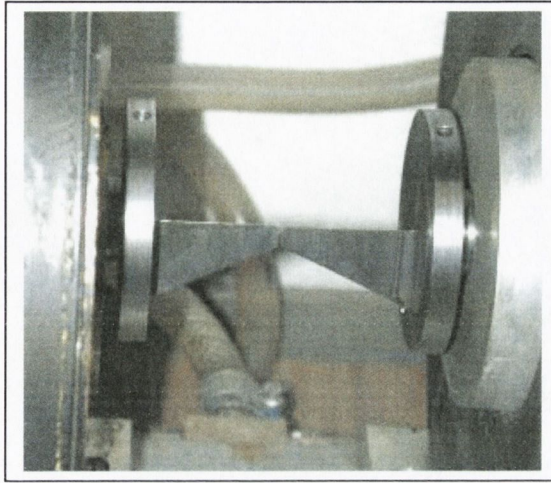


Figure 96. A single set of polar pieces utilized to magnetically pattern rotors.

4.2 Magnetizing and profiling rotors

4.2.1 Rotors magnetized using pulsed field

Swatch Company supplied several CoPt rotors cut into 12 poles and magnetized by a pulsed field in 6 (with and without a magnetic shunt) and 12 magnetic poles (without shunt). The magnetic shunt, made from the soft material FeNi, has the same shape as the rotor. The bulk magnetic properties of CoPt rotors were characterized using a 5 T SQUID magnetometer at room-temperature. Coercivity is 0.6 T and a remanence is 0.82 T. Fig. 97 shows the magnetic profile recorded using the magnetic profiler and Fig. 98 shows a

photograph of the rotor. The effect of the shunt is to enhance the stray field as shown in Fig. 97(b). A summary of stray field measured for these rotors and field gradient is shown in table 1.

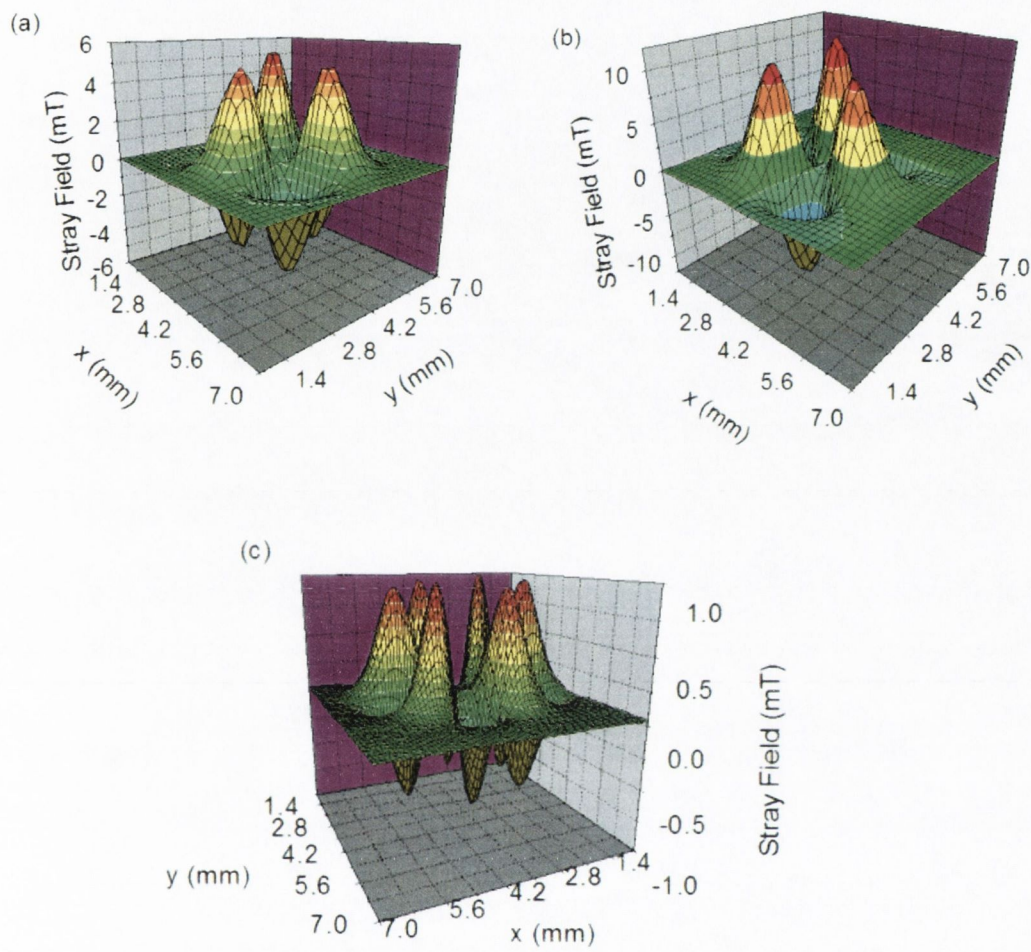


Figure 97. Magnetic profile of magnetized (a) 6 poles, (b) 6 poles with shunt and (c) 12 poles rotors.

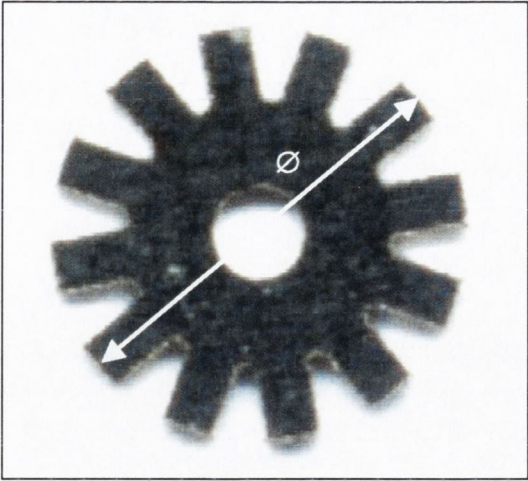


Figure 98. CoPt rotor 200 μm thick and 5 mm in diameter ($\varnothing$) supplied by the Swatch Company.

Table 1. Maximum stray field measured out of plane of the rotor.

Type	Rotor number	Maximum (minimum) stray field (mT)	Maximum field gradient (T m^{-1})
6 poles without shunt	1	3.6(-4.7)	3.7
	2	4.8(-5)	4.4
	3	5.3(-5.1)	4.6
6 poles with shunt	4	10(-10.6)	9.1
12 poles no shunt	5	0.9(-0.81)	2.0

4.2.2 Rotors magnetized using the magnetizing tool

We have successfully magnetized Nd-Fe-B rings, made of bonded Nd-Fe-B powder, into 12 poles as illustrated in Fig. 99. The rings were manufactured by the Sanhuan Magsound Company in China. Two sets of rings were characterized, with dimension (outer diameter, inner diameter, thickness) = (10, 7.5, 0.7) mm and (O, I, T) = (7, 5, 0.5) mm. The intrinsic magnetic properties were measured using the SQUID magnetometer. Room-temperature coercivity and remanence are 1.32 T and 1.2 T. Each pole was magnetized one at a time with a magnetic field of 2.0 T. Fig. 99(a) shows a Nd-Fe-B bonded ring and Fig. 99(b) the magnetic contrast seen through magnetic paper based on ferro-fluid.

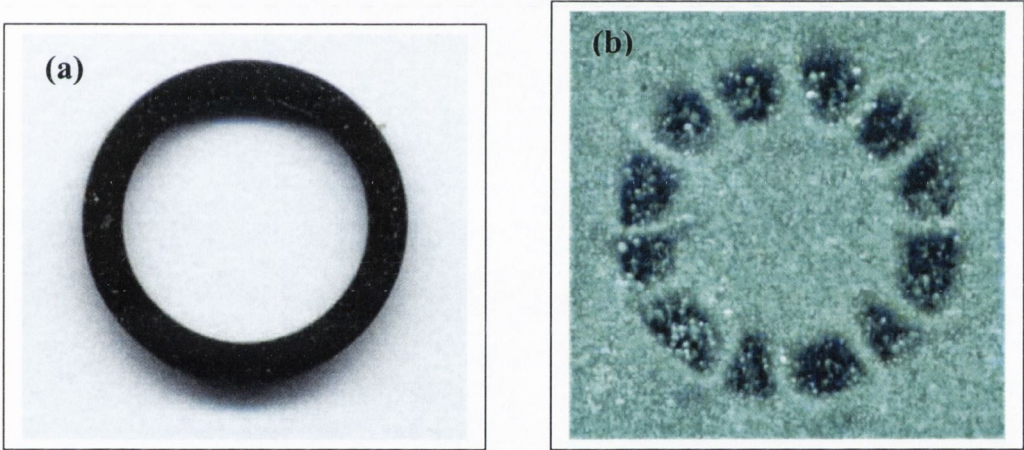


Figure 99. (a) A bonded Nd-Fe-B ring and (b) its magnetic contrast seen through a magnetic paper after magnetizing into pole pattern.

The magnetic profile of the Nd-Fe-B bonded ring is shown in Fig. 100. A stray field of 84 mT peak to peak was measured for the ring with 10 mm diameter and 56 mT for ring with 7 mm diameter, table 2.

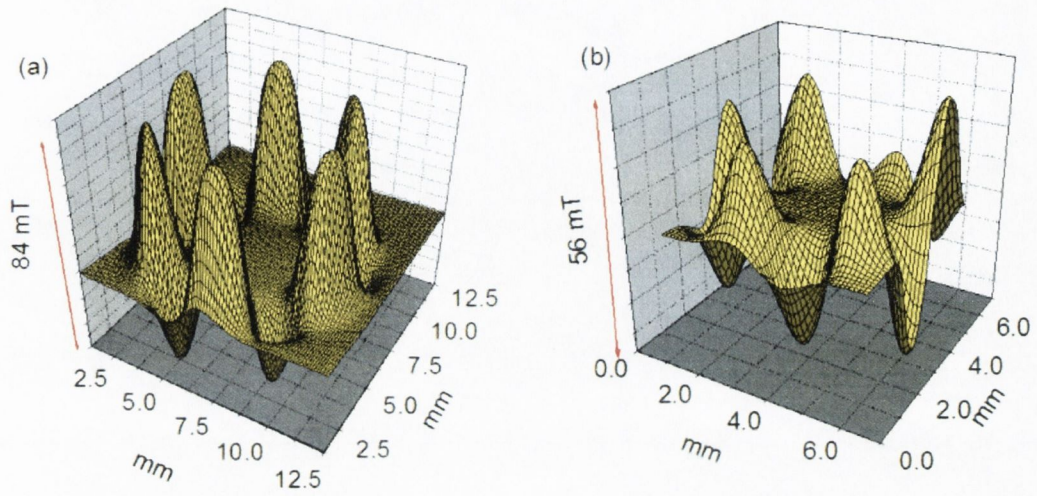


Figure 100. Magnetic profile of a 12 poles Nd-Fe-B based ring rotor of (a) 10 mm diameter and (b) 7 mm diameter.

Table 2. Stray field and field gradient of Nd-Fe-B ring magnetized using the magnetizing tool.

Dimensions (outer diameter, inner diameter, thickness) (mm)	Rotor number	Maximum/minimum stray field (mT)	Maximum field gradient (Tm ⁻¹)
(10, 7.5, 0.7)	1	42/-43	37.5
(7, 5, 0.5)	2	26/-25	22.6

4.2.3 Dual coercivity method

4.2.3.1 Electrodeposited CoPt

Two magnetic structures were investigated: a single set of stripes and double set of stripes with dual coercivity. We have used stripes here because it is easy to pattern them magnetically and the findings can directly be compared and extended to rotors.

Dual coercivity is a technique we have developed to prepare magnetic structures. The idea is to prepare magnetic stripes with material having two different coercivities so that the magnetization of a stripe can be inverted without affecting the neighbouring stripe. We have investigated two methods to obtain the dual coercivity in CoPt. First one is based on the fact that the coercivity of CoPt depends critically on the composition of the alloy and the second one based on the effect of annealing temperature on the room-temperature coercivity.

Unfortunately, we were not able to obtain a set of double stripes with different intrinsic coercivities by tuning the annealing time, since the membrane is very fragile. The preparation process requires the sample to be annealed twice. Residual stress is introduced in the membrane after the first annealing treatment preventing plating of the second set of stripes. In all our attempts, the sample breaks during second deposition process into the membranes.

4.2.3.2 Sample preparation

CoPt was electrodeposited from the ammino-complex bath and the details of the bath and annealing conditions were described in the chapter 3. The stripe pattern was obtained by using a shadow masking technique and the Ag film was used as a working electrode.

The two nearly equiatomic CoPt deposits were electrodeposited into each set of stripes from two different baths to obtain different coercivities (0.6 and 0.9 T) and were annealed under vacuum at 700 °C for 30 min. The stripe pattern consists of 60 μm long CoPt electrodeposited into a membrane template with 200 nm diameter pores. Fig. 101 shows the back contacts made for the electrodeposition of CoPt, each stripe was individually connected and selected during the deposition. Each wire connecting to the stripe in the membrane is also made of Ag. We have also deposited well-separated stripes from a single bath as shown in Fig. 102.

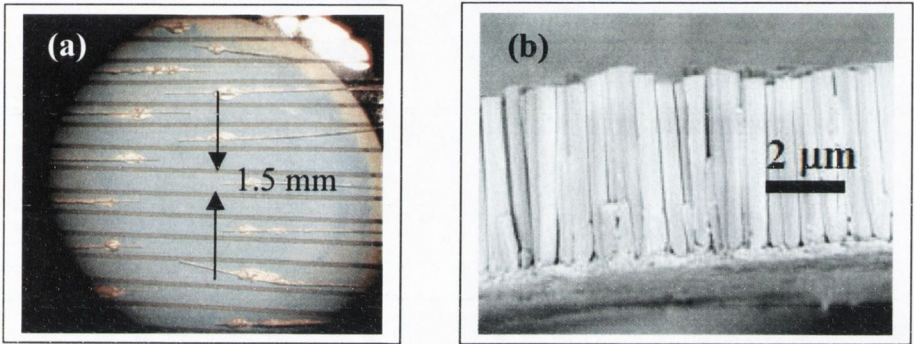


Figure 101. (a) Contact side of a membrane template and (b) cross section of CoPt deposited for a short period of time after the removal of the membrane template.

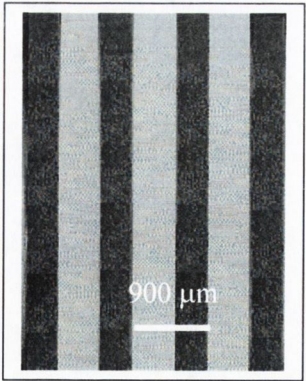


Figure 102. Top view of the set of stripes electroplated in a membrane template.

