Electrocrystallisation of CoFe Alloys
Under the Influence of
External Homogeneous Magnetic Fields

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To my beloved wife Kasia

and daughter Ola
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### The meaning of symbols used in text:

- **$a$**: crystal lattice constant
- **$a$**: activity
- **$a$**: constant
- **$A$**: electrode surface area
- **$A$**: nucleation rate constant
- **$\alpha$**: constant
- **$\alpha$**: roughness (Hurst) exponent
- **$B$**: magnetic flux density
- **$B_S$**: saturation magnetic flux density
- **$\beta$**: symmetry parameter (Butler-Volmer)
- **$\beta$**: width of the peak at half maximum intensity at $\theta$ angle
- **$\beta$**: growth exponent
- **$c$**: concentration
- **$c$**: constant
- **$\chi_m$**: molar magnetic susceptibility
- **$d$**: diameter
- **$d_{hkl}$**: interplanar distance
- **$D$**: diffusion coefficient
- **$D_K$**: weighted crystallite size
- **$\delta_D$**: diffusion layer thickness
- **$\delta_H$**: hydrodynamic layer thickness
- **$e$**: electron
- **$E$**: potential
- **$E^\circ$**: standard potential
- **$f$**: frequency
- **$f_0$**: resonance frequency of quartz oscillator
- **$F$**: Faraday’s constant ($96500 \text{ Cmol}^{-1}$)
- **$F_D$**: diffusion driving force
- **$F_G$**: gravity force
- **$F_L$**: Lorentz force
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<tr>
<td>$F_P$</td>
<td>paramagnetic concentration gradient force</td>
</tr>
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<td>$F_{\nabla B}$</td>
<td>magnetic field gradient force</td>
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<td>$H_c$</td>
<td>coercivity</td>
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<td>$\eta$</td>
<td>overpotential</td>
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<td>$i$</td>
<td>current density</td>
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<td>$i_0$</td>
<td>exchange current density</td>
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<td>$i_{lim}$</td>
<td>limiting current density</td>
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<tr>
<td>$I$</td>
<td>current</td>
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<td>$J$</td>
<td>magnetic polarisation</td>
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<td>remanence magnetic polarisation</td>
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<td>$J_s$</td>
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<td>$k$</td>
<td>constant</td>
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<td>$k_M$</td>
<td>electrochemical equivalent of M</td>
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<td>$l$</td>
<td>spatial size (length)</td>
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<td>$l_c$</td>
<td>critical length</td>
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<td>$\lambda$</td>
<td>wave length</td>
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<td>$m$</td>
<td>constant</td>
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<td>$m$</td>
<td>mass</td>
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<td>$M$</td>
<td>molar mass</td>
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<td>$\mu_0$</td>
<td>magnetic permability of a free space ($1.26 \cdot 10^{-6} \text{VsA}^{-1}\text{m}^{-1}$)</td>
</tr>
<tr>
<td>$\mu_q$</td>
<td>quartz shear modulus ($2.947 \cdot 10^{11} \text{g cm}^{-1}\text{s}^{-2}$)</td>
</tr>
<tr>
<td>$n$</td>
<td>Overstone number</td>
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<tr>
<td>$n$</td>
<td>order of reflection</td>
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<tr>
<td>$n$</td>
<td>Néel’s exponent</td>
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<tr>
<td>$N_0$</td>
<td>number of nuclei at saturation (saturation nucleus density)</td>
</tr>
<tr>
<td>$N(t)$</td>
<td>number of nuclei at time $t$</td>
</tr>
<tr>
<td>$\nu$</td>
<td>kinematic viscosity</td>
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<tr>
<td>$\theta$</td>
<td>incident angle</td>
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<tr>
<td>$\theta$</td>
<td>fraction of the surface area</td>
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<td>$\theta_{ex}$</td>
<td>extended area fraction</td>
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<td>$r$</td>
<td>radius</td>
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LIST OF SYMBOLS

\(R\) – universal gas constant (8.314 JK\(^{-1}\)mol\(^{-1}\))
\(R_{\text{rms}}\) – root mean square roughness
\(\rho\) – density
\(t\) – time
\(T\) – temperature
\(u\) – time at which nucleus has been born
\(w(l, t)\) – surface width
\(x\) – atomic (molar) fraction
\(\Psi\) – interaction energy
\(z\) – number of charges taking part in the electrochemical reaction

Abbreviations:
AES – Auger electron spectroscopy
AFM – atomic force microscope
\(b\text{ccc}\) – body centred cubic
BOS – background oriented schlieren
CA – chronoamperogram
CE – counter electrode
CV – cyclic voltamogram
DL – electrochemical double layer
EDX – energy dispersive X-ray spectroscopy
EQCM – electrochemical quartz crystal microbalance
FIB – focus ion beam
FM – Frank-van der Merve mechanism
\(f\text{cc}\) – face centred cubic
GC – glassy carbon
\(h\text{cp}\) – hexagonal close packed
HER – hydrogen evolution reaction
HOPG – highly oriented pyrolytic graphite
HRTEM – high resolution TEM
HT – Heerman-Tarallo model
<table>
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<th>Symbol</th>
<th>Description</th>
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<tr>
<td>ICP-OES</td>
<td>inductively coupled plasma optical emission spectrometer</td>
</tr>
<tr>
<td>MHD</td>
<td>magnetohydrodynamic</td>
</tr>
<tr>
<td>ML</td>
<td>monolayer</td>
</tr>
<tr>
<td>MN</td>
<td>Mirkin-Nilov model</td>
</tr>
<tr>
<td>MOKE</td>
<td>magneto-optical Kerr effect</td>
</tr>
<tr>
<td>ND</td>
<td>nano-diffraction</td>
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<tr>
<td>OPD</td>
<td>overpotential deposition</td>
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<tr>
<td>PIV</td>
<td>particle image velocimetry</td>
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<tr>
<td>RDE</td>
<td>rotating disc electrode</td>
</tr>
<tr>
<td>REF</td>
<td>reference electrode</td>
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<tr>
<td>SAD</td>
<td>selected area diffraction</td>
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<tr>
<td>SEM</td>
<td>scanning electron microscope</td>
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<tr>
<td>SH</td>
<td>Scharifker-Hills model</td>
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<td>Stranski-Krastanow mechanism</td>
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<td>SM</td>
<td>Scharifker-Mostany model</td>
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<tr>
<td>STM</td>
<td>scanning tunnelling microscope</td>
</tr>
<tr>
<td>TEM</td>
<td>transmission electron microscope</td>
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<tr>
<td>UPD</td>
<td>underpotential deposition</td>
</tr>
<tr>
<td>VSM</td>
<td>vibrating sample magnetometer</td>
</tr>
<tr>
<td>VW</td>
<td>Volmer-Weber mechanism</td>
</tr>
<tr>
<td>WE</td>
<td>working electrode</td>
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<td>XRD</td>
<td>X-ray diffraction</td>
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1. INTRODUCTION

The iron-group metals and alloys are of interest because of their magnetic properties [1-3]. They have found a wide application field in the storage technology, especially for reading/writing elements in the hard drive head [4,5], and in microelectromechanical systems (MEMS) [6]. The Fe-group alloys are characterized by their excellent soft magnetic properties [7]. Especially the CoFe system, which possesses the highest, among others, saturation magnetisation of 2.45 T and a relatively low coercivity of about $2 \times 10^{-5}$ T [2], is of interest. These properties are crucial for the further development in the storage technology, i.e. for the hard drive’s writing head. The reason is that the development of new magnetic recording materials has been accompanied by a substantial increase of their coercivity [8] and thus soft magnetic materials with a higher saturation flux density are necessary in order to write on them.

Electrodeposition is a very promising alternative to the physical vapour deposition techniques (PVD) to produce soft magnetic layers and microstructures. The advantage of electrodeposition in comparison to PVD processes is the fact that it is an inexpensive method compared to the latter one. Moreover, electrodeposition is the most appropriate process for the writing head fabrication since it allows to deposit high aspect ratio layers with a thickness ranging from a few monolayers up to more than 1 µm onto a complex geometry substrate [8]. However, in order to deposit a good quality layer of desired properties the deposition parameters have to be optimized.

It has been shown that the Fe-group alloy films with excellent soft magnetic properties can be electrodeposited from aqueous electrolytes [2,8,9] and the deposited layer properties could be tailored by a proper selection of the process parameters. But the electrodeposition of Fe-group metals and alloys from aqueous electrolytes could be accompanied by side reactions, mainly the hydrogen evolution reaction, which in turn significantly affects the deposit properties [2,10]. There are many parameters with which it is possible to tune the deposit properties, for example: the electrolyte composition, the pH value of the electrolyte, the temperature, the deposition potential or the current density [2,9,11].

A superposition of an external magnetic field during the electrodeposition has gained a considerable attention during the past decade [12,13], since it can affect the deposit properties. Mainly the morphology of the deposited layers is influenced [14-20]. But it has also been reported that a magnetic field applied during the deposition could texture the deposit [21-23], affect its phase composition [24] and reduce the internal stress of the layer [14,18]. Additionally,
when magnetic alloy layers are deposited under the influence of an external magnetic field, an in-plane anisotropy could be induced [2,14,16], which is of commercial importance [2]. Moreover, the very initial steps of the deposition could be affected by a superposed magnetic field as well [25-27]. Most of the above mentioned effects are caused by the Lorentz force driven convection, i.e. the magnetohydrodynamic (MHD) effect. But other magnetically induced effects, for example a field gradient force [28], could have a significant contribution to the layer formation.

Whilst the knowledge of uniform external magnetic field effects on the electrodeposition of single metals has been greatly improved during the past decade, an alloy deposition is still a challenging task. To the author’s best knowledge there is only one report available, besides own work, dealing with the deposition of CoFe alloys under the influence of external magnetic fields [125]. Due to a lack of understanding of mechanisms of a magnetic field impact on the deposition of CoFe alloys and their technological importance a detailed investigation is of demand. The aim of this work is to analyse in detail the effects induced by a homogeneous magnetic field with different strength and relative-to-electrode surface orientation on the electrodeposition of thin CoFe alloy films, including separate investigations of each constituent. This thesis is divided in three major parts.

The first one is devoted to a detailed analysis of the electrochemical processes, i.e. the influence of the magnetic field with respect to its flux density and relative-to-electrode surface orientation on the reactions rates, with a special attention given to the side reactions accompanying the metal reduction, i.e. the hydrogen evolution reaction. The latter one is known to have a significant impact on the layer’s properties development [2,10] and mechanisms governing the hydrogen formation and desorption from the electrode surface under the influence of a magnetic field, which is of considerable importance, will be studied as well.

In the second part, since the properties of thin films are determined mainly by nucleation processes, an extensive study of the very initial stages of electrocrystallization will be presented, i.e. the nucleation and growth processes under magnetic fields will be discussed. This will be performed by an analysis of the current density vs. time transients recorded during the potentiostatic deposition. The experimental dependencies will be examined by known theoretical models and the morphology evolution with the progress of deposition will be discussed on a microscopic investigations basis.

In the third part the influence of a magnetic field on morphology, chemical composition, crystal structure and texture, and magnetic properties will be extensively discussed. It has been shown
that a magnetic field superposition could texture the deposited layer [21-23]. Thus the anisotropic magnetic properties should be studied. The morphology of thin films, which could be affected by magnetic fields [14-20], is also known to have a great impact on the layer’s magnetic properties. Due to the complicity of these processes an attempt will be made in order to establish a cross link between the microstructure and the magnetic properties.
2. STATE OF RESEARCH

2.1. FUNDAMENTALS OF ELECTRODEPOSITION

Electrodeposition is an inexpensive method to obtain a variety of layers as well as microstructures [29]. This method allows depositing layers with a thickness ranging from a few nm to tens of mm. Metallization by electrodeposition is a well established technological method used to obtain functional layers as well as for decorative applications. Electrodeposition is also known as a method which allows depositing layers of non-equilibrium compositions and structures, intermetallic compounds, oxides, etc [30]. In the following sections the basic principles of electrodeposition will be discussed together with the parameters which may influence these processes.

2.1.1. Electrocrystallization

Electrodeposition is an electrochemical process which by definition occurs at the interface between the electrode surface and the electrolyte. In the electrolyte ions are present which can be reduced or oxidized at the electrode surface what is related to the charge transfer through the interface. Thus these processes are considered as heterogenic [31]. When a metallic electrode is immersed into the electrolyte solution containing metal ions (M$^{z+}$) the electrode will reach equilibrium with the metal ions according to the reaction:

$$M^{z+} + ze \leftrightarrow M$$ (2.1)

This equilibrium can be described by the equilibrium potential ($E_{w^{+}/o}^{a}$) through the Nernst equation [31]:

$$E_{w^{+}/o}^{a} = E_{w^{+}/o}^{0} - \frac{RT}{zF} \ln \frac{a_{M}}{a_{M^{z+}}}$$ (2.2)

where: $E_{w^{+}/o}^{0}$ is the standard potential, $R$ – the universal gas constant, $T$ – the temperature, $z$ – the number of electrons involved in the reaction, $F$ – Faraday’s constant, $a_{M}$, $a_{M^{z+}}$ – the activities of metal $M$ in the solid and metal ions in the electrolyte, respectively.

The direction of the reaction (2.2) can be affected by polarization of the electrode. At this point it is necessary to introduce the concept of the overpotential ($\eta$) which is defined as a potential
difference between the applied potential and the equilibrium potential. The sign of $\eta$ determines whether the reaction is cathodic (reduction – negative sign) or anodic (oxidation – positive sign). The electrochemical reaction rate can be expressed as a current density ($i$) and the electrode kinetics can be described by the Butler-Volmer equation [32]:

$$
\begin{align*}
    i &= i_0 \left\{ \exp \left[ \frac{\beta z F \eta}{RT} \right] - \exp \left[ -\frac{(1-\beta)z F \eta}{RT} \right] \right\} \\
    &= i_0 \left\{ \exp \left[ \frac{\beta z F \eta}{RT} \right] - \exp \left[ -\frac{(1-\beta)z F \eta}{RT} \right] \right\} \\
    &= i_0 \left\{ \exp \left[ \frac{\beta z F \eta}{RT} \right] - \exp \left[ -\frac{(1-\beta)z F \eta}{RT} \right] \right\}
\end{align*}
$$

(2.3)

where $i_0$ is the exchange current density and $\beta$ – the asymmetry parameter.

In expression (2.3) both reactions, i.e. reduction and oxidation, are considered, but, if $\eta$ is high enough, one of them can be neglected. The Butler-Volmer equation in the form of Eq. (2.3) assumes an equal concentration of reactants (metal ions) at the electrode surface and in the bulk electrolyte. This is only true when the mass transport of ions towards the electrode is faster than the charge transfer processes. In electrochemical systems it is often the case that the charge transfer processes are extremely fast compared to the transport of the reactants to or away from the interface. Thus the concentration of the electroactive species at the electrode surface will be significantly lower than that of the bulk electrolyte. This has to be considered in Eq. (2.3) by the correction of the concentration overpotential. Additionally, it is assumed that $\eta$ is negative enough to neglect the anodic part of Eq. (2.3).

$$
\begin{align*}
    i &= -i_0 \frac{c_s}{c_s^*} \exp \left[ -\frac{(1-\beta)z F \eta}{RT} \right] \\
    &= -i_0 \frac{c_s}{c_s^*} \exp \left[ -\frac{(1-\beta)z F \eta}{RT} \right]
\end{align*}
$$

(2.4)

Where $c$ is the concentration of metal ions and $s$ and * denominate surface and bulk, respectively.

The reduction of metallic ions at the electrode surface may lead to a layer formation. However the layer formation processes are complex and will be discussed in Chapter 2.1.3.

2.1.2. Mass Transport of Ions to the Electrode Surface

Before the ions can be reduced or oxidized at the electrode/electrolyte interface they have to be transported from the bulk electrolyte to the electrode surface. In Fig. 2.1 characteristic zones of the electrodeposition system are schematically shown together with their length scales. Starting from the bulk solution the following characteristic regions can be distinguished: bulk solution, hydrodynamic layer, diffusion layer and, at the interface, the electrical double layer (DL). In the bulk electrolyte the mass transport is governed by convection and migration, and a potential distribution occurs. The migration contribution to the mass transport of ions can be
suppressed by the addition of a supporting electrolyte [31]. In the hydrodynamic layer the velocity gradient is present but the mass transfer is also governed by convection. Going further towards the electrode surface the diffusion layer (concentration boundary layer) is formed where the mass transport is determined by diffusion. Finally the DL where the charge transfer occurs.

When the charge transfer processes are very fast compared to the transport of electroactive species the system is mass transport controlled and the reaction rate is determined by the transport rate of ions, i.e. by diffusion controlled processes. A concentration gradient ($\nabla c$) is formed in front of the electrode surface and a diffusion driving force arises ($F_D$). The rate of diffusion is proportional to the concentration gradient and can be expressed by Fick’s first law:

$$ J = -D \cdot \nabla c \quad (2.5) $$

where $J$ is the flux of the electroactive species, $D$ – the diffusion coefficient of the electroactive species and $\nabla c$ – the concentration gradient.

The concentration changes due to diffusion are described by Fick’s second law:

$$ \frac{\partial c}{\partial t} = D \cdot \nabla^2 c \quad (2.6) $$

where: $t$ is time.

By applying a potential step (cathodic) to the electrode the diffusion layer will be formed. Assuming a planar electrode which is uniformly accessible the cathodic diffusion-limited current can be expressed, according to Eq. (2.5) as follows:

$$ i = -zFD \left( \frac{\partial c}{\partial x} \right)_{x=0} \quad (2.7) $$

where $\frac{\partial c}{\partial x}$ is the concentration gradient normal to the electrode direction.

**Fig. 2.1.** Schematic representation of an electrodeposition system with its characteristic zones and length scales.
Now if we assume a linear concentration gradient (Nernst diffusion layer) and solve the second Fick’s law with following boundary conditions:

\[ t = 0, \quad c^* = c' \quad \text{(no electrode reaction)} \quad (2.8) \]
\[ t \geq 0, \quad \lim_{x \to \infty} c = c^* \quad \text{(bulk solution)} \quad (2.9) \]
\[ t \geq 0, \quad x = 0 \quad \text{(diffusion-limited current)} \quad (2.10) \]

we get the dependence of the current density changes with time known as Cottrell equation:

\[ i(t) = -zFc^* \sqrt{\frac{D}{\pi t}} \quad (2.11) \]

which predicts an exponential decay of current with time [31,32]. Equation (2.11) is valid only in a limited time range. At the beginning of the potential step the DL charging and nucleation processes might be significant and the current response will be obscured. Additionally, in a real diffusion-limited system, a current density decay to a limiting value called diffusion limited current density \( i_{\text{lim}} \) and a deviation from the Cottrell behaviour is expected. Moreover, if we consider a steady state condition, it is apparent that a limiting current density is proportional to the diffusion layer thickness (Eq. (2.12)). This clearly indicates that \( i_{\text{lim}} \) can be affected by changing the hydrodynamic conditions of the system which affect the diffusion layer thickness [31].

\[ i_{\text{lim}} = -\frac{zFD}{\delta_d} \quad (2.12) \]

2.1.3. Nucleation, Growth and Phase Formation of Electrodeposited Layers

The nucleation and the early stages of layer growth are of fundamental and theoretical interest. When thin films are deposited, the nucleation processes will determine the physical properties of the layer. Thus, the understanding of the earliest stages of film growth and of the influence of the deposition parameters is of great importance for the process development and optimisation. It is known that the deposition potential and the electrolyte composition [33-38], but also the hydrodynamic condition [39,40], affect the nucleation and the further growth of the layers. In order to better understand these effects the nucleation mechanisms will be discussed with a special attention given to nucleation and 3D diffusion-controlled growth processes.
In Fig. 2.2 the initial stages of electrocrystallization are shown. The metal ions present in the bulk electrolyte are hydrated and diffuse towards the electrode losing partially their hydration spheres [41]. In the Helmholtz layer the ions lose the rest of their hydration sphere and can finally be discharged and form ad-atom, adsorbed at the electrode surface. Before the ad-atoms are incorporated into the lattice they have to find energetically favourable sites in the vicinity which is done by surface diffusion. The preferred incorporation sites in electrodeposition are defects such as dislocations, vacancies, etc. It is also possible, mainly for single crystal or amorphous substrates, to incorporate the ad-atoms into a cluster and to form a stable nucleus [42].

The mechanism of nucleation and growth of the layer is determined by the interaction energies of the ad-atoms with the atoms of the metal substrate ($\Psi_{Me-S}$) and atoms of the same kind ($\Psi_{Me-Me}$), and the crystal lattice misfit between the substrate and the deposited layer. According to the classical models of nucleation and growth three limiting cases can be distinguished [43]. The Volmer-Weber (VW – island growth) mechanism (Fig. 2.3a) is observed when $\Psi_{Me-S} << \Psi_{Me-Me}$, irrespective of the lattice misfit. The Frank-van der Merve (FM) mechanism, a 2D layer-by-layer growth mode is observed when $\Psi_{Me-S} >> \Psi_{Me-Me}$, and the lattice misfit is negligible (Fig. 2.3b). An intermediate between the VW and the FM mode has been proposed by Stranski-Krastanov (SK). The SK mode is observed when $\Psi_{Me-S} >> \Psi_{Me-Me}$, but the lattice misfit is significant (Fig. 2.3c). At the beginning the 2D growth is observed but due to the lattice misfit the deposited layer is stressed and after a few deposited monolayers (MLs) a 3D island growth is observed in order to relieve the stress.
STATE OF RESEARCH

By in-situ STM studies Gündel et al. [44] have observed that the Fe film can be grown on Au(111) with a 2D growth mode. They have observed that the first two MLs show the non-equilibrium fcc structure \((a=3.43 \text{ Å})\) with a (111) plane parallel to the Au(111) fcc plane \((a=4.08 \text{ Å})\). In order to fit with the Au lattice, the fcc Fe(111) planes were rotated by 30° with respect to Au. This gives a misfit of -3% (compression) between the Au(111) fcc and Fe(111) fcc lattices. In the range of 2-5 MLs a transition from Fe(111) fcc to Fe(110) bcc \((a=2.87 \text{ Å})\) has been reported, with a nearly perfect layer-by-layer growth [44]. This growth mode is in agreement with the FM mechanism (Fig. 2.3b). Due to a lattice misfit it is expected that at a sufficient deposit thickness a shift from the 2D to the 3D growth mode will occur as predicted by the SK growth mechanism (Fig. 2.3c). Similar results have been reported for Co deposition onto an Au(111) substrate [45]. Kleinert et al [45], by in-situ STM investigations, have observed that after applying a potential step to the Au(111) electrode a formation of the epitaxial atomically flat Co bilayer takes place. From the atomic distances of the first ML it was concluded that this layer corresponds to the Co(111) fcc plane \((a=3.42 \text{ Å})\), which has to be rotated with respect to the Au(111) plane by ca. 30° as in the case of Fe (nearly the same lattice constant for both elements) in order to fit to the Au lattice. The epitaxial growth was observed up to about 4 MLs and then 3D growth has been reported. This growth mode follows the SK growth mechanism (Fig. 2.3c). Similar results regarding Co deposition onto an Au(111) electrode have been reported by Krause et al. [46]. Medndoza-Huizar et al. [47] have found, studying the electrocrystallization of Co onto a polycrystalline Au electrode, that the growth proceeds through successive steps, i.e. a 2D growth followed by a 3D diffusion-controlled growth has been reported, which is a typical case of the SK growth mechanism (Fig. 2.3c). It is also possible by selecting a proper substrate to observe the VW growth mechanism. For this purpose a glassy carbon (GC) or highly oriented pyrolytic graphite (HOPG), known to have a low metal-
substrate (Me-S) interaction [43], are chosen. This feature has been commonly employed to study the nucleation behaviour of metals followed by a 3D growth [36-39,43,48]. For example Grujicic and Pesic [37] studied the nucleation behaviour of Co onto a GC electrode by means of a current-time transients analysis and in-situ electrochemical AFM investigations. They have determined the influence of the electrolyte pH value, the concentration of Co$^{2+}$ and the deposition potential on the nucleation behaviour. Moreover the coordination of Co crystals formed at the electrode has been discussed on the basis of AFM investigations. The significance of the hydrogen co-reduction on the dimension of the Co nuclei has been emphasized.

It has been proposed that the nucleation and the early stages of growth can be studied by the analysis of the $i(t)$ transients obtained in a potentiostatic experiment [42,49,50]. The pioneer work in this field has been made by Fleischmann and Thirsk [51] who observed maxima followed by a current decay in the $i(t)$ transients obtained as an answer to a potential step applied to the electrode. They have proposed a so-called nucleation rate law, which stated that the nuclei at the active sites are formed according to the exponential dependence:

$$N(t) = N_0(1 - \exp[-At])$$

where $N(t)$ is the number of nuclei at time $t$, $N_0$ – the number of nuclei at saturation (saturation nucleus density) and $A$ – the nucleation rate constant.

In the nucleation rate law two limiting cases can be distinguished: (i) at $A<<1$ Eq. (2.13) reduces to $N(t)=N_0At$, i.e. ‘progressive nucleation’; (ii) at $A>>1$ Eq. (2.13) reduces to $N(t)=N_0$, i.e. ‘instantaneous nucleation’ (all nuclei are activated at the same time, $t\to0$). However the nucleation rate law in a form of Eq. (2.13) has been criticised by Deutscher and Fletcher [52]. This criticism was mainly related to the assumption that the whole electrode surface has the same nucleation activity but on the other hand allows the $N_0$ to be potential dependent. They have claimed that the electrode surface is not uniformly accessible for nucleation and that there is a distribution of the site activity which is potential-dependent. This activity distribution has been introduced to the nucleation rate law as ‘nucleation rate dispersion’. A large variety of models has been proposed to model the $i(t)$ transients based on Eq. (2.13) assuming different nucleus geometries and different rate-determining steps [42,49,50]. Because of this, the further discussion will be devoted to a specific situation, namely the nucleation followed by a 3D diffusion-controlled growth of hemispherical nuclei.
The starting point for the modelling of the \( i(t) \) transient is the expression of \( i(t) \) for a single nucleus growing under diffusion control, i.e. with a hemispherical diffusion zone as illustrated in Fig. 2.4. The current density to a single nucleus under diffusion-limiting conditions is expressed, regarding its small size similarly to the ultramicroelectrode [53]:

\[
i(t) = 2FDc^* \alpha(t-u)^{\frac{1}{2}}, \quad \alpha = 2\pi \left( \frac{2MDc^*}{\rho} \right)^{\frac{1}{2}} \tag{2.14}
\]

where \( M \) and \( \rho \) are the molar mass and the density of the deposited material, respectively and \( u \) – the time at which the nucleus has been born.

The next step is to consider multiple nucleations at the electrode according to the nucleation rate law. Assuming that the nuclei grow independently of each other the total current can be written as a sum of all individual nuclei currents [33]:

\[
I_{N,t} = \sum_{i=1}^{N} I_{i,t-u} \tag{2.15}
\]

where: \( N \) is the total number of nuclei, \( I_{i,t-u} \) – the current to an individual nucleus \( i \) of age \( t-u \).

It is easy to imagine that the growing centres and more importantly the diffusion zones surrounding them will interfere with time and Eq. (2.15) would not be valid anymore. This phenomenon is known as an overlap problem and a solution of it has been proposed by Scharifker and Hills [33]. They have implemented the concept of ‘planar diffusion zones’, i.e. before the overlap, when nuclei grow independently, they develop hemispherical diffusion zones, but at the moment of overlap the thickness of interacting diffusion zones has to be equal. In order to make this possible a 2D projection of the diffusion zones in the form of cylinders, where the linear diffusion is assumed, covering an equivalent area of the electrode proportional to the nucleus age has been made (Fig. 2.5a). This assumption reduces the problem of overlapping diffusion zones to a 2D one and the overlap can be treated by the Avrami theorem for a 2D overlap [54,55]. Accordingly to which real fraction of the surface area \( (\theta) \), to which diffusion occurs, can be expressed by the area fraction of diffusion zones without overlap (extended area fraction \( - \theta_{ex} \)) through Eq. (2.16) (Fig. 2.5b).

\[
\theta = 1 - \exp(-\theta_{ex}) \tag{2.16}
\]
Different models were proposed in order to analyse the $i(t)$ transients, which assume nucleation followed by a 3D diffusion-controlled growth, but all of them predict a similar $i(t)$ transients shape, i.e. after a sharp rising part a maximum is observed followed by an exponential decay (Cottrell behaviour).

One of the first and still widely used nucleation and 3D diffusion-controlled growth models has been proposed by Scharifker and Hills (SH) [33]. The SH model has been divided into two limiting cases: the progressive and the instantaneous one. In order to distinguish between these two limiting cases it was proposed to compare the experimental results with the theoretical ones in reduced current-reduced time coordinates for a progressive (Eq. (2.17)) and an instantaneous (Eq. (2.18)) mode.

\[
\left( \frac{i}{i_{\text{max}}} \right)^2 = 1.2254 \frac{t_{\text{max}}}{t} \left[ 1 - \exp \left\{ -2.3367 \left( \frac{t}{t_{\text{max}}} \right)^2 \right\} \right]^2 \quad (2.17)
\]

\[
\left( \frac{i}{i_{\text{max}}} \right)^2 = 1.9542 \frac{t_{\text{max}}}{t} \left[ 1 - \exp \left\{ -1.2564 \left( \frac{t}{t_{\text{max}}} \right) \right\} \right]^2 \quad (2.18)
\]

where: $i_{\text{max}}$ and $t_{\text{max}}$ are the current density and time coordinates of the maximum in the $i(t)$ transient, respectively.