4.2.3.3 Magnetic profile

Samples having dual coercivity were magnetized with field of 5 and 0.75 T using the process described in section 4 and then characterized using the magnetic profiler as illustrated in Fig. 103. Through this technique we obtained an alternating magnetic pattern.

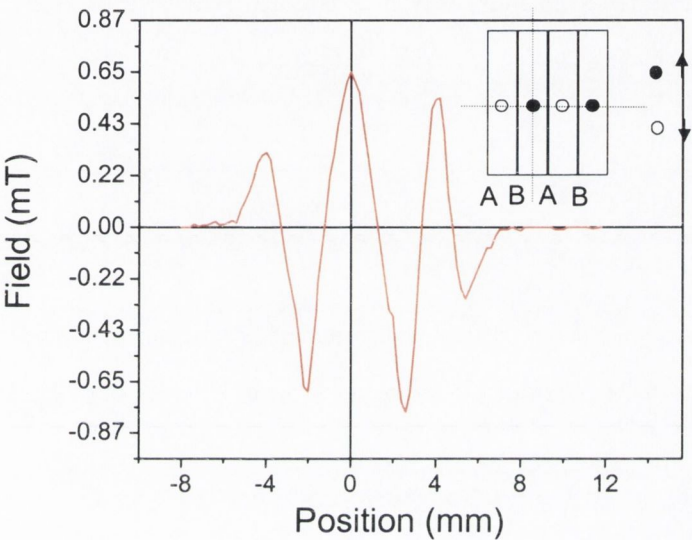


Figure 103. The magnetic profile of four stripes with alternating magnetization. “A” and “B” denote two groups of stripes with different coercivities.

We also used a single set of stripes with spacing comparable to the width. Here we magnetized all the stripes in the same direction with a 5 T field. Due to the dipolar characteristic of the stripes we have observed a negative stray field in the region between stripes as illustrated in Fig. 104.

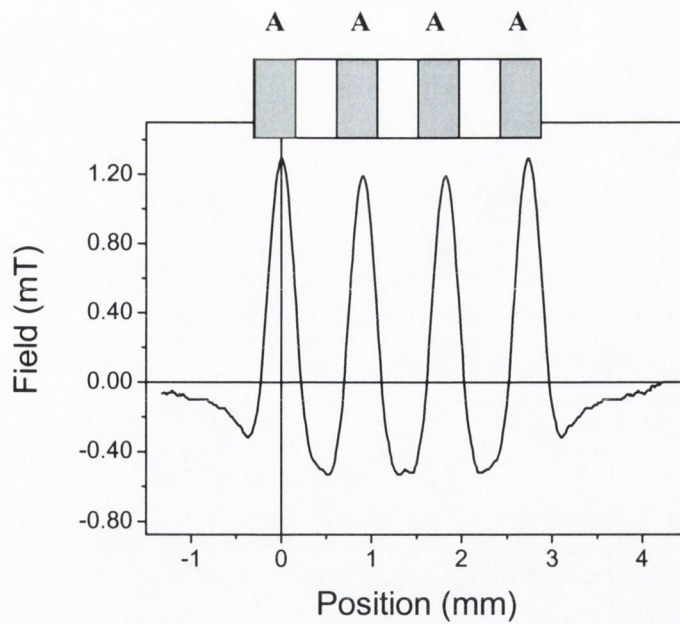


Figure 104. Stray field measured on a set of four stripes with spacing in between.

The use of a magnetic structure with two different compositions (dual coercivity) does not require the concentration of flux as required in the techniques involving the electromagnet tool and the pulsed field technique to produce magnetic patterns. The major advantage of this technique is that it can easily be extended to the micro and sub-micro scale since reversing the magnetization for one set of stripes is independent of the other.

4.3 Discussion

Topfer et al¹¹ reported on the characterization of multipoles made of Nd-Fe-B ($\mu_0 M = 1.16$ T) plate with dimensions $50 \times 50 \times 1$ mm³. They prepared a magnetic pattern with alternating magnetization using a 2 mm pitch size by pulsed magnetic field. The maximum stray field obtained was 0.35 T and maximum field gradient was 175 T m⁻¹. The stray field and field gradient were found to diminish with pitch pole size, for 1 mm

pitch pole size they measured a maximum stray field of 0.14 T and maximum field gradient 140 T m^{-1} .

Rotors made of CoPt are less effective to produce higher field gradients than Nd-Fe-B based rotors. However with the use of the FeNi shunt in CoPt rotors, the magnetic flux is concentrated and the stray field becomes comparable to our values for bonded Nd-Fe-B powders. In addition, the values we have obtained are smaller than those reported in the literature by Topfer et al. This is probably due to the fact that our samples are not fully saturated. They used a magnetizing tool made of parallel copper wires and pulsed currents of 39.3 kA for 120 μs , giving an estimated field of 7.5 T at a distance of 1 mm from the wires. The Nd-Fe-B samples in our studies have a coercivity of 1.3 T. The maximum applied magnetic field is only 2 T in our case which is clearly insufficient to fully saturate our samples. The CoPt samples supplied by Swatch were magnetized by a 2.2 T magnetic pulse.

An alternative process, which would allow the use of a relatively small magnetic field to fully saturate the material, is to explore the dependence of coercivity on the temperature or the Curie temperature of the material (T_C). By heating and cooling a magnetic material above the T_C under a magnetic field it is possible to saturate the sample with a relatively small field, typically few mT. For example, $\text{Nd}_2\text{Fe}_{14}\text{B}$ ¹² has $T_C = 312^\circ\text{C}$ and the tetragonal CoPt has $T_C = 567^\circ\text{C}$. To illustrate the use of the coercivity dependence on temperature, Nd-Fe-B has a temperature coefficient of coercivity^{6,7} of about $-0.37\% (\text{K})^{-1}$, therefore one can expect to have the coercivity reduced by half of its original value at room-temperature when magnetizing at 155°C . This would facilitate our magnetizing tool to completely saturate the samples. Another alternative is to use magnets with a nucleation type initial magnetization curve as illustrated in Fig. 62. Then a field of less than 3 times coercivity would be required.

The magnetic field can be calculated using the pole distribution according to the following equation¹³:

$$B(r) = -(1/4\pi) \{ \int \nabla \bullet M(r-r') / |r-r'|^3 d^3r' - \int M \bullet n(r-r') / |r-r'|^3 d^2r' \} \quad (1)$$

For a uniformly magnetized material $\nabla \bullet M = 0$ and only the surface contribution counts. Even then, there are only a few systems where the surface integral can be analytically solved. An example is the rod shown in Fig. 105 where the magnetic field can be calculated as:

$$B_x = B_r/2 \{ (L+X)[R^2+(L+X)^2]^{-0.5} - X(R^2+X^2)^{-0.5} \} \quad (2)$$

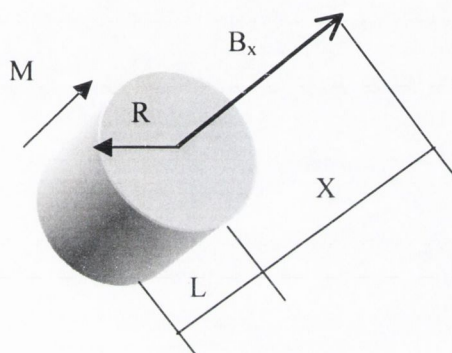


Figure 105. Magnetic field B_x due to a rod uniformly magnetized along its length.

Taking $B_r = 1$ T, $X = 0$, $R/L = 5$ we obtain $B_x = 0.1$ T at the centre of the circular surface of the rod. This shows that the stray field strongly depends on the geometry of the magnet. For a rod with small length the stray field is quite small compared to the remanence. Here, we use a program called “magnetic solver” by James Hilton² to calculate the expected profile for the stripe geometry. The program is based on equation (1). Fig. 106 shows a (a) single stripe and the magnetic field (b) B_z calculated along of

² Mr James Hilton is currently pursuing his PhD in the Physics Department, Trinity College Dublin.

the line A-B. It can be noticed that a single stripe shows a magnetic field B_z which has maximum in the center of the stripe and inverted sign near the edges of the stripe. The B_z profile of a single stripe can be used to determine the shape and intensity of a series of parallel and anti-parallel stripes. If the magnetization is pointing in the opposite direction, the intensity should be multiplied by -1. The profile is a linear function of the magnetization, therefore the magnetization and the stray field increase in the same manner.

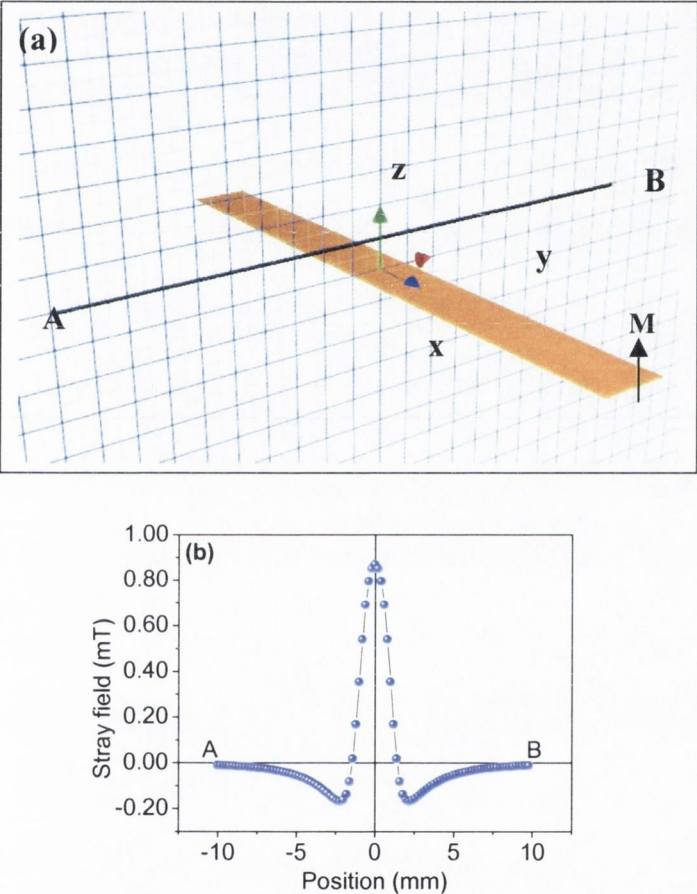


Figure 106. (a) A single stripe with dimensions $L = (20, 2, 0.012)$ mm and its (b) B_z field along the line A-B for a magnetization $M = (0, 0, 0.45)$ T.

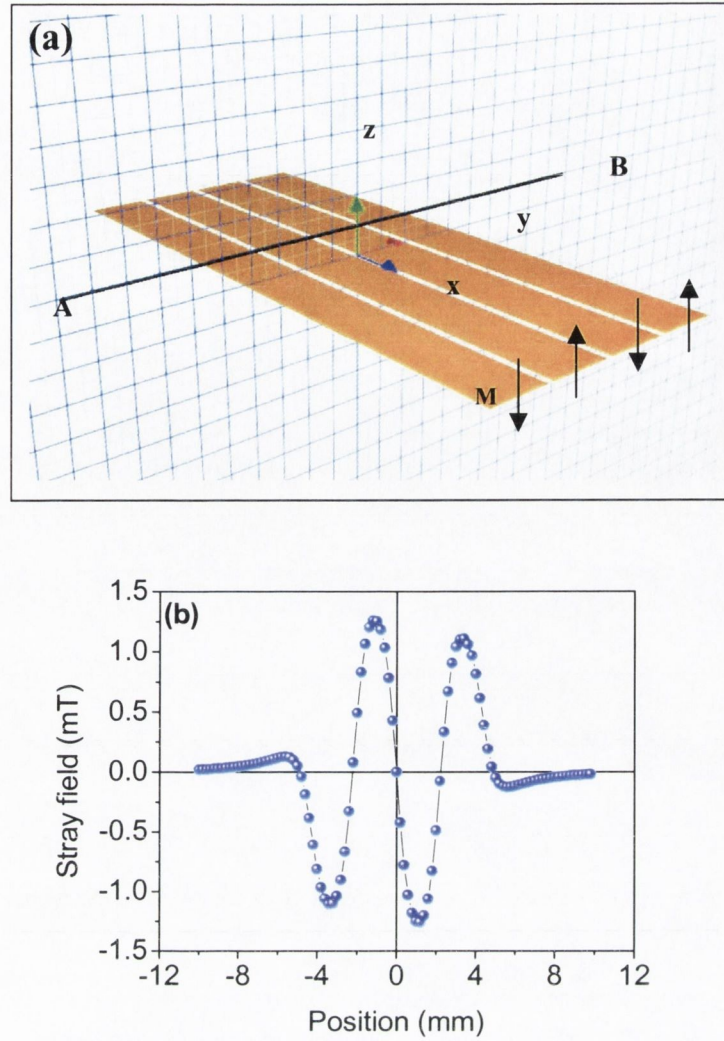


Figure 107. (a) A set of four stripes with alternation magnetization and each stripe having dimensions $L = (20, 2, 0.012)$ mm and the (b) B_z profile along of the line A-B for a magnetization $M = (0, 0, \pm 0.45)$ T.

The B_z profile of a set of 4 stripes is shown in Fig. 107. There are four main peaks which correspond to the center of the stripes and two small ones corresponding to the tail of the single stripe shown in Fig. 106. The profile was calculate using the “magnetic solver” program. The same profile can be obtained by using the superposition principle and the profile of one stripe.