The SH model has been extensively used to distinguish between the limiting nucleation and growth modes [26,34-37,56,57]. However it has very strong limitations which have to be considered before drawing any conclusions out of it. It has been shown [53] that the reduced coordinate plots hide some details of the $i(t)$ transient like a maximum current density which
might be higher than the one calculated by the Cottrell equation (Eq. (2.11)), which is a limit of
the SH model and the current can not exceed it, what has been commonly observed [20,38,53].
Another problem has been pointed out by Cao and West [58]: namely that at low deposition rates
where a deviation from a diffusion control occurs, an instantaneous nucleation could appear as a
progressive one in the reduced coordinate plots.
Soon after the SH model was published a correction to it has been proposed by Scharifker and
Mostany (SM) [59]. The correction essentially removed the restriction of the two limiting cases
analysis and allowed to analyse a whole variety of results which could lie in between of the
limiting ones. Originally the approach was based on the analysis of the singular point, i.e. the
coordinates of the maximum of the \( i(t) \) transient. This method however is not a perfect one since
the analysis based on one point may lead to a large error and assumes that the diffusion
coefficient value is known [60]. This idea has been modified and a fitting procedure to a whole
transient was proposed by the SM model expressed as follows:

\[
i(t) = zF_{c^*} \left[ \frac{D}{\pi} \left[ 1 - \exp\left( -\frac{\pi N_{o} D t \Theta}{8} \right) \right] \right]
\]

(2.19)

where: \( k = \left( \frac{8\pi M_{c^*}}{\rho} \right)^{\frac{1}{2}} \) and \( \Theta \) given by:

\[
\Theta = 1 - \frac{\left[ 1 - \exp\left( -\frac{At}{\lambda^2} \right) \right]}{At}
\]

(2.20)

The SM model has been also widely explored in the nucleation studies [34,35,56], although it has
the limitation regarding the current density values which can not exceed the Cottrell limit.
A similar approach to the nucleation and early stages of 3D diffusion-controlled growth has been
made by Mirkin and Nilov (MN) [61] and independently by Heerman and Tarallo (HT) [53].
They have proposed a correction to the SM model claiming that the equivalent diffusion layer
thickness has to depend not only on time but also depends on the nucleation rate constant [53].
This leads to the expression:

\[
i(t) = zF_{c^*} \left[ \frac{D}{\pi} \frac{\Phi}{\Theta} \left[ 1 - \exp\left( -\frac{\pi k N_{o} D t \Theta}{8} \right) \right] \right]
\]

(2.21)

where: \( \Phi \) is related to Dowson’s integral:

\[
\Phi = 1 - \frac{\exp\left( -\frac{At}{\lambda^2} \right)}{\sqrt{At}} \int_{0}^{\sqrt{At}} \exp \lambda^2 d\lambda
\]

(2.22)

and represents the retardation of the current density due to a slow nucleation.
On the basis of the presented models the nucleation parameters can be obtained together with their dependencies on the deposition parameters.

It is known that the deposition potential and the electrolyte composition [26,33-38,40,43,62], but also the hydrodynamic conditions [40,62], affect the nucleation and the further growth of the layers. It is established that the increase of the applied potential as well as of the concentration of electroactive species in the electrolyte increases $A$ and $N_0$. The organic additives have a great impact on the nucleation processes, for example even very small addition of thiourea to the Cu electrolyte increases the $N_0$ value [34]. The hydrodynamic conditions may significantly affect the nucleation rate [40,62]. It has been shown that a forced convection (flow cell, stirred cell) increases $A$ whereas $N_0$ remains unchanged when compared to the quiescent condition [62]. On the contrary, under sonicated conditions a retardation of $N_0$ has been reported [40]. There are also a few reports available regarding the influence of an external magnetic field, applied during the deposition, on the nucleation behaviour of the electrochemical system [25-27]. A clear effect of magnetic fields on the nucleation rate has been shown, which has been attributed to the convective effects induced by magnetic fields.
2.2. INFLUENCE OF AN EXTERNAL MAGNETIC FIELD ON THE ELECTRODEPOSITION PROCESS

A superposition of an external magnetic field during the electrodeposition has gained a considerable attention during the past decade [12,13]. It has been established that a magnetic field could significantly affect the deposition process. Mainly the mass transport is affected by magnetically induced forces. On the contrary, no significant effects of magnetic fields on the electrode kinetics are expected [63,64]. In the following sections the magnetic field impact on the electrochemical reactions as well as its influence on the deposited layer quality will be discussed.

2.2.1. Magnetically Induced Forces

It has been shown that superposed magnetic fields influence mainly the rate of mass transport of ions and, thus, can affect the morphology and the texture of the deposit [17-24,65-68]. Magnetic field effects on electrochemical reactions are widely accepted and summarized in various reviews [12,13,69]. The known magnetic forces which may affect the mass transport in the electrolyte are: the Lorentz force ($F_L$), the field gradient force ($F_{\nabla B}$) and the paramagnetic force ($F_P$).

The Lorentz force acts on moving ions in a magnetic field and appears when magnetic field lines cross the electric field lines (Eq. 2.23):

$$\vec{F}_L = \vec{i} \times \vec{B}$$  \hspace{1cm} (2.23)

where: $i$ is the current density and $B$ – the magnetic flux density.

The Lorentz force acts in the whole volume of the electrolyte and is accepted as the main driving force of the so-called magnetohydrodynamic (MHD) effect i.e. an enhanced convection in the magnetic field (this will be discussed in detail in chapter 2.2.2).

The field gradient force and the paramagnetic force, generated by a magnetic field, act on the magnetic ions and are independent of the direction of the applied magnetic field. These forces are derived by differentiating the energy density of an electrolyte in the presence of a magnetic field:

$$E = -\chi_m \frac{B^2}{2\mu_0} c^*$$  \hspace{1cm} (2.24)

where: $\chi_m$ is the molar susceptibility of ions, $\mu_0$ – the permeability of the free space.
The field gradient force \([70,71]\) acts on the magnetic ions to move them in the magnetic field gradient. \(F_{VB}\) is proportional to the magnetic flux density and its gradient, and depends on the magnetic properties of the electroactive ions. Paramagnetic ions move in the direction of the gradient and diamagnetic ones in the opposite way.

\[
\vec{F}_{VB} = \chi_m \frac{B \nabla B}{\mu_0} c^* \tag{2.25}
\]

\(F_{VB}\) can significantly affect the electrochemical processes. It was shown by Chaure et al. \([72]\) that a field gradient can significantly increase the oxygen reduction from alkaline media. It was observed by Sueptitz et al. \([73]\) that a field gradient arising from the magnetization of an iron wire in a homogeneous magnetic field can significantly reduce the active–passive transition potential.

The paramagnetic force was proposed by O’Brien and Santhanam \([74]\) and Waskaas and Kharkaas \([75]\). They observed that a uniform magnetic field acts on the electrolyte volume containing magnetic ions. When a gradient of the magnetic susceptibility occurs, as it does in the case of electrodeposition processes, it is supposed that the magnetic field causes an additional convection in the diffusion layer. The direction of \(F_P\) depends on the properties of the ions. According to Eq. (2.26), \(F_P\) has the same direction as the gradient of the paramagnetic ions \((\nabla c)\). Thus, in the case of electrodeposition paramagnetic ions are pushed away from the surface and diamagnetic ions are attracted to it.

\[
\vec{F}_P = \chi_m \frac{B^2}{2\mu_0} \nabla c \tag{2.26}
\]

Leventis and Dass \([76]\) have claimed that \(F_P\) is responsible for the concentration boundary layer formation at the microelectrode surface by the attraction of a paramagnetic species and can be stronger than the gravitational force. Enhanced mass transport during electrodeposition of paramagnetic ions in a uniform magnetic field caused by \(F_P\) was questioned \([77]\). Hinds et al. \([77]\) compared \(F_P\) with the diffusion driving force \(F_D\) and concluded that \(F_P\) is negligible and is not expected to play any significant role in mass transport. More recently, Coey et al. \([78]\) concluded that there is no first order concentration gradient force acting on diamagnetic or paramagnetic ions in a uniform magnetic field, but there is a second order correction related with a demagnetizing field. This second order body force is very low and is not expected to be observed in electrochemical experiments. They suggested that effects observed by O’Brien and
Santhanam [74], Waskaas and Kharkats [75], Leventis and Gao [76], and Krause et al. [79] are not related to the paramagnetic force, but to some other magnetic effect, for example a very small field gradient. It was also shown by Weier et al. [80], who repeated the experiments of Leventis and Gao [76], that the Lorentz force-driven convection is more likely the reason of such behaviour rather than the paramagnetic force. They have shown by numerical simulations and by interferometry and background oriented schlieren (BOS) method that the concentration boundary layer is formed because of a Lorentz force-driven convection which creates a stagnation point directly at the electrode surface.

2.2.2. Classical Magnetohydrodynamic Effect

As it was mentioned in a previous section, the $F_L$ acting in the hydrodynamic layer is accepted as the main driving force of the MHD-effect, i.e. an enhanced convection in the magnetic field. For diffusion-limited processes the MHD-effect causes a reduction of the diffusion layer thickness and an increase of the limiting current density ($i_{lim}$) [17,64,69,77,81-83]. Fahidy [84] was one of the first who made an attempt to model the MHD-effect and proposed a semiempirical solution to this problem. The dependence of the limiting current density with magnetic flux density has been established as power dependence:

$$i_{lim}^B = i_{lim}^{OT} + aB^m$$

(2.27)

where: $i_{lim}^{OT}, i_{lim}^B$ is the limiting current density obtained without and in a magnetic field, respectively, $B$ – the magnetic flux density applied parallel to the electrode surface and $a, m$ are empirical constants.

Aogaki et al. [85] have shown by solving the Navier-Stokes equation that the limiting current density increases as a power function of the magnetic flux density, with $m=0.5$. More recently, Leventis et al. [76], studying the influence of a magnetic field on the electrochemical reactions at milielectrodes, have derived a semiempirical solution of the limiting current density with the magnetic flux density, derived from the hydrodynamic Levich equation [31], which also predicts a power behaviour with $B$. This equation seems to be the most recent one and has been proven by other investigators [17,65,81]:

$$i_{lim} = 4.31 \cdot 10^2 \cdot z^{\frac{1}{2}} F A^{\frac{1}{2}} D^{-\frac{1}{2}} v^{\frac{1}{2}} c^{\frac{1}{6}} B^{\frac{1}{3}}$$

(2.28)
where: \( A \) is the electrode surface area, \( \nu \) – the viscosity of the electrolyte, \( B \) – the magnetic flux density applied parallel to the electrode surface.

Different semi-empirical models have been proposed, but most of the correlations between \( i_{\text{lim}} \) and \( B \) are power functions, where the power parameter lies in the range between 0.25 and 1.6 [77,81,85-87]. The reason for this may lie in the natural convection contribution to the mass transport [88], but also the dependence can scatter if the magnetic flux density range is not wide enough [89].

### 2.2.3. Micro- MHD Effect

A different effect has been introduced by Aogaki at al. [90] during studies of metal corrosion in high magnetic fields. In this study an influence of a magnetic field applied perpendicular to the electrode surface has been investigated. It was observed that during the chemical dissolution local galvanic cells are formed leading to a localized current flow. This in turn generates a Lorentz force as the cross product of current density and magnetic flux density (Eq. 2.23). As a result a localized convection is induced. This effect has been assigned as the micro-\textit{MHD} effect, since the convection is introduced on a microscale and propagates further, by a liquid viscous coupling and eventually induces a macroscopic fluid motion (Fig. 2.6) [66]. A similar effect has also been observed with polarized electrodes in the perpendicular to the electrode magnetic field, irrespective of the polarization direction, i.e. during both the deposition and dissolution of metals [66]. In this magnetic field-to-electrode configuration it is expected that the magnetic field lines are aligned parallel to the electric field, the Lorentz force is minimized and a bulk \textit{MHD} flow might be neglected. However, at the active sites, a distortion of

![Fig. 2.6. Schematic representation of macroscopic fluid flow induced by micro-\textit{MHD} cells [66].](image)

![Fig. 2.7. Schematic representation of microscopic micro-\textit{MHD} flow cells induced at the (a) cathodic and (b) anodic active site [66].](image)
the current distribution has been observed [66]. This in turn leads to a situation where the current flows no longer perfectly normal to the electrode surface, but there is also a parallel-to-electrode component (Fig. 2.7). As a consequence, a Lorentz force arises, and in turn, a localized convection is induced (Fig. 2.7).

The micro- \textit{MHD} effect was employed in explanation of different effects generated by an external magnetic field applied perpendicular to the electrode surface, for example morphological changes [91], influenced nucleation behaviour [25] or an increased desorption of hydrogen from the electrode surface [92] has been reported.

2.2.4. \textit{Nucleation, Growth and Phase Formation in the Presence of an External Magnetic Field}

It is known that the superposition of the magnetic field during the electrodeposition process can introduce significant changes in the deposit properties. Mainly the morphology of the deposited layers is affected [14-20]. It has been observed in numerous investigations that a superposition of a parallel-to-electrode external magnetic field reduces the layer roughness [14-16,18,20,93,94] and its grain size [14-16,18,95] as well. In this magnetic field-to-electrode configuration the Lorentz force is maximal leading to a strong \textit{MHD} stirring of the electrolyte. This has been assign to be responsible for the observed effects. It has been also shown that the Lorentz force-driven convection could increase the roughness of the deposited Cu layer. This has been proven by independent RDE measurements where a disk rotation at 10 rpm had the same effect as the magnetic field superposed parallel to the electrode surface [77]. On the contrary, in the perpendicular-to-electrode magnetic field an increased roughness has been reported [15,17,20]. The influence of the \textit{MHD} convection is not straightforward, since many overlapping effects have to be considered. A special attention has been given to the natural convection contribution to the overall flow pattern development which may significantly affect the deposit morphology [19,83]. At vertical electrodes with low magnetic flux density applied in a configuration that the Lorentz force counteracts the natural convection the overall mass transport toward the electrode could be suppressed [19,79]. Matsushima et al. [94], studying the Fe deposition in a parallel magnetic field, have observed that grains elongate in the field direction. Moreover, they have performed a dynamic scaling analysis [96,97] showing that the scaling
exponents are reduced in the parallel field. A similar observation for NiCu alloy deposition has been made by Tabakovic et al. [18].

A lot of attention has been focused on the side reaction occurring during the metal deposition, mostly the hydrogen evolution reaction (HER), in the presence of an external magnetic field. It has been shown that the HER rate is improved by a magnetic field irrespective of its relative-to-electrode configuration [19,83,92,98,99]. In the parallel-to-electrode magnetic field the mass transport of H$^+$ ions towards the electrode surface is increased and the desorption of the hydrogen bubbles is improved as well due to the MHD effect acting in the electrolyte [19,83,99]. This has been shown to have an impact on the layer morphology [19,83]. In this field configuration it has also been shown that the interface pH value is affected, i.e. a retardation of the interface pH value with $B$ has been reported [100,101], what in turn leads to a suppressed hydroxide formation and an improved layer quality. In the perpendicular-to-electrode magnetic field an increased desorption of hydrogen bubbles from the electrode surface has also been reported [79,92,98]. This effect has its origin in a specific current distribution in the bubble vicinity [92], resulting in a localized convection, analogous to the micro- MHD convection proposed by Aogaki et al. [66]. As a result of the increased hydrogen desorption the layer quality has been greatly improved [92].

There are also some reports regarding the nucleation of the layer in an external magnetic field. Matsushima et al. [25] have shown that a magnetic field applied perpendicular to the electrode surface retards the steady state nucleation rate. It has been explained by a micro- MHD convection arising due to a non-homogeneous current distribution at a nucleus. It was also observed that the steady state nucleation rate could be suppressed in the parallel-to-electrode configuration [26]. On the contrary, Ispas et al. [27], analysing the $i(t)$ transients obtained during potentiostatic deposition of Ni without and with a magnetic field, concluded that the steady state nucleation rate has been increased with magnetic field applied in the parallel-to-electrode configuration resulting in a finer grain structure of the deposited layer.

It was shown that a magnetic field applied during the deposition could texture the deposit [21-23], affect its phase composition [24] and reduce the internal stress of the layer [14,18]. Additionally, when magnetic alloy layers are deposited under the influence of an external magnetic field an in-plane anisotropy can be induced [2,14,16]. This effect is of commercial significance [2].
2.3. ELECTRODEPOSITION OF Co, Fe AND CoFe ALLOYS

2.3.1. Electrode Kinetics

The Fe-group metal deposition proceeds through successive steps which are related to a hydroxide species formation. These hydroxide species are present in the electrolyte as dissolved ones in an ionic state or adsorbed at the electrode surface. It is generally accepted that the reduction of Fe-group metals proceeds through a multistep-reaction pathway as follows [102]:

\[
M^{2+} + H_2O \leftrightarrow MOH^{\text{(aq)}}^+ + H^+ \quad (2.29)
\]

\[
MOH^{\text{(aq)}}^+ \leftrightarrow MOH^{\text{(ads)}}^+ \quad (2.30)
\]

\[
MOH^{\text{(ads)}}^+ + e \leftrightarrow MOH \quad (2.31)
\]

\[
MOH + H^+ + e \leftrightarrow M + H_2O \quad (2.32)
\]

where: \( M \) is Co, Ni or Fe, \((aq)\) and \((ads)\) stands for “dissolved” and “adsorbed”, respectively.

At low overpotentials the rate determining step is reaction (2.30), but, with increasing potential, it can be shifted and, at high overpotentials, the rate-determining step will be reaction (2.31).

When deposition is carried out from aqueous electrolytes and the standard potential of the deposited metal is negative, as it is in the Fe-group metals case, additional side reactions might occur. Typical side reactions which may take place during deposition of the Fe-group metals are as follows [101]:

\[
2H^+ + 2e^- \leftrightarrow H_2 \uparrow \quad (2.33)
\]

\[
2H_2O + 2e^- \leftrightarrow H_2 \uparrow + 2OH^- \quad (2.34)
\]

\[
xM^{z+} + yH_2O \leftrightarrow M_x(OH)_{y(z-y)^+} + yH^+ \quad (2.35)
\]

\[
xM_x(OH)_{y(z-y)^+} + (xz - y)H_2O \leftrightarrow xM(OH)_y + (xn - y)H^+ \quad (2.36)
\]

Reaction (2.33) is the hydrogen evolution reaction (HER) which consumes \( H^+ \) ions and thus increases the \( pH \) value at the electrode surface. If the applied potential is high enough, it is possible to decompose water (2.34) and generate \( OH^- \), which also increases in front of the electrode \( pH \) value. When the \( pH \) value is sufficiently high, additional reactions may occur which produce a buffering effect, i.e. a hydrolysis of the metal ion (2.35), generating \( H^+ \) ions and decreasing the \( pH \) value. If reaction (2.35) is not able to prevent a further increase of the \( pH \),
precipitation of the hydroxide (2.36) will occur and the deposit may be contaminated by hydroxide inclusions [10].

As it is already visible, the side reactions and the metal deposition reaction itself (2.29-2.32) could interfere, since the interface $\text{H}^+$ and hydroxides concentration might be affected by reactions according to equations 2.33-2.36. The situation becomes more complicated when more than one metal is being co-deposited, i.e. alloy deposition. It is known that the deposition of Fe-group alloys shows a so-called ‘anomalous behaviour’, i.e. the less noble metal is deposited preferentially than one would expect from the electrolyte composition [103]. The explanation of this behaviour is not straightforward and different models have been proposed in order explain this phenomenon [104-108], though all of them highlight the importance of the hydroxide species formation.

With respect to the deposited alloy system and deposition parameters the anomalous behaviour could be suppressed or even totally cancelled (low $p\text{H}$ values). For the CoFe alloy deposition the anomalous behaviour has been shown to be the lowest among other Fe-group alloy systems (almost negligible) [11,109,110].

2.3.2. Properties of the Electrodeposited CoFe Alloy

The electrodeposition of the Fe-group metals and alloys is of great interest because of their magnetic properties [1-3]. They have found a wide application field in the storage technology, especially for read/write elements in hard drive heads [4,5] and in the microelectromechanical systems (MEMS) technology [6]. The electrodeposition process is widely used to obtain soft magnetic layers [1]. Numerous investigations have been carried out related to the electrodeposition of Fe-group alloys, most of them concerned with the NiFe alloy system [1,111,112], but the CoNiFe [5,9,113,114] and CoFe [9,11,115-117] systems have also been investigated.

In Fig. 2.9a the saturation flux density ($B_s$) of the annealed bulk CoFeNi alloys in dependence of the chemical composition is shown [2]. The CoFe alloy possesses as excellent soft magnetic properties as the highest (among the Fe-group alloys) $B_s$ of 2.4 T and a relatively low coercivity ($H_c$) of about $2\times10^5$ T [7] and is of technological interest [117]. From Fig. 2.9a it is apparent that the composition range where the highest $B_s$ is reached lies between 53 and 73 at.% Fe. In this
composition range the alloy structure is cubic body centred (bcc) and is of the CsCl type ordered structure (B2). The Co-Fe phase diagram is shown in Fig. 2.9b [118].

![Fig. 2.9. Saturation flux density values (approximate) of annealed bulk CoFeNi alloys [2] (a) and Co-Fe phase diagram [118] (b).](image)

At low Fe content it is also possible to deposit a layer of fcc or even hcp structure as schematically shown in Fig. 2.10, where structures of electrodeposited CoFe layers are compared with those of a bulk material with respect to composition [119]. From Fig. 2.10 it is clear that the structures of electrodeposited layers are quite the same as those of bulk, only the fcc+bcc mixture has not been reported in the electrodeposits. The influence of plating parameters such as the electrolyte composition [2,9,11,115-117], the current density [2,116], the pH value of the electrolyte [2], etc. on the deposited CoFe layer properties (morphology, structure, magnetic properties) has been established. It was observed that an addition of sulphur [113] and/or boron [117] containing surfactants results in a contamination of

![Fig. 2.10. Comparison of the equilibrium phase diagram extrapolated to room temperature vs. that of the electrodeposited alloys [119].](image)
the deposit which lowers the saturation magnetization. Osaka et al. [117] have found that the oxidation of $\text{Fe}^{2+}$ to $\text{Fe}^{3+}$ leads to a precipitation of iron hydroxides which, incorporated into the deposit, also lower the saturation magnetization. Similar results have been obtained by Brankovic et al. [120] and a simple analytical model has been proposed linking the reduction of $B_s$ with $\text{Fe(OH)}_3$ incorporation into the layer. Another very important aspect of the Fe-rich alloy deposition is the internal stress state of as-deposited layers which is known to strongly affect their $H_c$ values [114,121]. It has been shown by numerous investigations that the value of $H_c$ is reversely proportional to the layer thickness, i.e. $H_c$ is reduced with the layer thickness [114,122]. This effect could be explained by a change in the internal stress state of the layer which has been shown to depend on the thickness, i.e. the stress is relieved with the layer thickness [123,124], but the grain size is increased [123].

It has been shown that CoFe layers with a $B_s$ of 2.4 T could be deposited [2,117], however, as-deposited layers exhibit a positive magnetostriction and are strongly stressed. Therefore, a post heat treatment is necessary to improve material characteristics [2].

To the best author’s knowledge there is only one report available treating the influence of magnetic fields on CoFe alloy deposition [125] besides the own investigations [93,110]. They mainly focus on the influence of the magnetic field on the electrochemical reaction rate, though some effects regarding the chemical composition, morphology and structure are given. Harrach et al. [125] have shown that the chemical composition of the deposit is unaffected by a magnetic field, irrespective of the relative-to-electrode orientation, if the magnetic flux density is lower than 1 T, but structural changes with magnetic fields have been reported. Also the morphology has been strongly altered by external magnetic fields. These effects have been linked to the Lorentz force driven convection [125]. However, no quantitative description of the magnetic field induced changes has been given and thus a detailed analysis of the magnetic field impact on the deposited CoFe alloy properties is necessary.
3. EXPERIMENTAL SETUP AND PROCEDURES

3.1. CELL DESIGN AND ELECTRODES

The electrochemical experiments were carried out in four different cell geometries. Most of the investigations were performed with the Teflon cell schematically shown in Fig. 3.1.

![Fig. 3.1. Schematic drawing of membrane cells. 1 – TEFLON cell, 2 – working electrode (Quartz or wafer), 3 – Pt counter electrode, 4 – reference electrode (Hg/Hg$_2$SO$_4$/K$_2$SO$_4$(sat.) – MSE), 5 – membrane (Nafion), 6 – Luggin capillary.](image)

In both cell geometries the cathodic and the anodic compartment are separated by the Nafion® membrane (5). The reason is that Fe$^{2+}$ ions present in the electrolyte solution may oxidize at the Pt counter electrode to Fe$^{3+}$ and contaminate the electrolyte. The membrane prevents the contamination by Fe$^{3+}$ in the cathodic part of the cell. It is known that the Fe$^{3+}$ ions present in the electrolyte may lead to an oxygen incorporation into the deposited layer [117] and changes in the deposit properties. The difference between cell (a) and cell (b) is that cell (a) has a relatively large volume (~50 cm$^3$), but the current distribution over the electrode surface is not uniform and edge effects are significant [92]. On the other hand, cell (b) has a smaller volume (~25 cm$^3$) but is designed to minimize the edge effects by utilization of the recessed electrode concept, which is known to have a nearly perfect primary current distribution [126]. As counter electrode a Pt sheet and as reference a saturated mercury sulphate electrode (Hg/Hg$_2$SO$_4$/K$_2$SO$_4$(sat.) – MSE, +640 mV vs. SHE) were used. To minimize the IR-drop in the electrolyte a Luggin capillary (Fig. 3.1.- (6)) was employed [31] at a distance of 1.5 mm away from the electrode surface.
As working electrode in these cells (Fig. 3.1) an AT-cut quartz crystal or a glass wafer evaporated with Au was used. A 200 nm thick, polycrystalline Au layer was evaporated on a 2 nm Cr adhesive layer. In the case of the AT-cut quartz crystal the evaporation was performed on both sides allowing a double sided electrical connection. The Au layer exhibits a strong degree of the (111) orientation (Fig. 3.2a). The crystallite size estimated from (111) peak by the Debye-Scherrer formula (Eq. 3.6) is about 50 nm. In Fig. 3.2b an exemplary AFM image of the Au substrate is shown. The topology of the Au is fine grained with a grain size of about 50 nm and a roughness ($R_{ms}$) of 3 nm.

Another cell used for in-situ interface pH value measurements is shown in Fig. 3.3. The method of the interface pH measurements developed by Deligianni and Romankiw [10] was employed. A flat pH electrode (1) (type INLAP 426) was covered with an Au mesh of 1000 meshes per square inch and a height of 5 µm (PLANO GmbH) which acts as a
experimental setup and procedures

working electrode (2). A Pt net as counter (3) and a MSE as reference electrode (4) were used. A Luggin capillary was placed at about 2 mm distance from the electrode surface. The experiments were carried out in a glass cell with a volume of about 80 cm$^3$. With this setup the magnetic field could only be applied in the parallel to horizontal electrode configuration (Fig. 3.3).

To confirm the hydrodynamic nature of the observed effects some of the experiments were performed with a gold rotating disc electrode (RDE) in a setup similar to the one shown in Fig. 3.3, but instead of the pH electrode a RDE was used. The RDE was prepared from a cold rolled Au sheet embedded in epoxy resin (1.1 cm$^2$). The Au-RDE was ground with emery paper (4000 mesh) and than polished successively down to the 40 nm silica suspension. The rotation rate was varied in the range of 0 to 10 rpm throughout an EG&G Model 616 RDE controller.

Another cell was a closed cubic glass cell for in-situ optical observations with dimensions of 10 mm x10 mm x10 mm schematically drawn in Fig. 3.4. As working electrode (WE) a Cu plate (1 cm$^2$) was used. The Cu electrode was successively ground with emery paper and polished with a diamond suspension down to 200 nm prior to the experiment. A gold foil as a counter (CE) and the MSE reference electrode (REF) were used. A reference electrode was connected to the cell via a Na$_2$SO$_4$-agar bridge at a distance of approximately 1 mm to the working electrode [127].