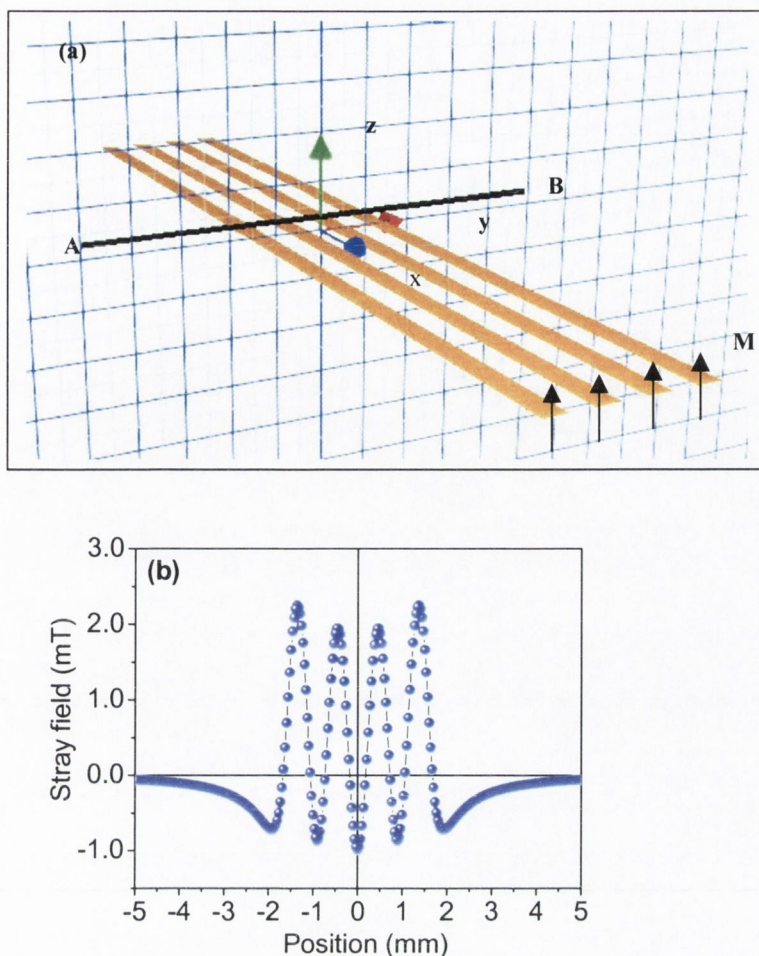


Figure 108. (a) A set of four stripes with spacing as large as the stripe width and magnetization $M = (0, 0, +0.45)$ T and the (b) B_z profile along of the line A-B. Each stripe has the dimensions $L = (20, 0.45, 0.012)$ mm.

Fig. 108 shows the magnetic B_z profile for a set of 4 stripes magnetized in the same direction with spacing as large as the stripe. An asymmetric alternating stray field is obtained in this configuration.

A direct comparison between the measured stray field of samples prepared from electrodeposited CoPt in the two structures, double set of stripes (Fig. 103), single set

(Fig. 104), and the calculated profiles shows a good agreement. The shape of the profiles measured is similar to the calculated ones. Also, the intensity of the stray field in the simulation is very close to those measured experimentally. The differences could be associated with the deviation in thickness, the estimated filling factor of the membrane (0.5) and the level of saturation of the stripes.

The structure consisting of a single set of stripes is quite easy to prepare compared to the structured using the double set. The structure with single set of stripes does not require two electrodeposition steps, which need different electrochemical baths and the magnetization can be done in one step. On the other hand, deposits carried out from the dual bath allow the preparation of structures, twice as dense as the single set of stripe structure, which allows to build more compact devices.

The use of a single pair of shaped polar pieces seems to be useful to magnetically pattern structures on a small scale. It is quite difficulty to position the rotor disc relative to the magnet in reduced dimensions and the accuracy of the pattern diminishes. More precise magnetization may be obtained with a sophisticated mechanical positioning system. For intermediate dimensions, the pulse field magnetization technique seems to produce excellent results, but there is a limitation on the construction of the coils required to produce the pulse current. Finally, the technique of the dual coercivity is a novel idea and can easily be extended to micron and sub-micron scale. This is likely to lead to new ways of preparing micro-motors in a near future or another application, which makes use of field gradient.

4.4 Bibliography

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Chapter 5

5 The influence of a magnetic field on the electrochemical rest potential

It has been known for well over 100 years that the electrochemical rest potential, E_0 , of an iron electrode may be modified by a magnetic field B^1 . Only lately has the phenomenon been re-examined with a view to explaining how the shift in rest potential $\Delta E_0(B)$ can come about^{2,3,4,5,6,7,8}. The direct effect of a magnetic field on the reduction potential of ferromagnetic iron is very small, amounting to only about 0.1 mV per tesla, whereas the observed shifts can be as high as 50 mV per tesla. Different investigators have proposed quite different origins of the effect.

Smaller effects are reported for electrodes of the other ferromagnetic elements cobalt and nickel, although there is disagreement whether the shift for these elements is cathodic, anodic or zero. Various ideas have been advanced to explain the effect. The problem can be framed in terms of the question 'Which force of magnetic origin acting in the electrolyte⁹ is responsible for the shift?'. Waskaas and Kharkats^{2,3,4} reported anodic shifts for iron in a variety of different electrolytes. The largest shift in 0.8 T was 45 mV in 1 M FeCl₃. No such effect appeared for diamagnetic electrolytes such as MgCl₂ or ZnCl₂, or for non-ferromagnetic electrodes such as copper and zinc. Cathodic shifts were reported for the other ferromagnetic elements cobalt and nickel. These authors concluded that the effect was limited to ferromagnetic electrodes immersed in paramagnetic solutions. Their explanation was based on the concentration gradient force $\mathbf{F}_{\nabla c} = \chi_m B^2 \nabla c / 2\mu_0$, which arises when a uniform magnetic field acts on a non-uniform concentration of magnetic ions of molar

susceptibility χ_m such as those that exist near the electrode in a diffusion layer. Here μ_0 is the permeability of free space $4\pi \times 10^{-7} \text{ A m}^2 \text{ T}^{-1}$.

Shinohara et al. used an Aogaki cell to study the shift in rest potential of iron. They found an anodic shift of 6 mV in a field of 6 T for 0.5 M NaCl. Their explanation was based on an increase in the cathodic corrosion current, via the Lorentz force $\mathbf{F}_L = \mathbf{j} \times \mathbf{B}$ which induces magnetohydrodynamic convection on a micron scale near the electrode, their 'micro-MHD effect'.

Perov et al used a differential cell with two iron electrodes connected by a salt bridge. The magnetic field was applied to only one of them, and an effect was observed for iron (35 mV at 0.4 T in 0.16 M FeCl_3), but no effect was detected for cobalt or nickel. Their explanation involved stray fields created by domain walls in the iron, and they suggested that the effect might be exploited as a possible magnetic field sensor.

Hinds et al determined the field-dependence of the effect in a variety of electrolytes, finding anodic shifts of up to 35 mV in 1.4 T for 1 M $\text{Fe}(\text{NO}_3)_3$. They also used an AC-method of detection, which allowed them to measure small anodic shifts of the order of 1 mV for cobalt and nickel, thereby overcoming the problem of a time-dependent drift in the rest potential as the electrode surface evolves when it is immersed in an aggressive electrolyte. They proposed an explanation in terms of the magnetic field gradient force $\mathbf{F}_{VB} = \chi_m c \nabla B^2 / \mu_0$, which could act either to enhance the cathodic corrosion current or to increase the concentration of paramagnetic ions in the vicinity of the electrode. The field gradients arise from the shape or surface roughness of the ferromagnetic electrode, and in the latter case the rest potential shift may be related to the local ion concentration via the Nernst equation

$$\Delta E_0 = (RT/nF)\ln[C_0(0)/C_0(B)] \quad (3)$$

In view of these disagreements regarding the origin of the effect, we have undertaken a systematic investigation, varying the electrolyte, the pH, the ionic strength, the dissolved oxygen concentration, the electrode roughness, rotation speed, and the direction and magnitude of the applied field from 0 to 5.5 T. Moreover, we also have investigated non-magnetic electrodes in order to clarify whether the magnetically-induced shift of rest potential really is restricted to iron and the other ferromagnetic elements. Previous studies on ferromagnetic electrodes suggest that the phenomenon is linked to the corrosion current at the electrode, with the largest shifts appearing for the most corrosion-susceptible systems^{2,3,5,6,8}. We have therefore investigated several non-ferromagnetic metals which are susceptible to corrosion, and we chosen zinc ($E^\ominus = -0.76$ V SHE), which is less noble than iron ($E^\ominus = -0.43$ V SHE) and corrodes easily in an acidic environment. Electrolytes for zinc were chosen to contain either paramagnetic (Cu^{2+}) or diamagnetic (K^+) cations. Effects of a magnetic field on the corrosion pattern of a zinc crystal have been reported by Shinohara et al.

The main experimental results for iron beg a series of questions:

- does the electrode have to be ferromagnetic?
- does it have to be corroding, and if so must the corrosion be under mass transport control?
- what magnetic force(s) influence(s) the mass transport, and how do they act?

The results for Zn compared to Fe help to explain the origin of the field-induced rest potential shift.

5.1 Experimental Methods

Most of the measurements were carried out in a standard three-electrode electrochemical cell using a Solartron SI 1280B potentiostat, but in some cases the potential difference between the working and reference electrode was measured with a Keithley 195 digital voltmeter. The working electrode was normally iron, the reference electrode was Ag/AgCl or Hg/HgSO₄, and the counter-electrode, when one was required for polarisation experiments, was Pt. The cell, of volume 50 mL, could be placed between the poles of a 300 mm electromagnet with a 60 mm gap, which produced a uniform field (< 1 part in 10^4 inhomogeneity over the cell) of up to 1.5 T, or in the 105 mm room-temperature bore of a superconducting magnet, which produced a uniform field (< 1 part in 10^3) of up to 5.5 T. The leads to the cell were twisted pairs arranged to minimize induced potentials due to time-varying magnetic fields. The field orientation was horizontal in the electromagnet and vertical in the superconducting magnet. The working electrode, typically 5×5 mm², could be mounted in either orientation. Some experiments used a rotating disc electrode of diameter 6 mm, or an electrode of diameter 1 mm which could be retracted by 8 mm within a teflon shield in order to limit convection. For precise measurements of small shifts the applied field was modulated at a frequency of 0.2 Hz and the voltage determined using lock-in detection.

In the following sections, all shifts of the rest potential are for a field of 1.5 T, unless stated otherwise. Also, all the potentials are quoted relative to the standard hydrogen electrode (SHE).

5.2 Rest potential shift of ferromagnetic electrodes

5.2.1 Rest potential shift of Fe electrodes

Fig. 109 shows a typical result for iron, where the rest potential is measured as the field is switched on and off. Apart from the anodic shift, ΔE_0 , it should be noted that

- i) There is an underlying cathodic drift of order 0.02 mV s^{-1}
- ii) The magnitude of ΔE_0 does not depend on the orientation of the 1.5 T field relative to the electrode; when this is changed from parallel to perpendicular to the electrode surface for the vertical electrode in the electromagnet, there is no change of ΔE_0 which is about 35 mV, Fig. 109(a) and 109(b).
- iii) While the response when switching the field on is practically instantaneous, a relaxation process with a characteristic time of order 20 s is evident when the field is switched off, especially in the parallel configuration. The time required to bring the field up to 1.5 T or to reduce it to zero is 10 s.

Table 7 summarises the shifts measured in different conditions with the field applied parallel to the surface of the iron electrode ($B_{\parallel}$ configuration). ΔE_0 ranges from zero up to 120 mV. In view of the uncertainties in the on/off measurement, values are quoted to the nearest millivolt. All shifts are anodic. The shifts in aerated and de-aerated electrolytes are compared.

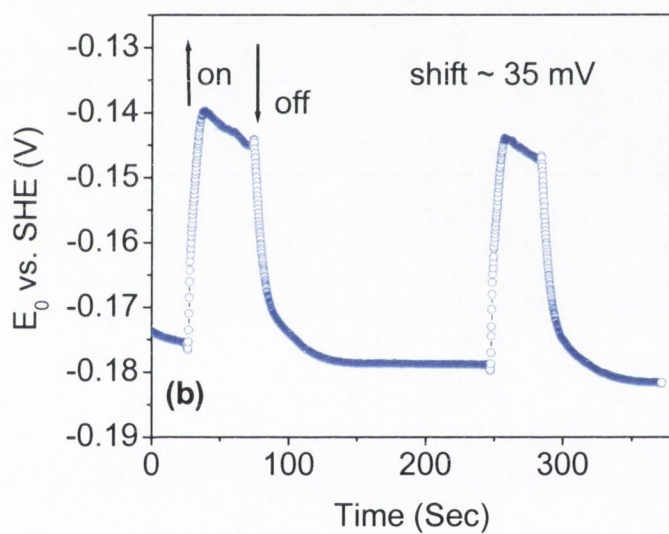
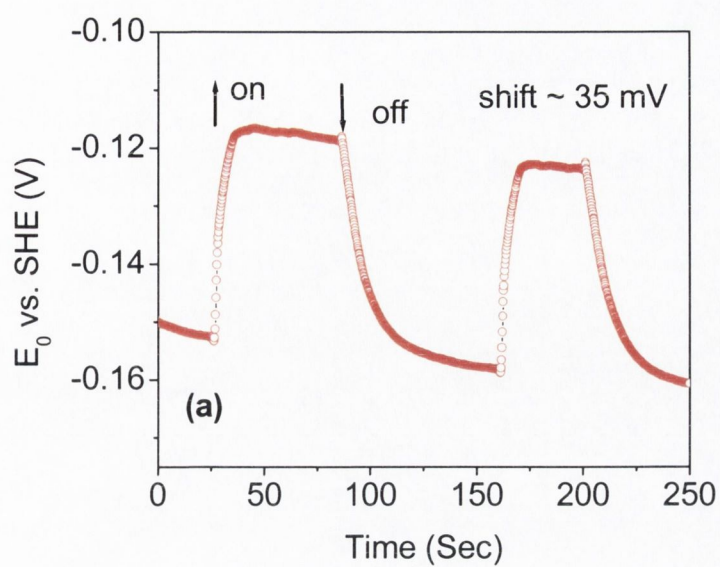


Figure 109. Shift of the rest potential of an iron electrode in 1 M $\text{Fe}(\text{NO}_3)_3$ as a 1.5 T field is switched on and off. (a) Field parallel to the electrode and (b) field perpendicular to the electrode surface

Table 7. Rest potential shift ΔE_0 measured for iron in 1.5 T in various solutions.