3.2. ELECTROCHEMICAL METHODS

- Potentiostatic and potentiodynamic measurements

The electrochemical experiments, i.e. cyclic voltammetry and chronoamperometry (potentiostatic deposition), have been performed in a three electrode cell configuration with a Bi-potentiostat (Jassile). The high magnetic field measurements have been conducted with the EG&G potentiostate (model 273A). In order to separate the metal deposition reaction from the overlapping side reactions, i.e. HER and water decomposition, which may occur during the Fe-group metal and alloy deposition the electrochemical experiments have been performed in
combination with an electrochemical quartz crystal microbalance (EQCM). This EQCM setup allows a simultaneous in-situ mass measurement. The EQCM measurements are very sensitive to the attached mass. When a monolayer or a film exhibits a rigid layer behaviour the EQCM provides reliable information on the deposited mass [128]. The quartz’s frequency shift is proportional to the attached mass according to Sauerbrey’s equation [129]:

$$\Delta f = -\frac{2\Delta m \cdot n \cdot f_0^2}{A \cdot \sqrt{\mu_q \cdot \rho_q}}$$  \hspace{1cm} (3.1)

where: $\Delta m$ is the deposited mass, $n$ is the Overstone number ($n=1$), $\mu_q$ is the quartz shear modulus ($2.947 \times 10^{11}$ g cm$^{-1}$s$^{-2}$), $f_0$ is the resonance frequency of the quartz oscillator (9.83 MHz), $\rho_q$ is the density of quartz (2.648 g cm$^{-3}$) and $A$ is the electrode area.

Most of the parameters are material constants, therefore, Sauerbrey’s constant $c_f$ can be introduce as:

$$c_f = -\frac{2n \cdot f_0^2}{\sqrt{\mu_q \cdot \rho_q}}$$  \hspace{1cm} (3.2)

The $c_f$ value for a given quartz resonance frequency of 9.83 MHz is equal to $2.2 \times 10^8$ Hz cm$^2$g$^{-1}$ [79]. This allows to rewrite Eq.(3.1) in the following form:

$$\Delta m = -\frac{\Delta f \cdot A}{c_f}$$  \hspace{1cm} (3.3)

In real systems an additional frequency shift may be observed due to a contribution of additional terms to the overall frequency [130]:

$$\Delta f = \Delta f_m + \Delta f_v + \Delta f_p + \Delta f_T + \Delta f_s + \Delta f_r$$  \hspace{1cm} (3.4)

where: $\Delta f_m$ is the mass change according to Eq.(3.1), $\Delta f_v$ is the viscosity effect, $\Delta f_p$ is the pressure effect, $\Delta f_T$ is the temperature effect, $\Delta f_s$ is the stress influence and $\Delta f_r$ is the roughness effect.

In order to use Eq.(3.3) to calculate the in-situ mass changes we will neglect the components related to viscosity, pressure and temperature, since the measurements are carried out at constant $p$ and $T$. No significant difference between the change of the frequency measured with and without electrolyte has been observed. Additionally, the viscosity of the electrolyte is close to the one of water and the changes during the deposition are too small in magnitude to introduce any significant frequency changes. This allows to neglect the viscosity influence. The damping caused by the roughness of the deposited layer can also be neglected, since the deposited layer thicknesses were only in the range from a few to a few tens of nanometers [79].
The measurements were carried out with an EQCM based on the Elchema frequency oscillator (EQCN-700) which has a frequency mixer implemented which in turn allows to use quartzes of not standardized frequencies. The reference frequency for the mixer has been provided through the wave generator (Hameg, HM8131-2). The frequency signal has been transformed to an analog signal by the self-constructed frequency-to-voltage converter and connected to the measurement system (Jassile).

The cell constructions used for the EQCM measurements are shown in Fig. 3.1. The EQCM has been calibrated using the Cu electrolyte containing a 0.01M CuSO$_4$/0.1M Na$_2$SO$_4$ solution of pH=3. An exemplary calibration curve is shown in Fig. 3.5. From Fig. 3.5 it is apparent that the dependence $\Delta f(\Delta m)$ shows a good linearity. The mass changes were calculated from a charge passed through the cell during the deposition, assuming 99% current efficiency. The value of $c_f$ averaged over a set of measurements is equal to $2.16 \times 10^8$ Hz cm$^2$ g$^{-1}$ which is in very good agreement with the calculated one and will be used further on.

Based on the in-situ mass measurements the deposition times to obtain a desired layer thickness have been estimated.

- Electrolytes

The electrochemical investigations have been performed with the electrolytes of compositions listed in table 3.1. In all cases the electrolyte’s pH value was set to 3 by sulphuric acid or sodium hydroxide. The sodium sulphate has been used as a supporting electrolyte to reduce the contribution of a migration component to the mass transfer [31]. The chemical composition of the electrolytes was chosen in a way to have the same ionic strength.
Table 3.1. Chemical compositions of the used electrolytes.

<table>
<thead>
<tr>
<th></th>
<th>Co</th>
<th>Fe</th>
<th>CoFe(A)</th>
<th>CoFe(B)</th>
<th>CoFe(C)</th>
<th>CoFe(D)</th>
<th>CoFe(E)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$c_{\text{CoSO}_4}$ / mM</td>
<td>6.5</td>
<td>0</td>
<td>6.5</td>
<td>6.5</td>
<td>6.5</td>
<td>6.5</td>
<td>6.5</td>
</tr>
<tr>
<td>$c_{\text{FeSO}_4}$ / mM</td>
<td>0</td>
<td>6.5</td>
<td>1.6</td>
<td>3.3</td>
<td>3.3</td>
<td>6.5</td>
<td>10.0</td>
</tr>
<tr>
<td>$c_{\text{Na}_2\text{SO}_4}$ / mM</td>
<td>100</td>
<td>100</td>
<td>98.4</td>
<td>96.8</td>
<td>96.8</td>
<td>93.5</td>
<td>90.0</td>
</tr>
<tr>
<td>$c_{\text{H}_3\text{BO}_3}$ / M</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
</tr>
</tbody>
</table>

As it can be seen from table 3.1 there are two different alloy electrolyte classes without and with boric acid which has been used as a buffer. The reason of the boric acid addition was a problem of depositing a thick layer from the alloy electrolyte with a high Fe concentration what will be discussed in detail further on.

- Magnetic fields

Homogenous horizontal magnetic fields up to 1 T have been applied during the deposition by an electromagnet (HV7 – Walker Scientific) which was powered by a programmable power supplier (Xantrex, XCD150-80). The magnetic flux density between the magnet poles has been measured with a Hall-probe H1-R (Magnetmesstechnik Jürgen Ballanyi). The magnetic field during the electrochemical experiments has been superposed in two different relative-to-electrode configurations: parallel and perpendicular to the electrode surface as schematically shown in Fig. 3.6a.

Some of the experiments have been performed at the high magnetic field facility (GHMFL) in Grenoble where the investigations could be carried out with a magnetic flux density up to 13 T. In this case the magnetic field has been applied vertically as schematically shown in Fig. 3.6b. In the case of the shadowgraph measurements a magnetic field of 650 mT was applied vertically,
perpendicular to the horizontal electrodes. A magnetic field was applied by a set of two large NdFeB magnets [131] in an arrangement that gives a very homogeneous magnetic field over the whole volume, i.e. the cell was placed in the magnets gap. The magnetic field arrangement employed in the shadowgraph measurements is schematically shown in Fig. 3.6c.

- In-situ \(\text{pH}\) measurements

The in-situ interface \(\text{pH}\) value measurements have been carried out in a setup shown in the Fig. 3.3. The Au-mesh used as a working electrode was 5 \(\mu\)m thick. This is far below the thickness of the diffusion layer. The \(\text{pH}\) electrode situated in close vicinity of the mesh (the Au-mesh lies directly on the \(\text{pH}\) electrode surface) allows \(\text{pH}\) measurements nearly at the interface [10]. The measurements have been performed with a \(\text{pH}\)-Meter (Knick, Calimatic 761) coupled with the potentiostat’s measurement card.

- Shadowgraph

The in-situ observations of the electrode surface during the deposition of Co have been carried out in a cell arrangement shown in Fig. 3.4. The cube cell was placed inside a shadowgraph optics employing a collimated light beam of a high-power LED (\(\lambda\sim632\) nm) [127] to enable direct surface observations during the deposition. The electrode/electrolyte interface pictures have been taken with a CCD camera (Dalsa) at 20 Hz frequency. The shadowgraph experimental setup is schematically shown in Fig. 3.7.

![Fig. 3.7. Schematic drawing of a setup used for shadowgraph experiments.](image)
All the electrochemical experiments have been carried out at room temperature.

### 3.3. DEPOSIT CHARACTERISATION

- **Morphology**

  The morphology of the deposited layers (~100 nm thick) has been observed with a scanning electron microscope (SEM – FEG Gemini Leo 1530) and with the help of atomic force microscopy (AFM – Nanoscope IIIa, Digital Instruments and XE-100, Park). The roughness of the layers has been determined by AFM. Cross sections of deposited layers were cut with focused ion beam (FIB) and observed under SEM (ZEISS 1540 XP). Thin foils of the film cross sections have been prepared for TEM investigation. The samples were face-to-face glued together and stabilized by a Si wafer. So prepared samples were polished and further thinned by ion milling (RES101-BALTEC). These thin foils have been investigated by transmission electron microscopy (TEM – Tecnai T20, 200 kV).

- **Chemical composition of alloy layers**

  The chemical composition of the deposited alloy layers was determined by inductively coupled plasma – optical emission spectrometry (ICP-OES) after dissolution in concentrated HCl. The composition was additionally proven by independent EDX investigations. Auger electron spectroscopy (AES) analysis was carried out in a Scanning Auger Microprobe PHI660 (Physical Electronics) with primary electrons of 10 keV at 40 nA, an energy resolution of $\Delta E/E = 0.6 \%$, and a beam diameter of about 400 nm. For depth profiling, the samples were sputtered by 1.5 keV argon ions with an equivalent sputtering rate in SiO$_2$ of about 2.8 nm min$^{-1}$. The Auger spectra were measured in areas of about 15 µm×10 µm.

- **Crystal structure and texture**

  The crystal structure and the texture of the deposited layers have been investigated by X-ray diffraction (XRD – XPertPro Philips, with Co$K_\alpha$ – $\lambda_{CoK_\alpha}$=1.79 Å and Cu$K_\alpha$ – $\lambda_{CuK_\alpha}$=1.54 Å). The structure was also determined by Laue diffraction methods under TEM, i.e. by selected area
diffraction (SAD) and nanodiffraction (ND) on selected grains. Based on the θ/2θ XRD patterns the interplanar distances were calculated according to the Bragg equation:

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

(3.5)

where: \( n \) is the order of reflection, \( \lambda \) – the wave length of X-rays, \( d \) – the spacing between parallel planes in the atomic lattice, \( \theta \) – the angle between the incident ray and the scattering planes.

On the basis of the θ/2θ XRD patterns the crystallite size has been estimated using the Debye-Scherrer formula [132] in the following form:

\[ D_K = \frac{0.94\lambda}{\beta \cdot \cos \theta} \]  

(3.6)

where: \( D_K \) is the weighted crystallite size, \( \beta \) – the width of the peak at half maximum intensity at the \( \theta \) angle.

- Magnetic properties

The magnetic properties, i.e. hysteresis curves, have been measured by means of vibrating sample magnetometry (VSM – Quantum Design PPMS). Magneto-optical Kerr microscope (MOKE) as well as laser MOKE magnetometer investigations have been performed in the longitudinal mode in order to determine the domain structure and to record the hysteresis curve as well.
4. RESULTS

4.1. INFLUENCE OF AN EXTERNAL HOMOGENEOUS MAGNETIC FIELD ON THE MASS TRANSPORT DURING ELECTRODEPOSITION

The influence of external magnetic fields on the mass transport will be divided into two parts. The first part is devoted to the effects observed for a pure metal reduction reaction (Eq. (2.1)). The second part, since the metal deposition reaction overlap with side reactions, is dedicated to the influence of magnetic fields on the side reactions, which may occur simultaneously with the metal reduction (Eq. (2.33-2.36)).

4.1.1. Influence of a Magnetic Field on the Metal Deposition

In the parallel-to-electrode magnetic field configuration electrical current lines are in great majority perpendicular to the magnetic field lines. The maximal Lorentz force will occur as a cross product between current and magnetic flux density. As a consequence, a MHD effect is induced and significant changes in the electrochemical behaviour are expected with magnetic field. On the other hand, when a magnetic field is applied in the perpendicular-to-electrode configuration the magnetic field and the electric field are aligned, in majority, parallel and the Lorentz force is expected to be minimized. Therefore, the MHD effect should not play a significant role and other possible magnetic field effects might be observed.

In this chapter the influence of a magnetic field applied in the parallel- and perpendicular-to-electrode configuration on the electrodeposition of Co, Fe and CoFe alloys is studied in detail. The electrochemical experiments in the magnetic field were carried out in the cell geometry shown in Fig. 3.1a. Some of the experiments were also performed with RDE to verify if the observed effects induced by the magnetic field are of hydrodynamic nature.

4.1.1.1. Cobalt

In Fig. 4.1 cyclic voltamograms (CVs) (a,c) and corresponding mass changes ($m(E)$) (b,d) obtained in the Co electrolyte (table 3.1) at different magnetic flux densities in both magnetic field-to-electrode configurations are shown.
Irrespective of the magnetic field-to-electrode configuration the current density-potential curves show three characteristic peaks in the cathodic region. The first one (I), with a maximum at a potential of about -1100 mV\textsubscript{MSE} is related to the reduction of oxygen (OR) \cite{133}, which is dissolved in the electrolyte despite N\textsubscript{2}-purging. The second peak, observed at a potential of about -1260 mV\textsubscript{MSE} (II), is linked to the hydrogen reduction reaction (HER). The third one (III) corresponds to the bulk Co deposition (overlapped by the HER). The onset of this peak is observed at a potential of about -1400 mV\textsubscript{MSE}. The maximum of the deposition peak occurs at a potential of -1480 mV\textsubscript{MSE}.

The mass increase is observed above a potential of ca. -1175 mV\textsubscript{MSE} (IV). After this point the mass increases linearly until the onset potential of the bulk deposition occurs. In this potential range the reduction of hydrogen \( E_{H/H^+} = -756 \text{ mV}_{\text{MSE}} \) is superposed. The calculated equilibrium potential from the Nernst equation (Eq. (2.2)) for the Co electrolyte is \( E_{\text{Co}/\text{Co}^{2+}} = -965 \text{ mV}_{\text{MSE}} \).
which is more positive than the measured one. The difference for both reactions is caused by the total overpotential.

Until the potential reaches about -1550 mV$_{\text{MSE}}$ the metal deposition reaction dominates. Above this potential the decomposition of water and the HER have a significant contribution to the total current.