Solution	Concentration (M)	pH	ΔE_0 (mV)	ΔE_0 (mV) (Ar saturated)	Comments
Fe(NO ₃) ₃	1.0	1.0	35	32	
FeSO ₄	1.0	1.0	10	7	
	0.1	1.0	2	2	
FeCl ₃	1.0	0.1	12	-	
H ₂ SO ₄	0.1	1.0	2	0	
KNO ₃	1.0	1.0	25	21	smooth electrodes
	3.0	1.0	32	19	
	3.0	0.0	126	120	smooth and rough electrodes
	1.0/3.0	7.0	0	0	smooth and rough electrodes

5.2.1.1 Chemical reactions associated with the rest potential shift of Fe

We have carried out a few experiments in order to identify the chemical reactions involved in Fe corrosion. More specifically, we have studied the reactions for Fe in KNO₃ where the largest rest potential shift is observed. We have carried out the corrosion of Fe electrodes in a 1 M KNO₃, pH 0.5 solution, inside a small closed chamber and used the following equation $P = N(RT/V)$, where (RT/V) is a set-up constant, N is the number of moles and P is the pressure. The reservoir was kept at room-temperature and the pressure measured. We did not observe any change in the pressure which indicates that there is no hydrogen evolution during the corrosion meaning that the reaction $2H^+ + 2e^- = H_2$ is negligible. Changes in pressure were observed when using Fe in a HCl (pH 0.5) solution. In addition, the colour of the solution after Fe corrosion is reddish-brown which is characteristic of N₂O₄ and known as an oxidizer with MP = -10.2 °C and BP = 22.4 °C. On

top of that, we also carried out mass spectrometer experiments which show peaks at 46 and 92 g/mol corresponding to NO_2 and N_2O_4 , respectively. Therefore, the likely half reaction in acid NO_3^- solution is the following:

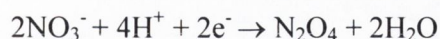
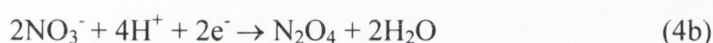


Fig. 110 illustrates the effect of pH changes of a deoxygenated KNO_3 electrolyte on the rest potential shift. The pH was adjusted by adding HNO_3 . The data show that large effects occur only when the pH is low. They suggest that paramagnetic (Fe^{2+}) ions in the electrolyte are not necessary for the observation of the rest potential shift. The iron electrode is strongly corroding when the pH is less than 3 in accordance with the following reactions:



Comparison of ΔE_0 for aerated and de-aerated electrolytes shows a systematically lower shift when the electrolyte is de-aerated by saturation with argon. For example, no shift at all is observed in de-aerated 0.1 M H_2SO_4 (pH 1), whereas the shift in the aerated acid is 2 mV.

In some cases, the rest potential shift was found to decay with time with the build up of corrosion products on the electrode surface. In the example shown in Fig. 111, the effect of the field had almost disappeared after 1000 s.

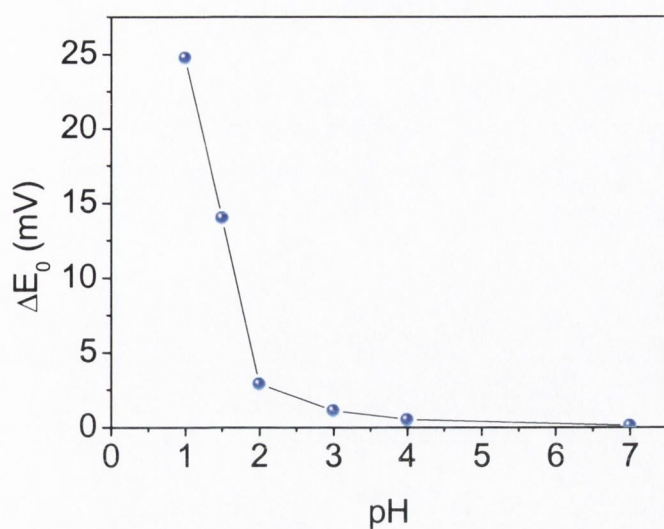


Figure 110. Variation as a function of pH of the rest potential shift in 1.5 T applied parallel to the surface of an iron electrode immersed in 1 M KNO_3 .

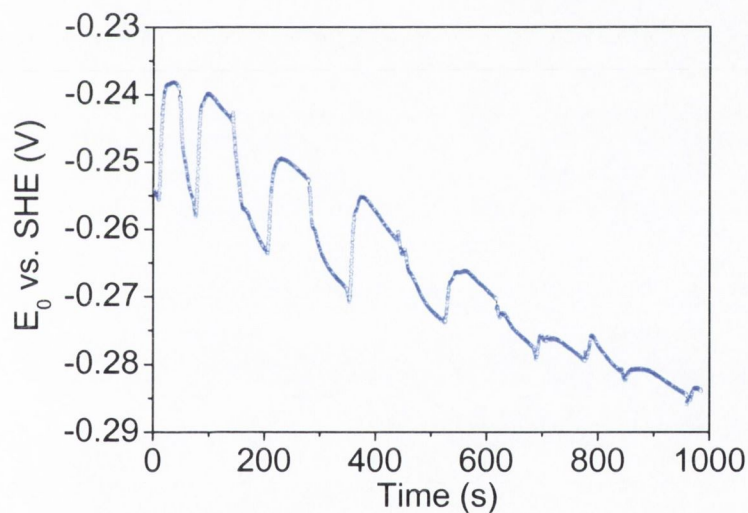


Figure 111. Time dependence of the rest potential shift ΔE_0 of an iron electrode in 1 M KNO_3 (pH 1). The shift decreases as the electrode is coated with corrosion products.

5.2.1.2 Corrosion rate of Fe in KNO₃ solution

We have prepared electrodes from 8.8 μm thick Fe films electrodeposited on one side of 5 mm x 5 mm smooth and rough Cu foils. The electrodeposited Fe films were found to follow the roughness of the Cu substrate. The corrosion rates were calculated based on weight losses and the experiments were carried out in 50 mL solutions containing 1 M KNO₃ with pH 1. The electrodes were left in the solution and the rest potential recorded as a function of time. The electrodes were identified as completely corroded when the rest potential increased sharply with time. Additionally, the complete corrosion was observed as the Cu foil was exposed. Fig. 112 shows the rest potential of four electrodes: two rough and two smooth, with and without a 1.5 T field applied in the plane of the electrode.

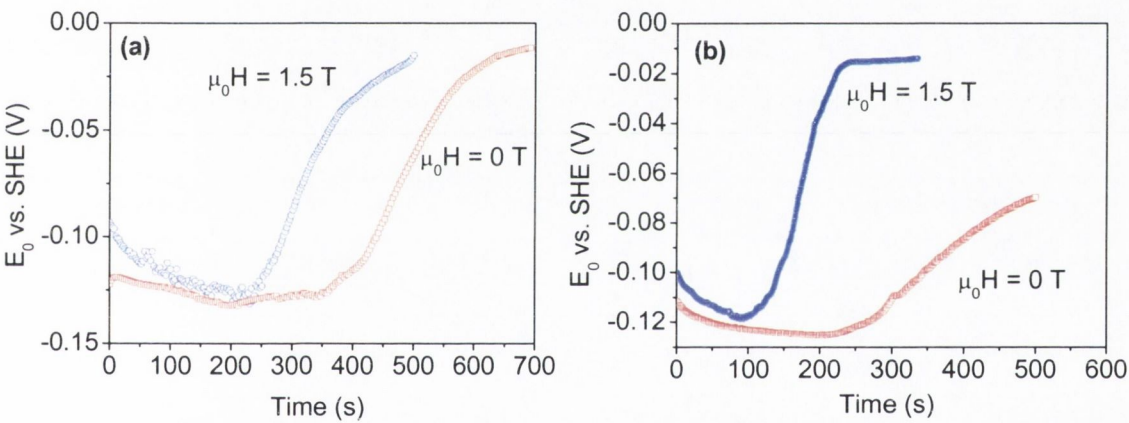


Figure 112. Dependence of the corrosion time on the applied field for (a) smooth and (b) rough electrodes with and without a 1.5 T field applied parallel to the electrode surface.

It is noticeable that smooth electrodes [Fig. 112(a)] take a longer time to corrode than rough electrodes and the overall effect of the magnetic field is to enhance the corrosion

rate. Also, the rest potential with applied field is always greater than without applied field as long as the electrode is not completely corroded. After complete corrosion, the rest potential goes to that of the copper substrate which is about -15 mV vs. SHE.

We also carried out potentiostatic corrosion experiments where the counter electrode was a Pt wire. In these experiments the cathode potential was kept fixed and the time needed to completely corrode the electrode was measured. Fig. 113 shows a typical result where the corrosion time is determined with and without a 1.5 T applied field in plane. As observed in the rest potential experiments the field acts in such a way as to increase the corrosion rate.

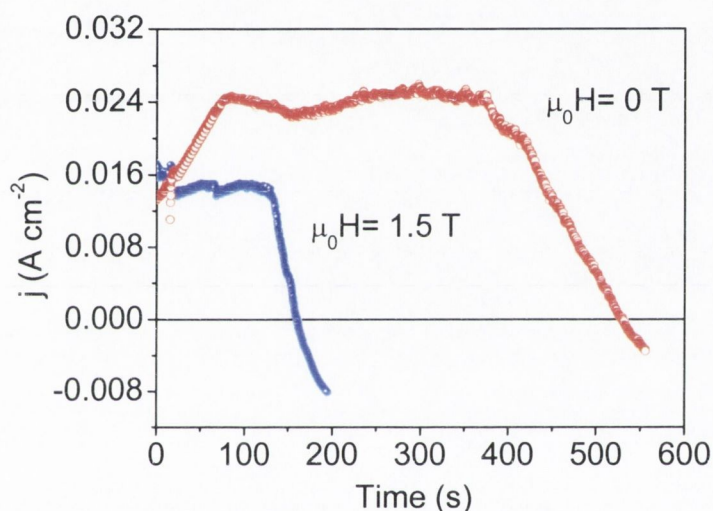


Figure 113. Dependence of the corrosion time on the applied field when a smooth electrode is set to -0.08 V vs. SHE. The 1.5 T field is applied in plane of the electrode.

In both situations, at constant potential (potentiostat) and open circuit (rest potential), the effect of an applied magnetic field is to increase the corrosion rate. Based on the weight losses the corrosion rate was determined and the results are shown in Fig. 114. For

potentials smaller than -0.4 V without an applied field rust forms on the electrode which blocks the corrosion. The values of rest potential were taken as the average over time since the rest potential drifts constantly.

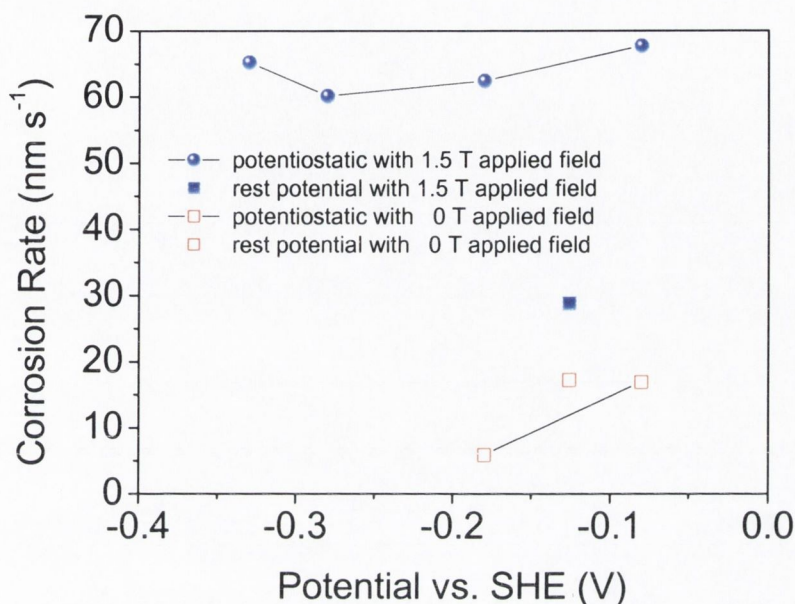


Figure 114. Corrosion rate measurements based on weight loss for smooth samples corroded at constant potential and at open circuit (rest potential). The 1.5 T field was applied in plane of the electrode.

5.2.1.3 The Corrosion rate dependence of Fe in KNO_3 solution on pH

Fig. 115 shows the corrosion rate as a function of the 1 M KNO_3 solution pH. At low pH the corrosion rate is large, about 0.2 A cm^{-2} . The effect of the magnetic field is to enhance the corrosion rate in the range of pH studied. The corrosion rate decreases as the pH goes towards neutral. This confirms that H^+ is one of the active ions involved in the corrosion process.

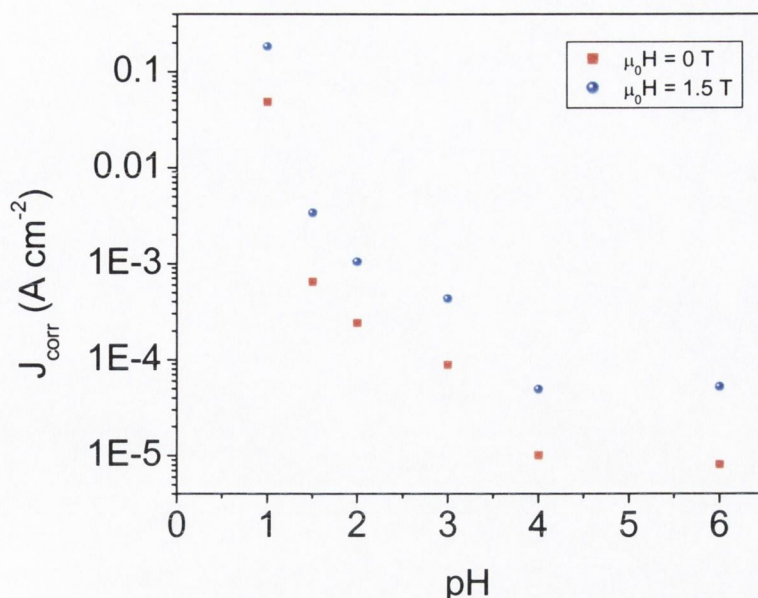


Figure 115. Corrosion rate dependence of Fe in 1 M KNO_3 solution on pH, with and without a 1.5 T applied field.

5.2.1.4 Morphology and composition of Fe electrodes after corrosion

The morphology of electrodes was studied on 0.5 mm thick Fe foils before and after exposure to a 1 M KNO_3 solution of pH 1. The electrodes were washed with deionised water after being removed from the solution to clean any residual salts. Fig. 116 shows the foil before and after corrosion. The tracks shown in Fig. 116(a) are the result of polishing with sand paper, grade 800, in a rotating polisher machine. The initial features of the foils are completely removed by the corrosion, as shown in the Fig. 116(b). One can see that the corrosion produces bumps and depressions which are characteristic of the formation of anodic and cathodic sites. During corrosion, there is an electronic corrosion current flowing through the electrode and an ionic current through the solution.

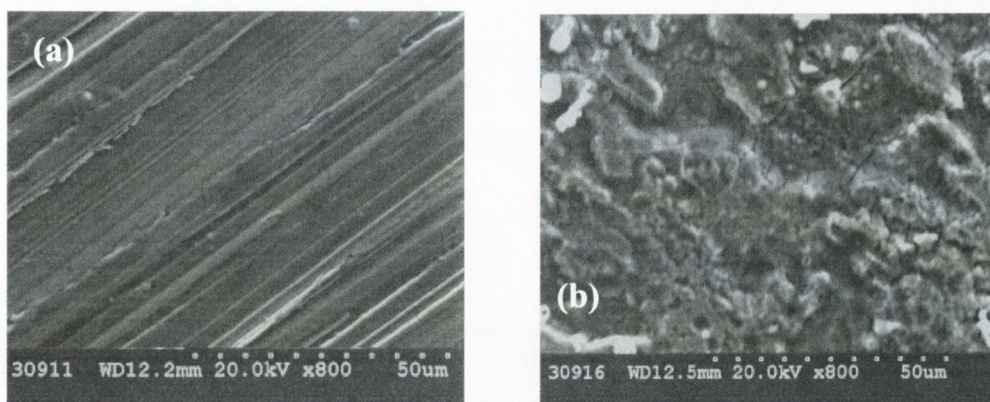


Figure 116. Micrograph of Fe electrode (a) before and (b) after corrosion in 1 M KNO_3 pH 1 solution.

EDS analysis of the corroded Fe surface reveal the presence of the elements N, O and K suggesting the presence of KNO_3 as shown in Fig. 117. It is also likely that the composition of the corrosion products is a combination of $\text{Fe}(\text{NO}_3)_x$ ($x = 2,3$), KNO_3 and metal hydroxides ($\text{Fe}(\text{OH})_x$).

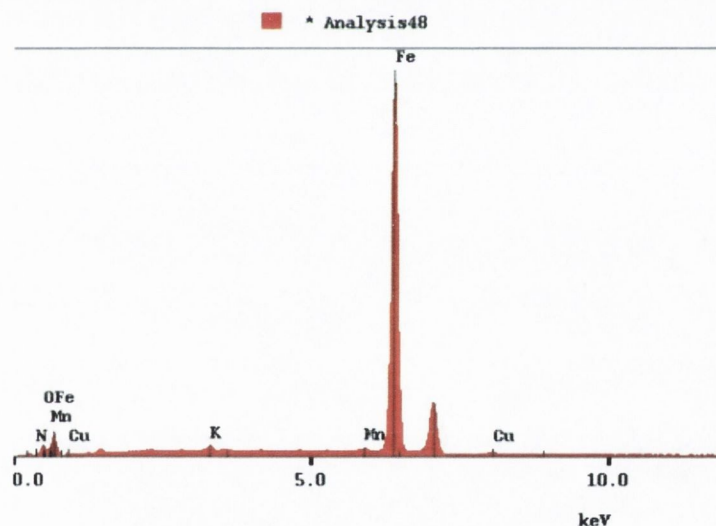


Figure 117. EDS of an Fe electrode after corrosion in a 1 M KNO_3 pH 1 solution.

5.2.1.5 Dependence of the rest potential on the roughness

The effect of roughness on the rest potential of Fe electrodes was investigated as illustrated in Fig. 118. The rough and smooth electrodes were inserted in a 1 M KNO_3 solution and the rest potential was measured as the magnetic field was switched on and off. When the iron electrode was deposited on a Cu substrate polished using 0.25 μm diamond paste, or roughened by a chemical process, the root mean square (rms) surface roughnesses determined by atomic force microscopy were 8 nm and 170 nm respectively. A comparison between the shift for the rough and smooth electrodes shows little difference, indicating that in this scale roughness does not play a significant role in the rest potential shift.

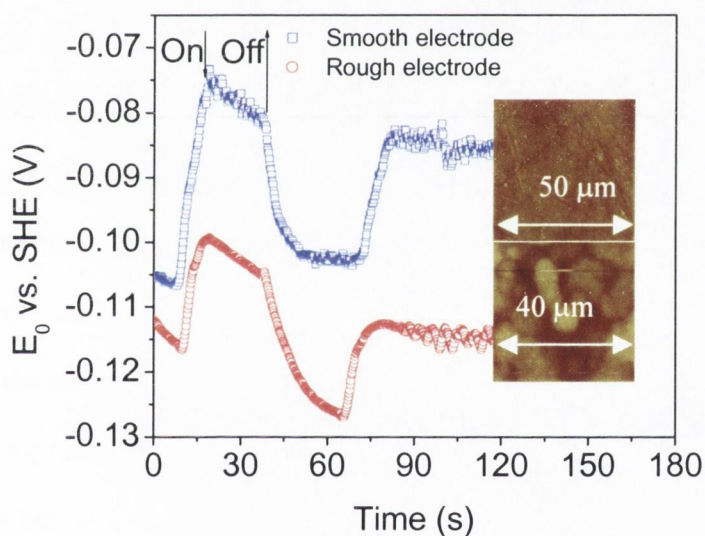


Figure 118. Rest potential shift of a smooth (8 nm rms) and a rough (170 nm rms) electrode in 1 M KNO_3 (pH 1) as the field parallel to the electrode surface is switched on and off.

5.2.1.6 Equivalence between the magnetic field effect and stirring

An anodic shift ΔE_0 comparable in magnitude to that obtained in the magnetic field can be obtained by rotating the electrode (RDE) or stirring the electrolyte. Fig. 119 shows ΔE_0 as a function of the rotation rate for a 6 mm diameter iron rotating disc electrode in the absence of any applied magnetic field. The rotating disc electrode is a well-known technique and one of the few systems where the limiting current due to mass transport can be analytically calculated (section 1.2.4). In 1 M KNO_3 at pH 1, the shift approaches a saturation of 90 mV above 1000 revolutions per minute (rpm). It is noteworthy that the field and rotation effects are not additive. For example, applying a field of 1.5 T when the electrode is rotating at 1000 rpm contributes an additional shift of less than a millivolt. The shift in 1.5 T is equal to that produced by rotation at 52 rpm. The rotation establishes conditions of forced convection which enhance mass transport to the electrode surface. The magnetic field acts similarly.

Another experiment using radial and axial convection was also carried out, where the electrode is shielded from large-scale convection using an insulating polymer sheath. In one case, the surface of a 1 mm diameter iron wire was flush with the polymer surface, thereby allowing radial convection to take place. To impose axial convection the wire was retracted 8 mm below the surface of the polymer creating a channel of 1 mm diameter. Observed anodic shifts in 1 M KNO_3 at pH 0.5 were about the same for both experiments (95 mV).

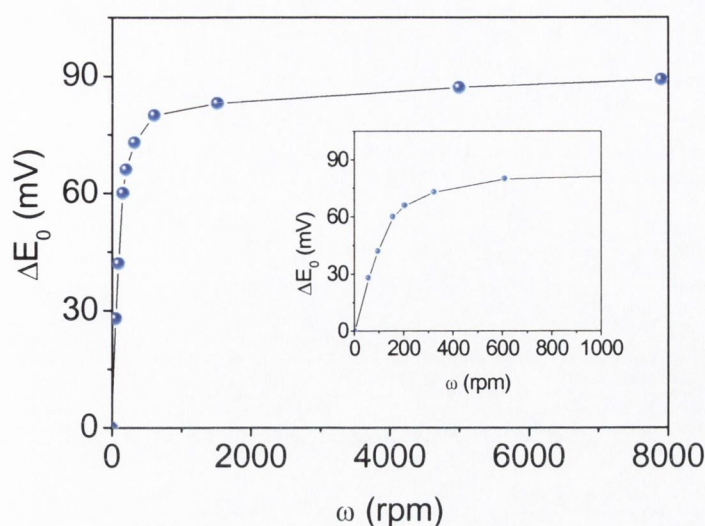


Figure 119. Variation of ΔE_0 with rotation rate for an iron rotating disc electrode in 1 M KNO_3 at pH 1.

Fig. 120 illustrates the field dependence of the rest potential shift for the KNO_3 solution in fields of up to 5.5 T applied parallel to the electrode surface. The effect approaches saturation at high field, varying approximately as $1 - \exp(-0.75B)$. This is quite different to the saturation magnetization itself. Fig. 121 shows the effect of the magnetic field on polarisation curves for the electrode in KNO_3 (pH 1). There is a clear difference between the effect of the field in the active regions of the cathodic and anodic curves. While there is no effect on the anodic current in the active region, the cathodic current is enhanced by more than a factor of two in the field which is also even more visible in the Tafel plot of an iron electrode in 3 M KNO_3 solution at pH 1 as shown in Fig. 122. As can be seen the field shifts the rest potential towards more positive values (anodic shift). In addition, in Fig. 121(a) the anodic polarization curve, in the absence of magnetic field, indicates a sharp

drop in the current at 0.7 V which is associated with the formation of a passive layer. This threshold is shifted anodically by 0.8 V in a field of 1.5 T.

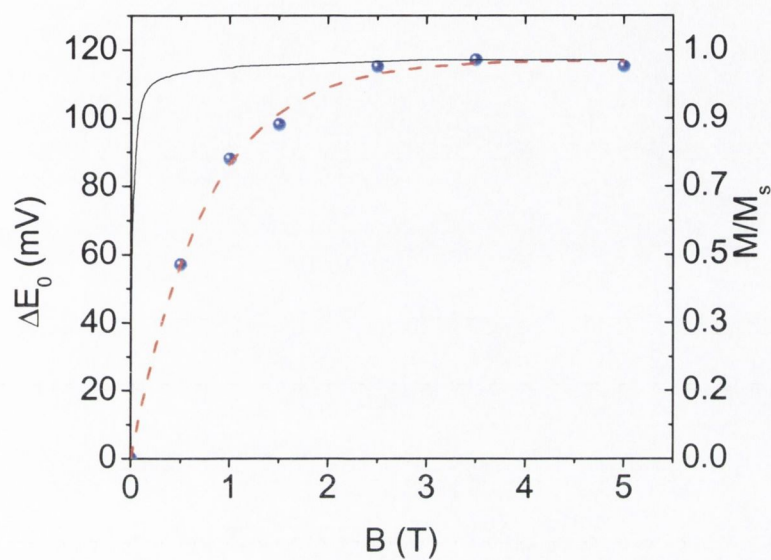


Figure 120. Variation of the rest potential shift of an iron electrode in 1 M KNO_3 at pH 1 as a function of applied magnetic field. The solid line shows the approach to magnetic saturation of the electrode in these conditions. The dashed line is guide to the eyes.

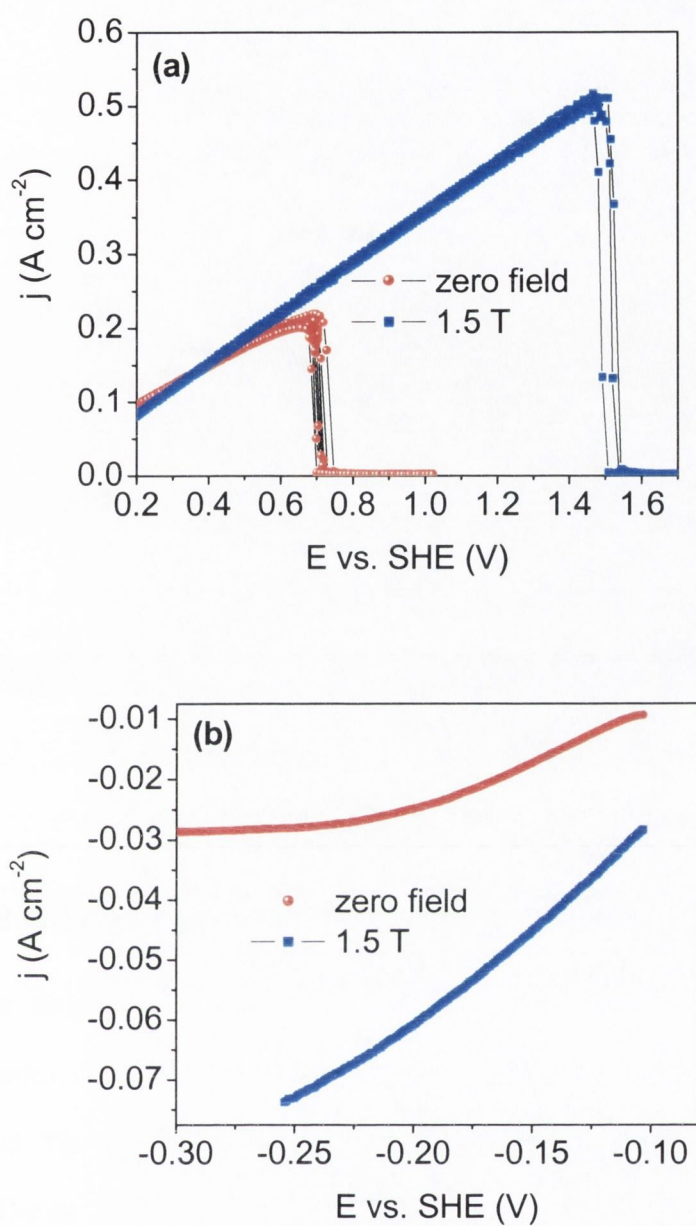


Figure 121. (a) Anodic polarization curves showing the passivation of iron in 1 M KNO₃ at pH 1 and (b) cathodic polarization curves with and without a 1.5 T applied magnetic field.

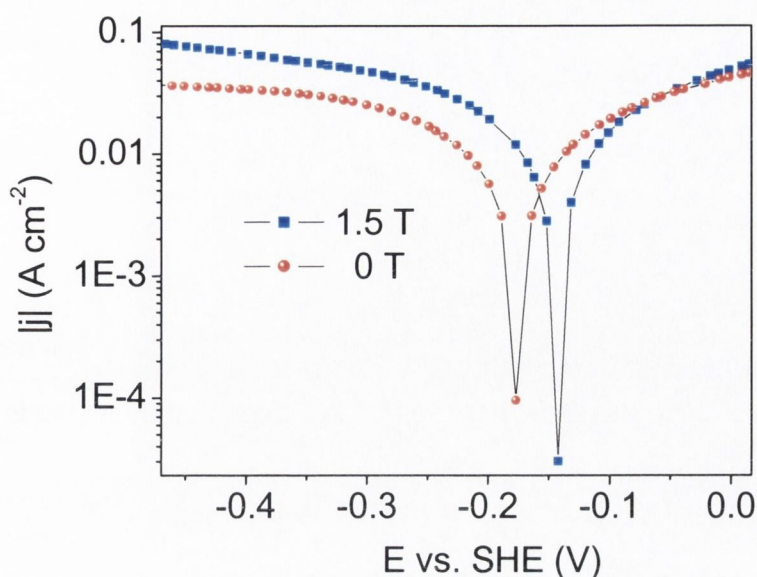


Figure 122. Tafel plot of a rough iron electrode in 3 M KNO_3 solution pH 1 with and without a 1.5 T applied magnetic field.