The parallel-to-electrode magnetic field affects the CV’s shape and corresponding mass changes significantly (Fig. 4.1a,b). It is evident that the first and the second peak maximum current density is increased in magnetic field (Fig. 4.1a). A similar observation is made regarding the Co deposition peak, i.e. an increased current density with field, but additionally the maximum position is slightly shifted towards more cathodic potentials. The increased diffusion-limited current density is far more obvious at the end of the potential scan and in the back scan current. This is an expected situation since the OR, HER, as well as Co deposition reaction are the in diffusion-controlled regime. The applied magnetic field induces MHD convection. As a result, the mass transport of ions towards the electrode is increased. This is also clear in the $m(E)$ plots (Fig. 4.1b – inset). No significant increase of the deposition rate was observed in the rising part of the peak, but at the end of the cathodic scan the deposited mass is higher in the parallel field. The same is noticeable in the back scan where the deposited mass and the $m(E)$ curves’ slopes are higher in this field configuration. Additionally, the mass increase is no longer observed from a potential of about -1300 mV$_{\text{MSE}}$ when a magnetic field is applied. At this potential, without a magnetic field, the mass increase is still significant. As a result, the mass deposited in this potential range is lower in a magnetic field compared with the situation where no magnetic field is applied (Fig. 4.1b). Contrary to the parallel-to-electrode configuration no significant influence of a magnetic field on the CV’s and the $m(E)$-curves in the perpendicular-to-electrode configuration was observed (Fig. 4.1c,d). Only a slight increase of the Co peak current density and a small retardation of the deposited mass on the plateau of the $m(E)$ plots recorded in the back scan with an applied magnetic field was observed.

Based on the CVs experiments, potentials for the potentiostatic depositions were chosen to ensure a mass transport control of the Co deposition reaction. The potentials were selected at the beginning ($E_1$), in the maximum ($E_2$) and at the end ($E_3$) of the bulk metal deposition peak (table 4.1).
Table 4.1. Potentials chosen for the potentiostatic experiments.

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Potential 1</th>
<th>Potential 2</th>
<th>Potential 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co and CoFe</td>
<td>-1400</td>
<td>-1480</td>
<td>-1600</td>
</tr>
<tr>
<td>Fe</td>
<td>-1500</td>
<td>-1550</td>
<td>-1650</td>
</tr>
</tbody>
</table>

In Fig. 4.2 the current time transients, \( i(t) \) (a,c), and the corresponding mass changes, \( m(t) \) (b,d), obtained at -1480 mV\(_{\text{MSE}}\) with different magnetic flux densities in both magnetic field-to-electrode configurations are shown. From \( i(t) \) transients (Fig. 4.2a,c) it is apparent that a stationary regime, irrespective of the magnetic field strength and configuration, is reached above 40 s. It is obvious that a magnetic field applied parallel-to-electrode increases the limiting current density and the deposited mass after 70 s. Such a result is in good agreement with the classical MHD theory, i.e. an additional convection is induced due to the Lorentz force (Eq. (2.23)) acting in the hydrodynamic layer. The additional convection reduces the diffusion layer thickness and increases the limiting current density for the mass controlled reactions [17,64,69,77,81-83].

In contrast, when a magnetic field was applied in the perpendicular-to-electrode configuration, no influence on the limiting current density was observed (Fig. 4.2c). But at the moderate deposition times an increased current density with magnetic field can be seen in this configuration (inset of Fig. 4.2c). On the other hand no significant influence of the perpendicular magnetic field on the \( m(t) \) transients shape was noticed (Fig. 4.2d). This effect is linked to the HER, which rate is clearly increased in this field configuration. This phenomenon will be discussed in detail in Chapter 4.1.2.

An interesting feature in the \( i(t) \) transients was observed. Instead of a Cottrell decay in the current with time [31], a deviation from this behaviour was noticed (Fig. 4.2a,c – indicated by arrows). The changes in the \( i(t) \) transient shape are commonly linked to nucleation and growth phenomena [50], which will be discussed in detail in Chapter 4.2.

In \( m(t) \) plots (Fig. 4.2b,d), irrespective of the magnetic the field-to-electrode configuration, a linear dependence is reached after about 40 s of deposition, which is in good correlation with the \( i(t) \) transients and reflects the steady state conditions.

The slopes of the linear parts of the \( m(t) \) transients represents the steady state deposition rates. By linear fits to these \( m(t) \) transient’s parts, Co partial current densities could be calculated and separated from the HER, which contributes to the measured current density (Fig. 4.2a,b).
calculation of the Co partial current densities is based on the Faraday law through the dependence (4.1):

\[ i_{Co} = \frac{dm_{Co}}{dt} \cdot k_{Co}^{-1} \]  

where \( i_{Co} \) is the Co partial current density, \( \frac{dm_{Co}}{dt} \) is the steady state deposition rate (slope of the linear part of the \( m(t) \) curve), \( k_{Co} \) is the electrochemical equivalent of Co.

Fig. 4.2. Chronoamperometric response (a,c) and corresponding mass changes (b,d) recorded during Co deposition at a potential of -1480 mV_{MSE} in parallel- and perpendicular-to-electrode configuration, respectively.

In Fig. 4.3 the calculated Co partial limiting current densities in dependence of the magnetic flux density obtained in the parallel-to-electrode configuration at different potentials are shown. Note that the data in Fig. 4.3 are presented in double logarithmic coordinates and show a good linearity. It is known on the basis of the classical MHD theory developed by Aogaki et al. [85] that the limiting current is a function of the magnetic flux density, in a form of \( i_B \propto B^n \) with \( n=0.5 \), when the magnetic field is applied perpendicular to the electric field. The slopes obtained by the linear fits are lower than the one predicted by the theory. But the absolute values of the \( n \)
RESULTS

Parameter may vary, the published $n$-values differ since the experimental conditions are not always comparable [20,79]. The reason may lie in the natural convection contribution to the mass transport [88], but also the dependence can scatter if the magnetic flux density range is not wide enough [89]. An almost linear dependence of the limiting current with $B$ up to 1T was observed by Ragsdale et al. [134] for the reduction of nitrobenzene and acetophenone at micro-electrodes. It was shown by Chopart et al. [65] for Cu electrodeposition, that the limiting current density dependence of the magnetic flux density is a power function where $n=1/3$. This was established for instance for Co deposition [17].

4.1.1.2. Iron

In Fig. 4.4 CVs (a,c) and corresponding $m(E)$ plots (b,d) obtained from Fe electrolyte (table 3.1) at different magnetic flux densities in both magnetic field-to-electrode configurations are shown. Similar to the Co case, the CVs show three characteristic peaks in the cathodic region, irrespective of the magnetic field configuration. The oxygen reduction (I) with a maximum at the potential equal to the one observed for the Co electrolyte (-1100 mV$_{\text{MSE}}$), the HER peak with a maximum at a potential of about -1420 mV$_{\text{MSE}}$ (II), and the bulk Fe reduction peak (III) are observed. The onset of the bulk Fe deposition peak is observed at a potential of about -1500 mV$_{\text{MSE}}$. The maximum of the deposition peak occurs at a potential of -1550 mV$_{\text{MSE}}$. It is apparent that the HER overpotential is higher in the Fe electrolyte than in the Co electrolyte, i.e. it is shifted to a more negative potential. This is expected since the hydrogen overpotential on Fe is higher than on Co [135].

A mass increase is observed above a potential of ca. -1325 mV$_{\text{MSE}}$ (IV). After this point increases linearly until the onset potential of the bulk deposition occurs. The equilibrium
potential for the Fe electrolyte calculated with the Nernst equation (Eq. (2.2)) is -1265 mV$_{MSE}$, which is more positive than the measured one. Until the potential reaches about -1600 mV$_{MSE}$ the metal deposition reaction dominates. Above this potential the decomposition of water and the HER have a very significant contribution to the total current.

![Fig. 4.4. CVs (a,c) and corresponding mass changes (b,d) obtained in the Fe electrolyte at different magnetic flux densities applied parallel and perpendicular to the electrode surface, respectively; dE/dt=20 mVs$^{-1}$.](image)

The parallel-to-electrode magnetic field affects the CV’s shape and corresponding mass changes significantly (Fig. 4.4a,b). The observed changes are qualitatively the same as in the case of Co electrolyte, i.e. an increased current density of all the peaks in a magnetic field is observed. The maximum potential of the Fe peak is slightly shifted to more cathodic one as well (Fig. 4.4a). The increased Fe diffusion limited current density is also visible at the end of the potential scan and in the back scan current. Since all considered electrochemical reactions are in the mass transport limiting regime the MHD convection increases the mass transport of ions towards the electrode.
This is also clear in the $m(E)$ plots (Fig. 4.4b): there is no significant increase of the deposition rate in the rising part of the CV’s peak but at the end of the cathodic scan as well as in the back scan direction the deposited mass is higher in the parallel-to-electrode field. Similarly to Co, the mass increase is no longer observed at a more cathodic potential (ca. -1390 mV$_{\text{MSE}}$) in magnetic field while without the field the deposition is still noticeable (up to ca. -1300 mV$_{\text{MSE}}$) (Fig. 4.4b). In contrast, no significant influence of a magnetic field on the shape of the CV neither the $m(E)$ plot was noticed in the perpendicular-to-electrode configuration (Fig. 4.4c,d). Only a slight increase of the Fe peak current density was observed.

Hinds et al. [77] studied the influence of a magnetic field on the electrodeposition of Cu and found that the MHD effect could be compared with the convective phenomena generated by a RDE. Similar dependencies of the limiting current density vs. applied potential were obtained with either a parallel-to-electrode magnetic field ($B=0.5\text{T}$) or a rotation rate of 10 rpm. They also stressed that the magnitude of these effects strongly depends on the electrode and cell geometry. Therefore, for a better demonstration of the convective origin of the shift of the cathodic peak with magnetic flux density in the parallel configuration (Fig. 4.4a) RDE experiments were performed. In Fig. 4.5 the cathodic parts of the CVs obtained with different rotation rates of the RDE are shown. It is obvious that the maximum current density at the peak is increased and the potential is shifted to more negative values with increasing rotation rate (Fig. 4.5). That is a direct proof that the shift of the bulk Fe deposition peak in the parallel-to-electrode magnetic field is due to the MHD effect acting in the electrolyte.

To analyze the influence of a parallel-to-electrode magnetic field in detail the deposition rates ($dm/dt$) were calculated by a graphical derivation of the $m(E)$ plots (Fig. 4.4b), where the potential is proportional to time through the scan rate (20 mVs$^{-1}$). In Fig.
4.6 the CVs (a) and the deposition rate vs. potential plots (b) obtained in the parallel-to-electrode configuration are shown.

From Fig. 4.6 it is apparent that the \( \frac{dm}{dt}(E) \) (b) curves correspond very well to the \( i(E) \) curves (a). Considering the \( \frac{dm}{dt}(E) \) plots, there is no significant difference between the curves obtained without and with field up to the onset potential of bulk Fe deposition. After that point the deposition rates are reduced in the field when compared to the case without field. This is also noticeable in the CVs (Fig. 4.6a) but at a much smaller magnitude. A similar effect of the rotation rate of RDE (Fig. 4.5) was observed. In the rising part of the \( i(E) \) peak a Lorentz force arises, which is proportional to the current density and which in turn generates additional convection. While the cyclic voltammetry is a dynamic technique [31,136], the rising part of the \( i(E) \) peak is in the mixed control regime (diffusion + charge transfer) and the Lorentz force magnitude changes with the potential. It is generally accepted that the reduction of iron proceeds through a multistep-reaction pathway involving the formation of hydroxide species (Eqs. (2.29-2.32)) [102]. An additional Lorentz force driven convection removes partially the adsorbed hydroxide species from the electrode surface. Due to that the electrode equilibrium is shifted resulting in reduced deposition rates (Fig. 4.6b) in the rising part of the \( i(E) \) peak (Fig. 4.6a) [26].
At the maximum of the $i(E)$ peak (Fig. 4.6a) the concentration of Fe$^{2+}$ ions at the interface reaches 0 and only the mass transport is the rate determining step. Above this point the expected exponential decay occurs until the limiting current density is reached [31]. In this part of the curve, where the mass transport dominates, an additional convection induced by the magnetic field increases the mass transport of ions towards the electrode surface and an expected increase in the current density as well as in the deposition rate is observed. The shifted electrode equilibrium in the rising part of the peak and the increased current density after the peak maximum in the parallel field explain the shift of the $i(E)$ peak maximum potential to more cathodic values. As it was already discussed in the back scan of the CV the diffusion current is increased in the parallel field (Fig. 4.6a), what can also be easily seen in the $dm/dt(E)$ curves (Fig. 4.6b). But, as already mentioned, the deposition is prevented at more negative potentials with field than without, i.e. a longer plateau in $dm/dt(E)$ without field is observed. During the cathodic sweep of the CV, in the potential range where the bulk Fe deposition occurs, the $pH$ value at the electrode surface reaches a high extend in comparison to the bulk value [101]. It was observed that the interface $pH$ value in the back scan of the CV recovers faster in the parallel magnetic field due to the MHD effect acting in the electrolyte (the influence of the magnetic field on the interface $pH$ value will be discussed in Chapter 4.1.2). As explained before a bulk Fe deposition at a potential below the $i(E)$ maximum in the mixed control regime (diffusion + charge transfer). An additional Lorentz force-driven convection partially removes the hydroxide species from the electrode surface and shifts the electrode equilibrium. This, in turn, leads to a more negative potential at which the deposition is no longer observed in field when compared to the case without field. A longer plateau in the $dm/dt(E)$ curve obtained without field corresponds well to the $i(E)$ plot where the diffusion current density in the CV back scan holds to a more positive potential when compared with the one recorded with field applied in the parallel-to-electrode configuration.

The RDE experiments revealed a similar dependence of the rotation rate (Fig. 4.5). It can be concluded that this is a hydrodynamic effect. The effects obtained with the RDE are of a much higher magnitude but the experiments in the magnetic field were performed with a vertical electrode and the RDE was horizontal and faced downward. In the case of vertical electrodes the contribution of the natural convection has to be considered [131], which may act opposite to the Lorentz force and reduce the transport of ions towards the electrode [17,79].
The same way as in the Co case deposition potentials for the potentiostatic experiments was chosen, i.e. at the beginning ($E_1$), at the maximum ($E_2$) and at the end ($E_3$) of the bulk metal deposition peak (table 4.1).

In Fig. 4.7 the $i(t)$ (a,c) and the corresponding $m(t)$ transients (b,d) obtained at -1550 mV$_{\text{MSE}}$ for different magnetic flux densities in both magnetic field-to-electrode configurations are shown. As expected, a magnetic field applied in the parallel-to-electrode configuration increases the limiting current density and deposition rate in the stationary regime (Fig. 4.7a,b). This result is linked to the MHD effect acting in the electrolyte.

On the other hand, the perpendicular-to-electrode field does not affect the $i(t)$ plot shape (Fig. 4.7c). Only a slight retardation of the deposition rate with field was observed (inset of Fig. 4.7d). Analysing the $i(t)$ transients (Fig. 4.7a,c), irrespective of the magnetic field-to-electrode configuration, a current density peak (I), which indicates nucleation and growth phenomena, is seen.
This peak is affected by a magnetic field applied parallel-to-electrode (inset of Fig. 4.7a), i.e. the magnetic field reduces the current density of the peak maximum and shifts it to shorter times. This effect has its consequences in the $m(t)$ transients (Fig. 4.7b), i.e. a parallel magnetic field decreases the deposited mass in the early beginning of the deposition (up to ca. 27 s). At high enough magnetic flux densities ($B \geq 0.8$ T) a second current maximum (II) can be noticed on the $i(t)$ transient indicating further nucleation and growth processes. These phenomena are discussed in detail in Chapter 4.2.