5.2.2 Other ferromagnetic electrodes

The field-induced shifts of rest potential were also studied for other ferromagnetic electrodes: cobalt and nickel. In order to measure small shifts we employed the use of an ac method. The magnetic field is modulated by a sinusoidal current with small frequency (0.2 Hz). The ac component of the rest potential is then decoupled and processed using a lock-in amplifier which gives the amplitude of the signal in the same frequency of the magnetic field. This method is applicable where the response of the electrochemical cell is linear, which is the case for small shifts. If the electrochemical cell has a non-linear response to the field harmonics are generated which make the use of a lock-in amplifier inappropriate. Anodic shifts in 1 M nitrate solutions for cobalt and nickel were observed, of 0.8 mV and

0.7 mV respectively. A large shift of 10 mV was found for cobalt in CoSO₄ solution. Data on cobalt and nickel are summarised in table 8.

Table 8. Rest potential shifts ΔE_0 measured for cobalt and nickel in 1.5 T in various solutions.

Electrode	Solution	Concentration (M)	pH	ΔE_0 (mV)	Comments
Cobalt	CoSO ₄	1.0	4.0	10	
	Co(NO ₃) ₂	1.0	5.4	0.8	ac method
Nickel	NiSO ₄	1.0	4.0	0.0	
	Ni(NO ₃) ₂	1.0	4.2	0.7	ac method

5.3 Rest potential of non-magnetic electrodes

5.3.1 Magnetic field effect on the rest potential of Zn

Experiments were carried out in a standard three-electrode cell with a 6 mm x 6 mm zinc working electrode, an Ag/AgCl reference electrode and a Pt counter electrode. All the potentials measured are quoted relative to SHE and are calculated by adding 0.22 V to values measured vs. Ag/AgCl. We also have carried out rotating disc electrode experiments to have controlled mass transport of oxidizing species towards the electrode. In this case a 6 mm diameter zinc disc was used. The counter electrode is only needed for the potential sweeps. The cell, of volume 50 mL, was placed between the poles of a large 1.5 T electromagnet, or in the 105 mm diameter room-temperature bore of a 5.5 T superconducting magnet.

Typical data for a vertical zinc electrode in a 1.5 T horizontal, in plane field are shown in Fig. 123. Here the zinc electrode is actively corroding and an anodic shift of 5 mV is observed in 1 M KNO₃ adjusted to pH 1 with HNO₃, but there is no field effect in 1 M ZnSO₄ or in 0.1 M H₂SO₄. A large anodic shift of 42 mV is observed in a 16 mM solution of CuSO₄. Further measurements on the acidified KNO₃ solution with the applied field parallel to the surface of the vertical electrode show that the rest potential varies as:

$$E_0(B) - E_0(0) \propto B^n \quad (5)$$

where $n = 0.8$ (Fig. 124). As the electrode corrodes there is a slight change in colour near the electrode surface. Consequently, we noticed that the electrolyte was visibly agitated near the electrode surface when the magnetic field was ≥ 1 T, especially when the

pH was < 1 . The electrode showed signs of corrosion after treatment in acidified KNO_3 (Fig. 124, inset b). The spots shown in the inset are characteristic of the formation of anodic and cathodic corrosion sites which drive corrosion.

The effect of stirring the solution in the absence of a magnetic field was investigated using a Zn rotating disc electrode in acidified KNO_3 . An anodic shift in rest potential is observed, which increases with rotation rate (Fig. 125). The magnitude of the shift achieved by rotating a disc electrode was significantly greater than that induced by the magnetic field over most of the range of rotation rates (up to 9000 rpm). Rotating the downward facing electrode at 100 rpm produces a similar shift to that induced by the 1.5 T field. At a rotation rate of 1000 rpm, the additional shift caused by the applied magnetic field was much less than 1 mV. A direct comparison between the effect of the field on the rest potential and RDE experiments reveals an important similarity. The shape of the rest potential shift dependence on the magnetic field (Fig. 124) is similar to that of the rest potential shift dependence on the rate of rotation (Fig. 125). Both rotation and magnetic field act in such a way as to increase the mass transport of oxidizing species.

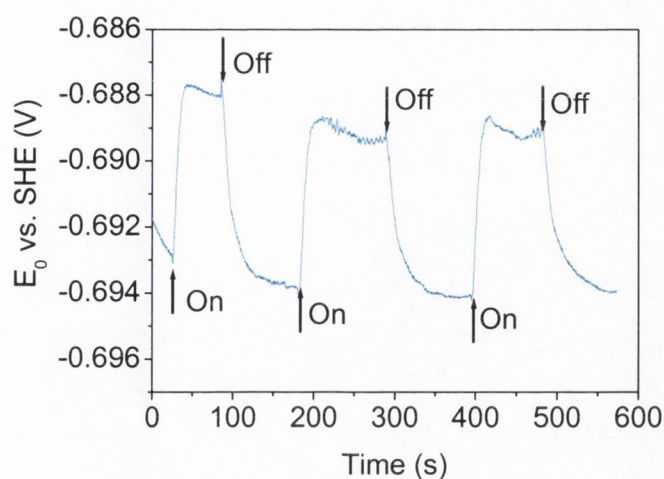


Figure 123. Shift of the rest potential of a zinc electrode in 1 M KNO_3 (pH 1) as a 1.5 T field is switched on and off. The field is in plane of the electrode, which is mounted vertically.

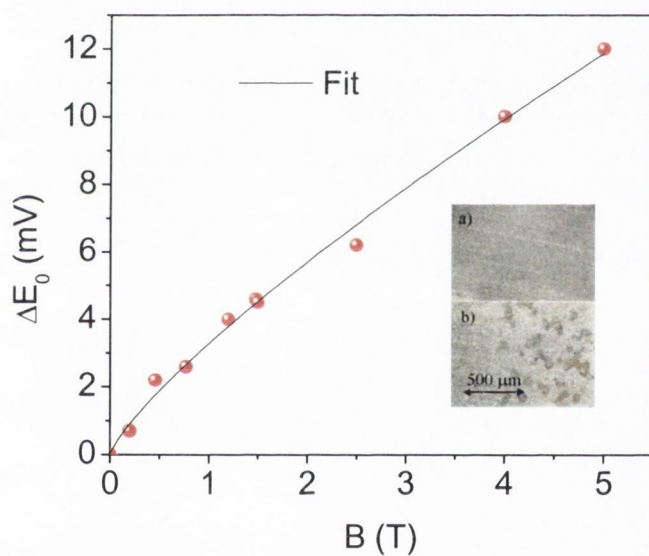


Figure 124. Magnetic field dependence of the rest potential shift for a zinc electrode in 1 M KNO_3 (pH 1). The fit is $\Delta E_0 \propto B^{0.8}$. The inset shows the electrode surface (a) before and (b) after exposure to the electrolyte in a 1.5 T field.

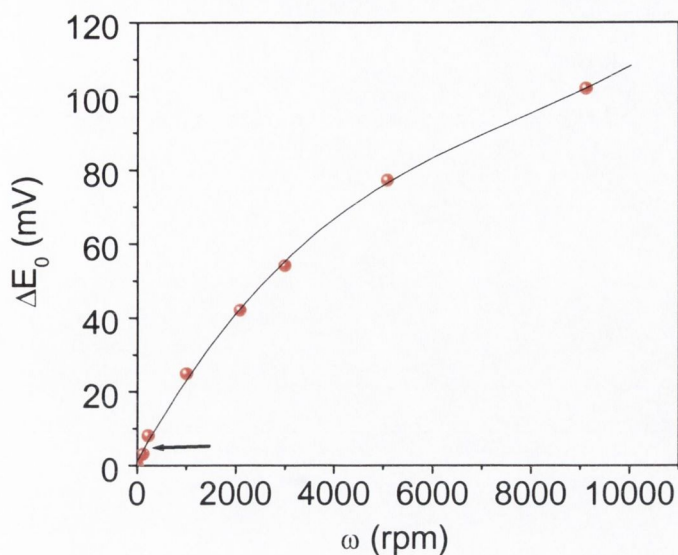


Figure 125. Variation of the rest potential of a Zn rotating disc electrode in 1 M KNO_3 (pH 1) with rotation rate. The shift obtained in 1.5 T is shown by the arrow.

The effect of an applied magnetic field on the voltammogram of a zinc electrode in an acidified 1 M KNO_3 solution is shown in Fig. 126. The cathodic current arising from the reduction of NO_3^- is enhanced by the field, but the anodic dissolution current of zinc is unaffected. In contrast, no effect of magnetic field on either the cathodic or the anodic branch is found in 0.1 M H_2SO_4 . The corrosion current density, j_{corr} , was measured directly by either extrapolating the linear portion of the Tafel curve to the rest potential or measuring the mass loss due to corrosion. The results are summarized in table 9.

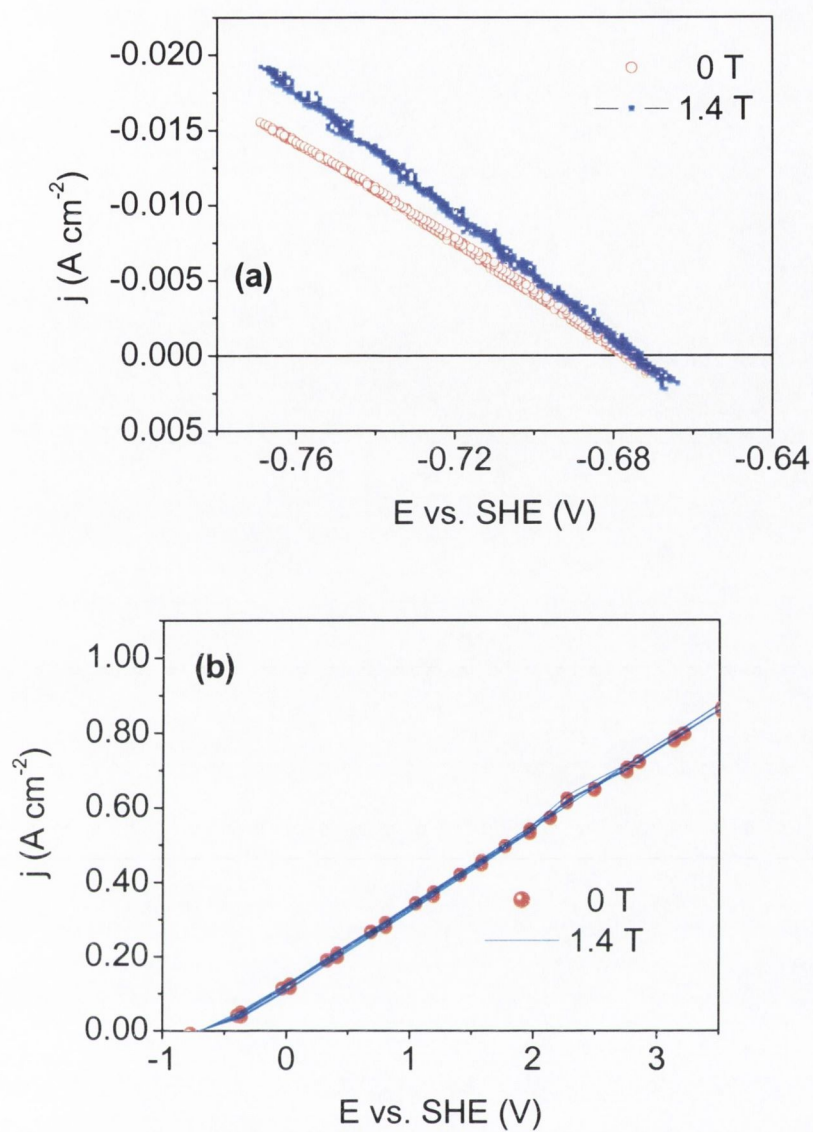


Figure 126. (a) Anodic and (b) cathodic voltammograms of a Zn electrode in 1 M KNO₃ pH 1 with an applied field of 1.4 T.

Table 9. Rest potential and related data for a zinc electrode. The solution concentrations are 1 M.

Solution	pH	E_0 (mV vs. Ag/AgCl)	j_{corr} (A m ⁻²)	ΔE_0 at 1.5 T (mV)	ΔE_0 at 1000 rpm (mV)
KNO ₃	1.0	-695	220	5	25
ZnSO ₄	7.0	-730	0.042	0	0
CuSO ₄	7.0	-680	0.053	42	165
H ₂ SO ₄	1.0	-680	230	0	0

5.3.2 Rest potential shift of non-magnetic electrodes other than Zn

The field-induced shifts of rest potential were also studied for a series of non-magnetic electrodes other than Zn. These were chromium, manganese, copper and stainless steel. The field induced shift in the rest potential for magnetic and non-magnetic stainless steel, alloys largely composed of iron but with significantly higher corrosion resistance, were less than 1 mV in conditions where pure iron gave a 35 mV shift. Data are summarised in table 10 showing that ferromagnetic electrodes are not needed to observe a shift in rest potential, which is in line with the findings for Zn. With the exception of Mn all of the other electrodes failed to show a significant shift. Aluminium and chromium are known to easily passivate in acidified solution, thereby blocking the corrosion.

Table 10. Rest potential shifts measured for electrodes other than iron.

Electrode	Solution	Concentration (M)	pH	ΔE_0 (mV)	j_{corr} (A m^{-2})
Chromium	KNO_3	1.0	1.0	0	< 0.001
Manganese	KNO_3	1.0	0.6	9	36
Aluminium	HCl	1.0	0.0	0	1.9
316L stainless steel (non-magnetic)	$\text{Fe}(\text{NO}_3)_3$	1.0	1.0	0	< 0.001
430L stainless steel (ferromagnetic)	$\text{Fe}(\text{NO}_3)_3$	1.0	1.0	0	< 0.001

5.4 Discussion

Much of the data presented for Fe points to a close link between the rest potential shift and corrosion. Iron is known to be particularly unstable in concentrated $\text{Fe}(\text{NO}_3)_3$ solutions where the largest effects are observed at $\text{pH} = 1$, corroding at rates of order a micron a minute. The sensitivity to pH, electrode roughness and dissolved oxygen concentration and the absence of an effect for stainless steel, whether ferromagnetic or not, all point in the same direction.

Another feature that emerges from the data is the equivalence between the field effect and enhanced convection (Fig. 119). The trend of the dependence (Fig. 120) resembles that found for the enhancement of electrodeposition currents in the mass transport limited regime^{10,11,12}.

In order to better establish the link with corrosion, we have determined the corrosion current at the rest potential as a function of pH in KNO_3 . This was measured by electroplating a thin layer of Fe onto a Cu electrode, and then measuring the time taken for

it to dissolve completely. Alternatively, the slope (R_p , the polarization resistance) of the $E:j$ curve was measured at E_0 , and the corrosion current was derived from the Stern-Geary expression

$$j_{\text{corr}} = (1/R_p)(\beta_a\beta_c)/[2.303(\beta_a+\beta_c)] \quad (6)$$

where β_a and β_c are the anodic and cathodic Tafel slopes respectively. The Stern-Geary coefficient $[(\beta_a\beta_c) / 2.303(\beta_a+\beta_c)]$ was estimated by weight loss measurements at low pH.

Fig. 127 shows a plot of j_{corr} vs. ΔE_0 for iron, measured for a 1.5 T applied field parallel to the surface of the electrode in 1 M KNO_3 solution at different pH values which are the same pHs as shown in Fig. 110. The highest corrosion rate corresponds to pH 1. The trend of the data establishes the primary conditional link between the field shift and the corrosion current. The link is conditional because the corrosion rate needs to be mass transport limited.

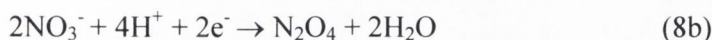
Active corrosion occurs in electrodes where there is no passive layer. At low pH the anodic dissolution of iron



is balanced by a cathodic reaction such as:



or



We have observed that all measured rest potentials for Fe are within the range from 0 to -0.4 V vs. SHE. It can be seen from the Pourbaix diagram of iron in water (Fig. 128) that these potentials are in the corrosion region in acidic solutions. The direction of the shift ΔE_0

depends on whether the cathodic or anodic reaction is more easily enhanced by the field. If both were equally sensitive there would probably be no shift. However, if one of the reactions is mass transport limited, and the other activation controlled, the mass transport limited current will be sensitive to field-induced convection, and the corrosion (rest) potential will have to shift in the sense required to increase the activation controlled reaction rate to match it. In corroding systems, anodic dissolution reactions are usually kinetically controlled while cathodic reactions may be either kinetically or mass transport controlled. In the case of iron, Fig. 122 shows that the cathodic current arising from nitrate reduction (Eqn. 8b) is mass transport controlled, while the anodic dissolution reaction is activation controlled. This results in an anodic shift in rest potential in the presence of a magnetic field, as illustrated by the Evans diagram in Fig. 129.

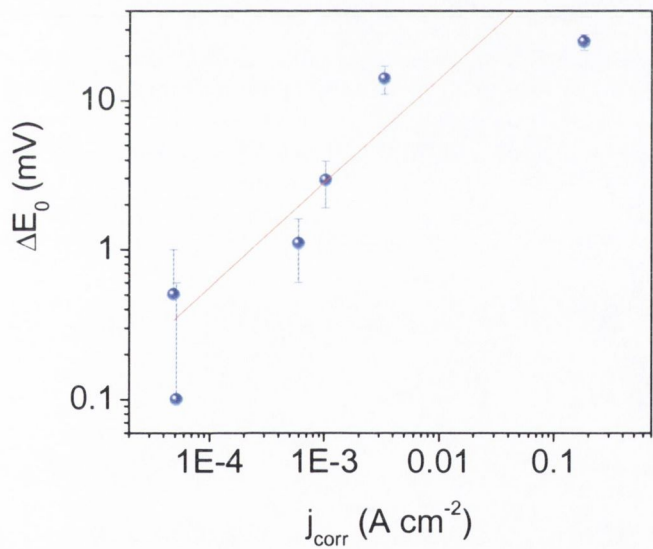


Figure 127. Relationship between ΔE_0 and the corrosion current j_{corr} for electrodes corroding under cathodic mass transport control.

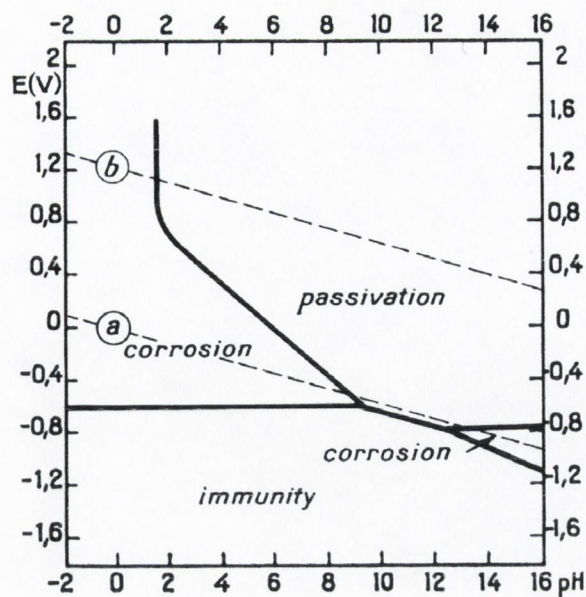


Figure 128. Pourbaix diagram for iron.

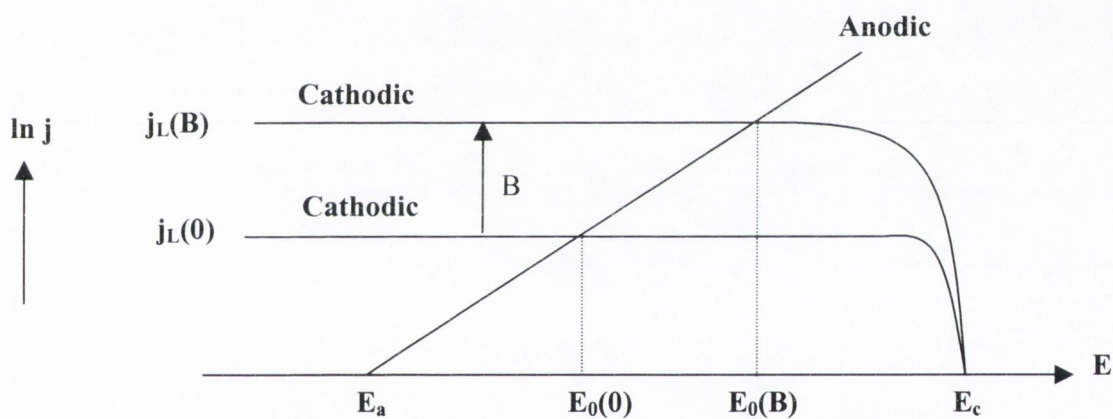


Figure 129. Evans diagram showing the effect of an applied magnetic field on the rest potential. An anodic shift is observed because only the cathodic reaction is sensitive to the applied magnetic field. Here, j_L , B and E_0 stand for limiting current density, magnetic field and rest potential.

Since the hydrogen ion reduction (Eqn. 8a) is not mass transport limited, the applied field cannot increase its rate. This is consistent with the observation that there is no shift at all for a de-aerated H_2SO_4 solution at pH 1. The small shift in aerated acid solutions is explained by enhancement of the reduction of O_2 in acid media ($\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$), which is mass transport controlled. It is interesting to note that hydrogen or nitrate ions do not provoke a shift by themselves; there is no effect for H_2SO_4 (pH 1, argon saturated), or for KNO_3 at pH 7, but when the nitrate solution is acidified to pH 1 there is a large field-induced shift (table 7). Here, the nitrate ions provide the mass transport limitation, while the hydrogen ions are required for the nitrate ion reduction (Eqn. 8b).

Another important effect of the field is also observed in the voltammograms. When the potential is increased anodically the corrosion rate increases and therefore the concentration of Fe^{2+} also increases near the surface of the electrode. The concentration builds up to the point where the solution becomes supersaturated and the precipitation of corrosion products may occur on the surface of the electrode, forming a passive layer. The application of a magnetic field induces convection near the electrode, reducing the local concentration of Fe^{2+} , and pushing the passivation potential of the supersaturated solution towards more positive values, as observed in Fig. 121(a).

Additionally, the equivalent circuit of the galvanic cell can be represented by the electrical diagram in Fig. 130 where R_f , R_b , C_{dl} , A and B are the Faraday resistance, the bulk resistance (ohmic drop), the double layer capacitance and the external leads to the galvanic cell, respectively. The dashed box represents the electrode/solution interface.

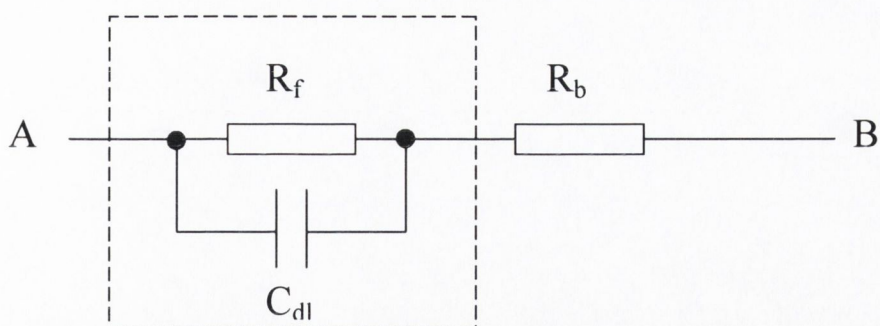


Figure 130. Electrical diagram of a low frequency galvanic cell.

The Faraday resistance (R_f) represents the charge transfer in the electrode/solution interface. In the case of corrosion shown in Fig. 121(a), for small overpotentials R_f is much smaller than R_b in the activation region, resulting in a linear dependence in the plot j vs. E . Therefore the only resistance seen between the points A and B is R_b . The passivation occurs as follows: as the potential is swept towards more positive values the concentration of corrosion products builds up near the electrode surface to the point where it reaches the supersaturated limit and then salts precipitate on the surface of the electrode blocking the charge transfer. The precipitation is followed by a sharp drop in current which is associated with the transition in the resistivity of the interface electrode/solution, thereby R_f becomes much bigger than R_b ($R_f \gg R_b$). The application of the field enhanced convection which requires higher corrosion rates in order to reach the same supersaturated solubility limit near the electrode. Therefore the passivation potential is pushed to more positive values. The magnetic field does not change the bulk solution resistance as can be observed from the slope of the plot j vs. E , Fig. 121(a).

The decay of the effect over time, shown in Fig. 111, is related to the build up of corrosion products on the electrode surface. This gradually modifies the mass transport regime from convective diffusion in a fluid to diffusion through a porous barrier, which becomes increasingly unaffected by the field-induced flow. Additionally, the density of anodic and cathodic sites diminishes. These are consistent with the slow underlying cathodic drift in rest potential, which reflects the reduced efficiency of the cathodic mass transport process with time.

The fact that observed anodic shifts in 1 M KNO₃ at pH 0.5 were about the same (95 mV) for both 8 mm retracted and non-retracted wire experiments using the PTFE sheath suggests that the magnetic field induced stirring occurs near the electrode surface on a scale much less than 1 mm.

Turning to the observation in Zn. The dominant corrosion reactions of Zn in acidified KNO₃ and CuSO₄, are:



Cathodic



Since the anodic dissolution reaction (9a) is activation controlled, while the cathodic reactions (9b) and (9c) are mass transport limited (Fig. 126), any enhancement of the cathodic corrosion current by the field will necessarily produce an anodic shift in the rest potential. No shift was observed in ZnSO₄ because it is not sufficiently corroding, nor in

H₂SO₄ because the cathodic reaction (9d) is not mass transport limited. No magnetic field effect on the electrode kinetics was observed, in line with investigations by Devos et al¹³. The equivalence of a 1.5 T field to a rotation rate of 100 rpm confirms that the effect of the field is equivalent to gentle stirring, as observed in magnetohydrodynamic effects on electrodeposition¹⁴.

At this point in the discussion we turn to the first of the questions posed at the beginning of this chapter. If the origin of the effect is related to corrosion then the association with iron may be simply coincidental. It so happens that iron corrodes rapidly in Fe(NO₃)₃ and KNO₃, and at low pH, but there may be no requirement for the electrode to be ferromagnetic. To settle the question ‘Does the electrode have to be ferromagnetic?’ we have seen that there is a field-induced shift in the rest potential of the non ferromagnetic corroding electrodes Zn and Mn. No effect is observed in open circuit experiments for elements such as copper, which is more noble than iron, despite the fact that Tafel plots with and without field suggest a small anodic shift for Cu in nitrate solutions in experiments carried out by Shinohara et al.¹⁵, indicating that the nobility of Cu suppresses the rest potential shift. We have chosen zinc and manganese, which are less noble than iron and corrode easily in an acid environment. The standard reduction potential for the reaction $M \rightarrow M^{2+} + 2e^-$ is -0.76 V for Zn, -1.03 V for Mn and -0.43 V for Fe. We find no shift for Zn in ZnSO₄ nor in H₂SO₄, but there is a shift of 4 to 5 mV for Zn in KNO₃ acidified to pH 1. Corrosion of zinc both in ZnSO₄ and in H₂SO₄ which is associated with reaction (8a) is not mass transport limited. However, the corrosion in acidified KNO₃ is mass transport limited (8b), hence the observed field effects for both Zn and Mn. The field-dependence, shown in Fig. 124, can be fitted to $B^{0.8}$ up to the highest fields, as the shift is monotonically

increasing in 5 T. Rotating disc electrode measurements indicate that the shift can be as large as 100 mV for a rotation rate of 10000 rpm (Fig. 125). Furthermore, as we have seen a large shift $\Delta E_0 = 42$ mV for Zn in 16 mM CuSO₄ at 1.5 T. In copper sulphate, there is a mass transport limited cathodic corrosion current as Cu displaces Zn according to the reaction: $\text{Cu}^{2+} + \text{Zn} \rightarrow \text{Cu} + \text{Zn}^{2+}$.

The rest potential shift can be analysed as follows (appendix A): the cathodic current density, which is mass transport limited, varies as $j_c = nFDc_0/\delta$ where D is the diffusion coefficient and c_0 the concentration of oxidizing species in the bulk solution and δ is the diffusion layer thickness. The anodic current density varies with potential E as $j_a = j_0 \exp[\alpha nF(E-E_a)/RT]$, where α is the anodic electron transfer coefficient, j_0 is the exchange current density and E_a is the equilibrium potential for the anodic reaction. Equating these, and taking the ratio for the equations in zero field and in field B gives $\exp[\alpha nF\Delta E_0/RT] = j_c(B)/j_c(0) = \delta(0)/\delta(B)$. Taking logarithms, $j_L(B) = j_L(0) + \beta B^n$ and setting $\ln(1+x) \approx x$ yields the expression for the rest potential shift, to first order

$$\Delta E_0 = (RT/\alpha nF)\gamma B^n \quad (10)$$

The power law describing the field enhancement of the cathodic current and the rest potential shift are identical, at least for small changes.