For a clarification of the origin of the magnetic field influence on the $i(t)$-transients shape, chronoamperometric experiments with an Au-RDE were performed. In Fig. 4.8 $i(t)$ transients for the deposition of Fe at -1550 mV$_{\text{MSE}}$ with different rotation rates of RDE are shown.

As it was expected, the limiting current density is increased with the rotation rate. The shape of the $i(t)$-transients obtained with the RDE is very similar to those obtained with a superposed magnetic field, i.e. after a sharp increase of the current density, a decay occurs followed by the $i(t)$ peak. The $i(t)$ peak maximum is decreased with increasing of rotation rate (inset of Fig. 4.8), what is in good correlation with results obtained with a magnetic field (Fig. 4.7a). This is again a direct proof that the magnetically induced effects are of...
hydrodynamic origin, i.e. the \textit{MHD} effect acting in the electrolyte.

The Fe partial currents were calculated as in the Co case from the steady state deposition rates (Eq. 4.1). In Fig. 4.9 the calculated Fe partial limiting current densities are shown in dependence of the magnetic flux density obtained at different potentials in the parallel-to-electrode configuration. The linearity of the double-log plot is obvious in Fig. 4.9, the \( i \propto B^n \) dependence of the limiting current with magnetic flux density holds supporting the \textit{MHD} effect behaviour (Eq. 2.27). During the deposition at -1650 mV\textsc{MSE} without a magnetic field the mass increase is prevented after about 40 s (not shown) resulting in the Fe limiting current becoming equal to 0. This is due to a very high interface pH value (see Chapter 4.1.2), sufficient for spontaneous hydroxide formation, which precipitate and block the electrode surface preventing further deposition. When a magnetic field is superposed in the parallel configuration a Lorentz force induced convection removes the hydroxides from the electrode surface allowing further deposition. That is a reason why the linear dependence obtained at this potential is so steep \((n=0.95)\).

4.1.1.3. Cobalt-Iron Alloys

Figure 4.10 shows CVs (a,c) and corresponding \( m(E) \) plots (b,d) obtained from the CoFe(B) electrolyte (table 3.1) at different magnetic flux densities in both magnetic field-to-electrode configurations. Similar to the Co and Fe cases, the \( i(E) \) curves show three characteristic peaks in the cathodic region, irrespective of the magnetic field configuration. The oxygen reduction (I), the HER peak with a maximum at a potential of about -1300 mV\textsc{MSE} (II), and the bulk alloy reduction peak (III) are observed (Fig. 4.10a,c). The maximum of the HER (II) peak is slightly shifted towards more negative potentials when compared with the Co electrolyte (Fig. 4.1a,c) but is lower than in the Fe electrolyte (Fig. 4.4a,c). The HER overpotential is increased with Fe concentration in the electrolyte \[110\]. The onset of the bulk alloy deposition peak is observed at a potential of about -1400 mV\textsc{MSE}, and is equal to the one obtained with Co (Fig. 4.1a,c). The maximum of this peak (III) is observed at a potential of -1480 mV\textsc{MSE} (equal to Co). The mass increase is noticed, irrespective of a magnetic field, above a potential of ca. -1175 mV\textsc{MSE} (IV), which is the same as in the case of Co (Fig. 4.1b,d).
RESULTS

Fig. 4.10. CVs (a,c) and corresponding mass changes (b,d) obtained in the CoFe(B) electrolyte at different magnetic flux densities applied in the parallel- and perpendicular-to-electrode configuration, respectively; $dE/dt = 20 \text{ mV s}^{-1}$.

The parallel-to-electrode magnetic field affects the CV and $m(E)$ shape significantly (Fig. 4.10a,b). The changes are qualitatively the same as in the Co and Fe electrolytes, i.e. an increased current of the oxygen reduction (I) and HER (II) peaks, except the bulk alloy deposition peak (III). Regarding the bulk alloy deposition peak (III) the situation becomes more complicated than with pure elements. The peak maximum current density is surprisingly reduced in the magnetic field but the rising part of it is unaffected. Moreover, the maximum of the peak potential is slightly shifted to more negative values as already observed for the Fe electrolyte (Fig. 4.4a). At the end of the scan in the cathodic direction as well as on the way back the current density is increased with parallel field (Fig. 4.10a). This is a clear influence of the MHD effect acting in the electrolyte, i.e. an increased transport of ions towards the electrode. The changes in the CV shape have a consequence in the $m(E)$ plots shape. At the onset potential of the alloy deposition peak an
increased deposition rate in $m(E)$ is observed (Fig. 4.10b). At the potential range where no difference in the $i(E)$ plots is observed, i.e. in the peak rising part (up to ca. -1450 mV_{MSE}), no changes in the deposited mass with magnetic field are seen. After that point the current density of plots recorded with the superposed magnetic field is reduced. Consequently the deposited mass is slightly lower in the field. This situation is reversed and the current density and deposition rate is increased with magnetic field above a potential of about -1500 mV_{MSE} resulting with the same mass deposited at the vertex potential.

In the back scan of the CV where the increased diffusion limited current density is observed (Fig. 4.10a) the deposited mass in the field is higher and the $m(E)$ dependency is steeper (Fig. 4.10b), i.e. higher deposition rates in the field are obtained. This is in agreement with the classical MHD theory, i.e. increased deposition rates with magnetic field applied in the parallel-to-electrode configuration are expected [85]. Additionally, similarly to the Co and Fe case, the mass growth is no longer observed above a potential of about -1300 mV_{MSE}, when the magnetic field is applied. At this potential without magnetic field the mass increase is still significant. This results in nearly equal masses deposited in the plateau potential range without and with the parallel magnetic field (Fig. 4.10b). In the perpendicular-to-electrode configuration no influence of a magnetic field in CVs neither in $m(E)$ curves was noticed (Fig. 4.10c,d).

Fig. 4.11. $dm/dt(E)$ plots obtained without and with a magnetic field ($B=1T$) applied in the parallel-to-electrode configuration (a) and CVs obtained with RDE at different rotation rates (b); CoFe(B) electrolyte, $dE/dt=20$ mVs$^{-1}$. 

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The CoFe deposition rates were calculated from the $m(E)$ plots in the same way as it was done for Fe. In Fig. 4.11a the $dm/dt(E)$ plots calculated for CoFe deposition without and with a magnetic field ($B=1$T) applied in the parallel-to-electrode configuration are shown. The shape of the $dm/dt(E)$ curves corresponds well with the CVs (Fig. 4.10a). The magnetic field impact on the deposition rate is similar as in the Fe case (Fig. 4.6). In the rising part of the bulk metal deposition peak the deposition rate is reduced in the parallel-to-electrode magnetic field, the peak maximum is shifted to a more negative potential and the diffusion current in the CV back scan is increased in the field (Fig. 4.11a). But instead of an increase in the current density of the bulk metal deposition peak maximum a retardation is observed. As expected the current densities obtained without a magnetic field in the potential range where the bulk metal deposition peak is observed (Fig. 4.10a) are significantly higher than the ones obtained in the Fe electrolyte (Fig. 4.4a). This results in a higher Lorentz force and a stronger convection in the CoFe electrolyte, which, in turn, amplifies the retardation of the deposition rate due to a more pronounced shift in the electrode equilibrium. Additionally in the alloy case two co-deposited metals and two MeOH$^+$ species adsorbed at the electrode surface have to be considered, i.e. CoOH$^+$ and FeOH$^+$. The adsorption of both species is competitive, they have different hydrolysis constants and adsorption abilities [106,137]. The ratio of the adsorbed species is most probably also affected by the additional convection what induces an additional shift to the electrode kinetics. Sasaki and Talbot [138] have found, in studies on Fe-group metals and alloys deposition, that the deposition rate is retarded with the rotation rate of the electrode. They have worked with much higher concentrations (approximately 50 times higher) where the rate determining step is charge transfer. This strongly suggests that an additional convection can affect the electrode equilibrium. In the back scan of $dm/dt(E)$ (Fig. 4.11), as it was already observed for Fe (Fig. 4.6b), the deposition rate is increased in the parallel magnetic field but the deposition is interrupted at a more negative potential (ca. -1450 mV$_{MSE}$) than in the case without magnetic field (ca. -1240 mV$_{MSE}$), i.e. a longer plateau in the $dm/dt(E)$ plot is observed in the back scan without a magnetic field. This again strongly suggests that the electrode equilibrium can be affected by the additional convection induced by the Lorentz force in the potential range more positive than the CV peak maximum (Fig. 4.10a). Additionally, it is known [139] that the stability of metal hydroxides is $pH$ dependent. It was found, the same as for Fe, that the interface $pH$ value in the CV back scan recovers faster in the parallel-to-electrode magnetic field (see Chapter 4.1.2) what could also affect the electrode equilibrium. These effects are much more pronounced in the alloy electrolyte.
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than in the case of pure Fe deposition, what supports the hypothesis that also the ratio of FeOH\(^+\)/CoOH\(^+\) adsorbed at the electrode surface is affected by additional convention. To confirm the hydrodynamic origin of the observed effects the RDE experiments were performed (Fig. 4.11b). The influence of the rotation rate is almost the same as that of the superposition of a parallel magnetic field, i.e. the peak maximum is shifted to more cathodic potential and its current density is reduced with the rotation rate (Fig. 4.11b – indicated by an arrow). In the back scan of the CV increased diffusion current and a shorter plateau is noticed with rotation rate. The decreased deposition rate in the rising part of the peak is much more pronounced with the RDE (Fig. 4.11b) when compared to the magnetic field impact (Fig. 4.10a), where almost no influence in this part of the CVs was observed. The potentiodynamic behaviour of the other non-buffered electrolyte CoFe(A) (table 3.1) is qualitatively the same, but the effects introduced by a magnetic field are smaller in magnitude.

![Graph](image)

**Fig. 4.12.** Position of the CV bulk CoFe deposition peak maximum (Fig. 4.10a) in dependence of the magnetic flux density applied in the parallel-to-electrode configuration; dE/dt=20 mVs\(^{-1}\).

In Fig. 4.12 the dependences of the current density (\(i_{\text{peak}}\)) and the potential (\(E_{\text{peak}}\)) of the bulk metal deposition peak maximum vs. magnetic flux density applied in the parallel-to-electrode configuration for CoFe(A) and CoFe(B) electrolytes are shown. A shift of the CVs peak maximum is obvious irrespective of the electrolyte composition, i.e. the decreased peak maximum current density and its potential shift towards more negative values. It becomes also apparent that the magnitude of the changes depends on the chemical composition of the
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electrolyte, i.e. it is proportional to the Fe concentration (more pronounced influence of a magnetic field in the CoFe(B) electrolyte – Fig. 4.12). This supports the hypothesis that a Lorentz force driven convection affects the ratio of metal hydroxides (FeOH\(^+\)/CoOH\(^+\)) adsorbed at the electrode surface. Also the maximum current density of the bulk metal deposition peak is proportional to Fe concentration. This can be explained by the fact that the Co concentration is constant in both electrolytes and only the Fe concentration is twice as high in the CoFe(B) electrolyte. The current density is proportional to the overall concentration of electroactive species [31,110].

As described in the experimental part (Chapter 3.2) two different classes of electrolyte were used, i.e. without and with addition of boric acid. In Fig. 4.13 CVs (a,c) and corresponding \(m(E)\) plots (b,d) obtained for the CoFe(C) electrolyte (table 3.1) at different magnetic flux densities in both magnetic field-to-electrode configurations are shown.

Fig. 4.13. CVs (a,c) and corresponding mass changes (b,d) obtained in the CoFe(C) electrolyte at different magnetic flux densities applied in the parallel- and perpendicular-to-electrode configuration, respectively; \(dE/dt=20\ mV\ s^{-1}\).
The shape of the CV (Fig. 4.13a,c) is clearly affected by the addition of a buffer. The HER (II) and the bulk alloy reduction (III) peaks are visible. A magnetic field applied in the parallel-to-electrode configuration influences the CV and the corresponding $m(E)$ plot shape. The current density of the bulk metal deposition peak is increased in this field configuration (Fig. 4.13a). This has a consequence in the $m(E)$ response (Fig. 4.13b). Above a potential, where the mass growth is noticed (ca. -1250 mV$_{MSE}$), the amount of material deposited in the field is higher and the deposition rates are increased (steeper dependences) as well. The same dependence holds also for the back scan of the CV resulting in a higher mass in the plateau potential range deposited in the parallel field. Increased current densities as well as deposition rates in the parallel field are a clear indication of MHD effect acting in the bulk electrolyte, i.e. an increased mass transport of ions towards the electrode surface. No significant influence of a perpendicular-to-electrode magnetic field was noticed (Fig. 4.13c,d).

The influence of the electrolyte composition on the potentiodynamic behaviour in alloy electrolytes, CVs and corresponding mass changes obtained without a magnetic field in CoFe(B) and CoFe(C) electrolytes were compared (Fig. 4.14). The difference between the CoFe(B) and the CoFe(C) electrolytes is the addition of boric acid only, but the metal ions concentration is the same (table 3.1). It is apparent that, irrespective of a buffer addition, the HER and the bulk alloy deposition peaks are visible. The addition of a buffer does not significantly affect the onset of the mass growth as well as the onset of HER and the bulk alloy deposition peak. The current densities in the potential range, where the bulk alloy deposition peak occurs, are quite similar, but the HER peak current is increased by the buffer addition. The water decomposition onset potential is slightly shifted in a more positive direction by the boric acid addition what is in agreement with results obtained by other groups [10,111,140]. This increased HER rate and an earlier onset of
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Water decomposition is also obvious from the \( m(E) \) curves. The mass of alloy deposited from the buffered electrolyte is lower and the reduction of the deposition rate in the cathodic direction scan occurs at a more positive potential, what suggests that the metal deposition reaction is strongly overlapped by the HER and the water decomposition. The reduced deposition rate of the alloy and the increased HER rate is a straightforward effect of the boric acid addition which buffers the \( pH \) value at the interface (lower interface \( pH \) value with buffer). As a result a higher HER as well as a reduced current efficiency of the alloy deposition is observed (influence of the buffer addition on the HER and the interface \( pH \) value is discussed in more details in Chapter 4.1.2).

In the same way as in the Co and Fe cases the deposition potentials for the potentiostatic experiments were chosen, i.e. at the beginning \( (E_1) \), at the maximum \( (E_2) \) and at the end \( (E_3) \) of the bulk alloy deposition peak (table 4.1).