The results establish that a ferromagnetic electrode is *not* essential for the observation of the rest potential shift effect. What is important is that the electrode should be actively corroding and the corrosion should be mass transport limited. This conclusion is reinforced by the observation of a shift for non-magnetic electrodes, summarised in table 10. A shift is observed for manganese and zinc electrodes, but not for Al and Cr which are protected by a

passive layer. No shift is observed in the rest potential of copper because the rest potential of copper lies in the region in which the cathodic reaction is not mass transport limited.

We now consider how the field acts to increase the cathodic corrosion current. It is convenient to discuss this in terms of the forces acting on the electrolyte in the presence of a magnetic field, mentioned in the beginning of this chapter. The concentration gradient force $\mathbf{F}_{\nabla c}$ is discounted for the following reasons: diffusion in a concentration gradient is driven by an entropic force $\mathbf{F}_d = -(RT/c)\nabla c$ which is in the opposite direction to $\mathbf{F}_{\nabla c}$, but is over five orders of magnitude greater at room-temperature; the ratio $\mathbf{F}_d/\mathbf{F}_{\nabla c} = 2\mu_0 RT/\chi_m B^2$ is $\approx 2.7 \times 10^5$ for a field of 1.5 T and a typical molar susceptibility of $10^{-8} \text{ m}^3 \text{ mol}^{-1}$. The concentration gradient force cannot therefore be expected to exercise any appreciable influence on the convection. Furthermore, the results for zinc in KNO_3 demonstrate that it is possible to observe a shift in a system that contains no magnetic cations. The field gradient force is also ruled out as a primary factor by the observations on zinc, which show that a field-induced shift of rest potential can be observed for non-magnetic electrodes provided they corrode under mass transport control. The applied field was deliberately arranged to be uniform over the cell, so that any field gradients will only appear in the vicinity of the edges or rough surfaces of ferromagnetic electrodes.

That leaves the Lorentz force, $\mathbf{F}_L$, which is known to induce magnetohydrodynamic flow, thereby enhancing the currents during electroplating^{16,17}, or more generally in a mass transport limited regime. Much of the phenomenology at the rest potential is similar to that found for electroplating in a field. Although apparently no *net* current flows at the rest potential and hence the net force $\mathbf{F}_L = \mathbf{j} \times \mathbf{B}$ should be zero, the effects on the balancing cathodic and anodic currents are different as shown in Fig. 129. Some sites on the electrode

(Fig. 116(b) for Fe and Fig. 124(b) for Zn) act as cathodes and others as anodes allowing a flux of current between them. An electronic current goes through the electrode and an ionic current flows from different anodic and cathodic sites on the electrode surface on a microscopic scale, therefore it is possible to enhance vortex flow on a small scale near the electrode surface. This is the idea behind Aogaki's 'micro MHD effect'. We consider that small-scale magnetohydrodynamic flow is the principal factor accelerating the mass transport limited cathodic reaction, which in turn produces the field-induced rest potential shift. The time for these flows to decay and the concentration of the corrosion products to reach a zero field state, according to Fig. 109, is of order 20 s. The surface potential differences may also contribute to drive near-surface flow via electrokinetic effects, and the flow associated with these currents will also be modified by the magnetic field¹⁸, but this force is also associated with the existence of Lorentz force.

This is not to say that the field gradient force cannot play some role in the case of iron, and other ferromagnetic electrodes. Roughening the electrode will increase the concentration of paramagnetic species Fe^{2+} and O_2 in its vicinity, because of the large field gradients present. There will also be field gradients near the edges and corners. In the first case, assuming sinusoidal roughness on a scale of 20 μm for example, the field gradients ∇B are of the order 10^4 T m^{-1} and the forces $\mathbf{F}_{\nabla B}$ are of order 10^5 N m^{-3} . The forces near the edges, where $\nabla B \approx 10 \text{ T m}^{-1}$, are three orders of magnitude smaller. The field gradients due to surface roughness are likely to modify the concentrations of paramagnetic species near the electrode, and hence the electrode potential, but this effect is difficult to disentangle from the straightforward increase in corrosion rate due to roughening.

The increase in potential shift on changing from de-aerated to aerated solutions raises the possibility of a modest effect of the field gradient on paramagnetic O_2 . Unlike NO_3^- , oxygen is uncharged and therefore unaffected by the Lorentz force, which would suggest that the field gradient force could be responsible for the additional shift in aerated solutions.

5.5 Conclusions

Our primary conclusion is that the field-induced shift of rest potential is associated with corrosion currents in the mass transport limited regime, and does not depend in any essential way on the electrode being ferromagnetic or the electrolyte being paramagnetic. It is a coincidence that iron and the other ferromagnetic metals corrode easily. A consequence is that the effect is unlikely to provide a stable electrochemical method of sensing magnetic fields.

The corrosion must be active, and one of the corrosion currents should be mass transport limited in order to observe the anodic shift. The field-induced shift can be taken as a signature of mass transport limitation in corroding systems.

The primary mechanism of the shift is the magnetohydrodynamic stirring provided by the Lorentz force. It is not clear on what scale this stirring takes place, but it acts to enhance the mass transport limited cathodic current, and the rest potential shifts in an anodic sense thereby increasing the activation controlled anodic dissolution current to match.

A modest effect of the field gradient force on paramagnetic O_2 is suggested by the reduction of the rest potential shift upon de-aeration. However, it remains a challenge to distinguish field gradient and Lorentz force effects in such complex dynamic systems.

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Chapter 6

6 Further work

Throughout this thesis, the fact that electrodeposited $L1_0$ magnets have magnetic comparable to $L1_0$ sputtered magnets was demonstrated. Furthermore, electrochemistry allows the preparation of thick films and occupies, as a technique, a unique position between vapour deposition and bulk preparation techniques.

Electrodeposited FePt, in the current state, can fit well into high density media applications. These applications require corrosion-resistant thin films with high room-temperature coercivity. There are some studies covering the preparation of $L1_0$ FePt by sputtering (see Chapter 1). For possible MEMS applications, enhancement in the thickness films and the reduction of the required annealing temperature of FePt still need to be addressed. Future work should focus on searching for possible new electrochemical baths for the electrodeposition of ordered FePt and the development of methods for the preparation of thick as-deposited films with enhanced magnetic properties. Thick FePt films may be obtained by plating into membrane templates as demonstrated for CoPt in the present work. Metallic additives such as Cu, Pb, Zn may be required to reduce the annealing temperature enhance coercivity in FePt films.

There is a window of coercivities between as-deposited $Co_{80}Pt_{20}(P)$ (0.35 T) and annealed $L1_0$ CoPt (1.3 T). A breakthrough is needed to access intermediate values of coercivity without high temperature annealing. Meanwhile, one can exploit the use of localized annealing to obtain high coercivity. In this case only the region containing the electrodeposited material or the device needs to be annealed, keeping the other integrated parts within the admissible temperatures ($< 300\text{ }^{\circ}\text{C}$), using lasers or on-board local heaters

to produce local heating. The design and study of this alternative annealing process should be device-driven since the success will depend on the position of the device on the integrated system. Research should be focussed to identify the minimum distances required for a particular annealing temperature.

The microswitch can already be prepared by using $\text{Co}_{80}\text{Pt}_{20}(\text{P})$. The steps for the implementation of this device may include the preparation of masks for lithography, the design of the coils to deliver the switching magnetic field and the incorporation of electrical functionality which requires electrical contacts. Low resistance electrical contacts can be obtained by using Ag or Au.

The main driving force on the rest potential shift is the Lorentz force as discussed in chapter 6. However, it is possible that there is an additional contribution to the effect associated with the presence of O_2 in solution and the field gradient for ferromagnetic electrodes. Oxygen is paramagnetic and uncharged, therefore it cannot be affected by the Lorentz force. Consequently, a study involving a magnetic field gradient and O_2 would help to quantify their contribution to the rest potential shift of ferromagnetic electrodes. Also, fuel cells appeared as an alternative source for the always demanding need for clean sources of energy. A fuel cell is a device which extracts energy from the reaction between O_2 and H_2 according to the equation $2 \text{H}_2 + \text{O}_2 \rightarrow 2 \text{H}_2\text{O}$. Efficiency is always an issue whatever the source of energy. A study targeting the effect of the field gradient on the kinetics of O_2 reduction may help to improve fuel cell performance, enhancing the efficiency.

Chapter 7

7 List of publications

The publications related to this work are the following

1. G. Hinds, F.M.F. Rhen, J.M.D. Coey, "Magnetic field effects on the rest potential of ferromagnetic electrodes", IEEE Transactions on Magnetics, **38**, 3216 (2002).
2. F.M.F. Rhen, G. Hinds, C. O'Reilly and J.M.D. Coey, "Electrodeposited FePt Films", IEEE Transactions on Magnetics, **39**, 2699 (2003).
3. F.M.F. Rhen and J.M.D. Coey, "Structural characterization and magnetic properties of electrodeposited CoPt alloys", Journal of Magnetism and Magnetic Materials, **272-276**, E883 (2004).
4. F.M.F. Rhen, G. Hinds and J.M.D. Coey, "Magnetic field effect on the rest potential of zinc", Electrochemistry Communications, **6**, 413 (2004).
5. N.B. Chaure, P. Stamenov, F.M.F. Rhen and J.M.D. Coey, "Oriented cobalt nanowires prepared by electrodeposition in porous membrane", J. Magn. Magn. Mater, in press (2005).
6. F.M.F. Rhen, E. Backen and J.M.D. Coey, Thick-film permanent magnets by membrane electrodeposition, J. Appl. Phys. **97**, 113908 (2005).
7. F.M.F. Rhen, D. Fernandez, G. Hinds and J.M.D. Coey, "The influence of a magnetic field on the electrochemical rest potential", in press, Journal of the Electrochemistry Society (2005).

Other publications

1. M. Venkatesan, F.M.F. Rhen, R. Gunning, and J.M.D Coey, "Effect of Fe, Cu, Zr, and Ti on the magnetic properties of SmCo-1:7 magnets", IEEE Transactions on Magnetics, **38**, 2919 (2002).
2. M. Venkatesan, U.V. Varadaraju, A.P. Douvalis, C.B. Fitzgerald, F.M.F Rhen, J.M.D. Coey, "Enhanced magnetoresistance in $\text{Sr}_2\text{FeMoO}_6$ by combustion synthesis", Journal Materials Chemistry, **12**, 2184 (2002).
3. F.M.F. Rhen, M. Venkatesan, I.R. Harris and J.M.D Coey, "Effect of ZrB_2 additions on SmCo-1:7 high temperature magnets", Journal of Applied Physics, **93**, 8683 (2003).
4. M. Venkatesan, J. Buschbeck, F.M.F. Rhen and J.M.D. Coey, "Effect of annealing on magnetic properties of Nd-Fe-B films", Journal of Magnetism and Magnetic Materials, **272-276**, E881 (2004).

Patent

S2004/0809, "Thick film permanent magnets", Trinity College Dublin, Irish patent submitted in December 2004.

Appendix A

The rest potential analysis

The rest potential (E_0) corresponds to the point where the anodic current density is balanced by the cathodic current density ($j_c = j_a$). This is illustrated by the Evan's diagram in fig. 131.

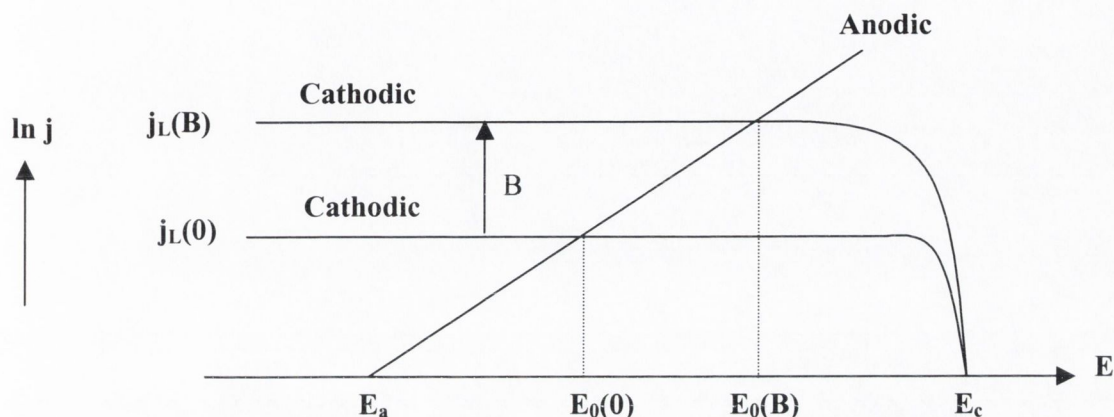


Figure 131. Evans diagram showing the effect of an applied magnetic field on the rest potential.

An anodic shift is observed because only the cathodic reaction is sensitive to the applied magnetic field. Here, j_L , B and E_0 stand for limiting current density, magnetic field and rest potential.

Assuming that the anodic current is activation controlled, according to Butler-Volmer¹ equation the anodic current density is given by:

$$j_a = j_0 \exp [(\alpha n F / RT) (E_0 - E_a)] \quad (1)$$

Here α is the anodic charge transfer coefficient, j_0 is the exchange current density, E_0 is the rest (corrosion) potential and E_a is the formal potential of the electrode.

For cathodic current limited by mass-transport $j_c \sim j_L$. Then, for zero field and a B field

$$\exp [\alpha nF (E_0(0)-E_a)/RT] = j_c(0) = j_L (0) \quad (2)$$

$$\exp [\alpha nF (E_0(B)-E_a)/RT] = j_c(B) = j_L (B) \quad (3)$$

Dividing (3) by (2) and defining the rest potential shift as $\Delta E_0 = E_0(B) - E_0(0)$

$$\exp [\alpha nF (\Delta E_0)/RT] = j_c(B)/j_c(0) \quad (4)$$

Taking the logarithms and rearranging

$$\Delta E_0 = (RT/\alpha nF) \ln [j_c (B)/ j_c(0)]$$

Now, using the current dependence on the field in the form $j_L(B) = j_L(0) + \beta B^n$

$$\Delta E_0 = (nF/\alpha) \ln \{ 1 + [\beta/j(0)] B^n \}$$

We can expand $\ln(1+x) \sim x$ for small values of x yielding the expression for the rest potential shift to the first order

$$\Delta E_0 = (RT/\alpha nF) \gamma B^n \quad (5)$$

$$\text{where } \gamma = [\beta/j(0)]$$

¹ Eliezer Gileadi, *Electrode Kinetics for Chemists, Chemical Engineers, and Materials Scientists*, VCH Publishers, Inc, printed USA, (1993).