![Graphs showing i(t) and m(t) transients](image)

**Fig. 4.15.** \( i(t) \) (a,c) and corresponding \( m(t) \) (b,d) transients recorded during the CoFe alloy deposition at a potential of -1480 mV\textsubscript{MSE} in parallel- and perpendicular-to-electrode configuration, respectively; CoFe(B) electrolyte (table 3.1).
In Fig. 4.15 exemplary $i(t)$ (a,c) and corresponding $m(t)$ transients (b,d) obtained at a potential of -1480 mV$_{MSE}$ from the CoFe(B) electrolyte with different magnetic flux densities in both magnetic field-to-electrode configurations are shown. As it was expected, a magnetic field applied in the parallel-to-electrode configuration increases the limiting current density and the deposition rate in the steady state conditions (Fig. 4.15a,b) due to the MHD effect acting in the electrolyte. On the other hand the perpendicular-to-electrode field does not affect the limiting current neither the steady state deposition rate nor the deposited mass (Fig. 4.15c,d). An increased current density was observed with magnetic field in moderate times (20 – 60 s), but at the same time no changes in the $m(t)$ transients were noticed. This clearly indicates that the HER rate is increased in this field configuration (see Chapter 4.1.2). The shape of $i(t)$ transients (Fig. 4.15a,c), irrespective of the magnetic field strength and configuration, shows an $i(t)$ (I) peak similarly to the Fe deposition indicating the nucleation and growth phenomena. This peak is slightly affected by the parallel-to-electrode magnetic field, i.e. a weak retardation of the peak current density with magnetic field is noticed (Fig. 4.15a). On the contrary, no influence of the perpendicular-to-electrode magnetic field on the $i(t)$ peak was found (Fig. 4.15c).

In Fig. 4.16 the $i(t)$ (a,c) and the corresponding $m(t)$ transients (b,d) obtained at a potential of -1480 mV$_{MSE}$ from the CoFe(C) electrolyte with different magnetic flux densities in both magnetic field-to-electrode configurations are shown. The only difference in the electrolyte composition between the CoFe(B) and the CoFe(C) is the addition of boric acid to the later one (table 3.1). The shape of the $i(t)$ transients is similar for both electrolytes, i.e. the $i(t)$ peak is observed indicating the nucleation and growth phenomena. The current densities obtained for the CoFe(C) electrolyte (Fig. 4.16a,c) are much higher than the ones obtained in CoFe(B) electrolyte (Fig. 4.15a,c) (about 3 times) but the deposited mass is only slightly higher (Fig. 4.16b,d). This indicates that the HER and the water decomposition are greatly enhanced by the buffer addition what was already noticed during the potentiodynamic polarisation experiments. A magnetic field affects the shape of the $i(t)$ transients obtained from the CoFe(C) electrolyte in both configurations. When a magnetic field is applied in the parallel-to-electrode configuration the limiting current density as well as the steady state deposition rate are increased (Fig. 4.16a,b) due to the MHD effect acting in the electrolyte. Moreover, the $i(t)$ peak is also affected by the parallel magnetic field, i.e. the current density of the peak maximum is decreased by a magnetic field (inset in Fig. 4.16a). This will be discussed in more detail in Chapter 4.2.
A perpendicular-to-electrode magnetic field affects the $i(t)$ transients shape as well, i.e. the limiting current density is increased in the field (Fig. 4.16c) but no significant changes in the $m(t)$ transients in this field configuration were noticed (Fig. 4.16d). This clearly shows that the HER rate is increased in the perpendicular-to-electrode magnetic field which is discussed in more detail in Chapter 4.1.2.

The limiting current densities for the alloy deposition were calculated, similarly to Co and Fe, from the steady state deposition rates (Eq. 4.1). The calculations were supported by the chemical composition analysis of the deposited layer, which was found to be unaffected by the magnetic field, and the knowledge that the composition is constant with the layer thickness [110,141] (for details see Chapter 4.3.1). The alloy partial limiting current density vs. magnetic flux density applied in the parallel-to-electrode configuration dependencies obtained at a potential of $-1480 \text{ mV}_{\text{MSE}}$ in parallel- and perpendicular-to-electrode configuration, respectively; CoFe(C) electrolyte (table 3.1).
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-1480 mV$_{\text{MSE}}$ from used electrolytes are shown in log-log coordinates in Fig. 4.17. Irrespective of the electrolyte composition the linearity in the dependencies is obvious, clearly indicating the MHD effect impact on the alloy deposition reaction [85], which increases the deposition rate through the improved transport of ions towards the electrode surface.

The electrodeposition of Fe-group alloys is very often found to be anomalous, i.e. the less noble metal is deposited preferentially or the deposition of the nobler one is inhibited [103-109,138]. To verify, if this is the case, the relation between the composition of the deposit and the composition of the electrolyte ($x_C = \frac{C_C}{C_C + C_{Co}}$, where $C$ is the molar concentration) was examined according to the procedure described by Brenner [103]. In Fig. 4.18 the relations between the composition of the deposit referred to the more noble Co and the composition of the electrolyte are shown. According to Brenner’s alloy codeposition classification [103], points which lie below the composition reference line represent the so called anomalous deposition, i.e. the deposition of the more noble metal is inhibited or the less noble metal deposition is enhanced. As it may be seen from Fig. 4.18.

![Fig. 4.17](image1.png)

**Fig. 4.17.** CoFe alloy partial limiting current density vs. magnetic flux density in log-log coordinates obtained with used electrolyte (table 3.1); -1480 mV$_{\text{MSE}}$, parallel-to-electrode magnetic field.

![Fig. 4.18](image2.png)

**Fig. 4.18.** Relation between composition of the deposit and composition of the electrolyte; full points and empty points represent unbuffered and buffered electrolytes, respectively.
4.18, the deposition at -1400 mV$\text{MSE}$ and -1480 mV$\text{MSE}$ seems to be only slight or not anomalous, irrespective of the buffer content, which is in good agreement with the literature data [11,109]. In the case of the highest applied potential of -1600 mV$\text{MSE}$ for the unbuffered electrolyte, it is clear that the deposition is anomalous. Moreover, the anomalous behaviour strongly depends on the electrolyte concentration, i.e. a more anomalous behaviour is observed with a higher Fe$^{2+}$ concentration. It was found that in front of the electrode, the $\text{pH}$ reaches a very high value in comparison to the bulk situation, especially with a high applied potential. It was also shown that this $\text{pH}$ value is proportional to the Fe$^{2+}$ concentration (for details see Chapter 4.1.2). The increased interfacial $\text{pH}$ value (up to about 12) is sufficient for the precipitation of the hydroxide species [135]. From the above considerations it might be concluded that the deposition of the CoFe alloy with the highest applied potential is anomalous and proceeds according to the model suggested by Dahms and Croll [104], which assumes the precipitation of the metal hydroxides. The magnetic field superposition during the deposition does not change the behaviour of the system, the chemical composition of the deposit is unaffected by a magnetic field irrespective of its strength and configuration (for details see Chapter 4.3.1).

4.1.1.4. Summary

To summarize the influence of the magnetic field on the metal deposition reaction in steady state conditions, the current enhancement parameter was used to make the magnetic field influence evident because it is very sensitive even for small differences:

$$\text{current enhancement} = \frac{i^B_{\text{lim}} - i^0_{\text{lim}}}{i^0_{\text{lim}}} \times 100\% \quad (4.2)$$

where: $i^0_{\text{lim}}$ is the partial (metal or alloy) limiting current density obtained without magnetic field, $i^B_{\text{lim}}$ is the partial (metal or alloy) limiting current density obtained with superposed magnetic field.

The influence of the magnetic flux density, relative to the electrode surface configuration, and the applied potential on the current enhancement for the Co (a), the Fe (b) and the CoFe(A) (c) electrolyte are shown in Fig. 4.19. It is obvious that a magnetic field applied in the parallel-to-electrode configuration leads to a strong current enhancement, i.e. almost linear dependence of the current enhancement with the magnetic flux density is observed for all of the electrochemical
systems. This effect is related to the Lorentz force acting in the hydrodynamic layer, i.e. an additional convection is induced (MHD effect) which increases the mass transport of ions towards the electrode surface and as a consequence, the limiting current densities for the mass transport controlled reactions [17,20,64,65,79,88,101]. In this configuration the current enhancement is also potential-dependent, i.e. it increases proportionally with the potential. During the deposition of the alloy in the parallel magnetic field at -1600 mV\textsubscript{MSE} (Fig. 4.19c) the current enhancement parameter reaches extremely high values, i.e. about 500%. This effect can be explained as follows: during the deposition at -1600 mV\textsubscript{MSE} a very high pH value in front of the electrode surface is reached, which is sufficient for a Fe(OH)\textsubscript{2} precipitation (see Chapter 4.1.2). The precipitated hydroxides block the electrode surface and further deposition is inhibited. When a magnetic field is superposed in the parallel-to-electrode configuration, the depletion of the H\textsuperscript{+} concentration at the electrode surface is compensated by the MHD effect and the hydroxide formation is suppressed. The additional convection induced by the Lorentz force may also remove some of the precipitates from the electrode surface leading to a higher deposition rate.

Fig. 4.19. Current enhancement changes with a magnetic field obtained for Co (a), Fe (b) and CoFe(A) (c) electrolyte (table 3.1) at different potentials and magnetic field-to-electrode configurations.

Considering the alloy deposition at the highest applied potential without the magnetic field superposition it was found that the deposition rate obtained from the CoFe(A) electrolyte is strongly inhibited and the deposition from the CoFe(B) electrolyte is almost prevented (not shown). In this case it is obvious that even a very small change of the deposition rates, which are directly proportional to the alloy limiting current densities, leads to a very high extend of the
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current enhancement parameter (Fig. 4.19c). It is the same case for the Fe deposition at -1650 mV_MSE, but the current enhancement is so huge (more than 1000%) that the results obtained at this potential are not shown.

When a magnetic field is applied perpendicular to the electrode surface there is almost no influence on the metal deposition reaction. A retardation of the current enhancement in the range of 10-20% is observed for Fe (Fig. 4.19b) and alloy deposition (Fig. 4.19c). It seems that the retardation is proportional to the magnetic flux density. In this magnetic field-to-electrode configuration the Lorentz force is very small, but, nevertheless, it can not be neglected, especially because of the edge effects at the electrode. It was found by Cierpka et al. [142] for the similar geometrical system that even in a seemingly parallel electric and magnetic field, the Lorentz force-induced motion dominates the flow. It is possible that the retardation of the deposition rates arises from the fact that the induced Lorentz force acts against the natural convection and thus the mass transport of ions towards the electrode surface is decreased [17,79].

Fig. 4.20. Current enhancement changes with a magnetic field obtained for unbuffered (a) and buffered (b) alloy electrolytes (table 3.1) at -1480 mV_MSE and both magnetic field-to-electrode configurations.

In Fig. 4.20 the influence of magnetic fields on the current enhancement parameter calculated at -1480 mV_MSE for the unbuffered (a) and buffered electrolytes (b) are shown. It is apparent that the changes induced by a magnetic field are qualitatively the same, irrespective of the buffer addition. A parallel-to-electrode magnetic field increases the CoFe limiting current density and a perpendicular magnetic field has a very low influence on the current enhancement parameter. The magnitude of changes obtained in the perpendicular-to-electrode configuration with the buffered
electrolytes (Fig. 4.20b) is higher than with the unbuffered one (Fig. 4.20a). The total current density obtained in the buffered electrolyte (Fig. 4.16c) is much higher (at least 3 times) than in the unbuffered one (Fig. 4.15c). Moreover, the total limiting current density is increased in the perpendicular-to-electrode configuration (Fig. 4.16c) as well. This clearly shows that the edge effects play a significant role in this magnetic field-to-electrode configuration: the higher the current density the higher the Lorentz force and its influence on the electrochemical reactions.

4.1.2. Influence of a Magnetic Field on the Hydrogen Evolution Reaction (HER) and the pH Value at the Interface

The electrodeposition of Fe-group metals and alloys from aqueous solutions can be accompanied by side reactions, i.e. HER (Eq. 2.33) and water decomposition (Eq. 2.34). These may lead to changes of the surface concentration of hydrogen and hydroxyl ions and, therefore, of the surface pH value. The changes in the surface pH value may in turn affect the electrode kinetics (Eqs. 2.29-2.32) [104-108]. Moreover, the properties of a deposited layer can be affected by the interface pH value variation, for example, the crystal structure of the electrodeposited Ni and Co layers is pH dependent [143,144]. If the interface pH value reaches a very high extend compared to the bulk then a precipitation of metal hydroxides (Eq. 2.36) may occur [10], which in turn incorporate into the deposit. For instance, Osaka et al. [117] have shown that contamination of hydroxides into deposited soft magnetic Co$_{35}$Fe$_{65}$ films reduces the saturation magnetization of the deposit. The simultaneous evolution of hydrogen gas at the electrode has a significant impact on the layer morphology. For example, holes left after hydrogen bubble could be observed [19,20,79,83,92].

A superposition of a magnetic field may affect the HER [19,20,79,83,92,98,99] and thus the interface pH value [100,101]. For a better understanding of this influence a detailed analysis is needed. This chapter is devoted to investigations on the influence of magnetic fields on HER.

For a detailed analysis of the magnetic field impact on the HER with respect to its strength and relative to the electrode configuration, HER limiting currents were calculated as the difference between the total current density and the metal partial current density \( i_{lim,HER} = i_{lim,total} - i_{lim,metal} \). The current enhancement parameter (Eq. 4.2) has been used to visualize the influence of magnetic fields on the HER. In Fig. 4.21 the HER current enhancement, obtained for the Co (a) and the Fe (b) electrolytes at \( E_1 \) and \( E_2 \) potentials (table 4.1), in the cell geometry shown in Fig.
3.1a, is plotted vs. the magnetic flux density. The data set obtained at the highest applied potential is not shown because at this potential the water decomposition reaction (Eq. 2.34) has a significant contribution (for details see Chapter 4.1.1) and a calculation of the HER partial current density is not possible.

In Fig. 4.21 the HER current enhancement parameter, obtained at -1480 mV_{MSE} for alloy electrolytes of different composition (table 3.1), is plotted vs. the magnetic flux density. The influence of a parallel-to-electrode magnetic field is qualitatively the same for unbuffered electrolytes, irrespective of their composition. An increase of the HER rate is observed (Fig. 4.21a,b and Fig. 4.22a) due to the MHD effect acting in the electrolyte, which increases the H\(^{+}\) transport towards the electrode surface. The HER is mass transport controlled at the pH level of 3, which is an expected behaviour \[17,20,79,110\]. On the contrary, when boric acid is present in the electrolyte the influence of the magnetic field applied in the parallel-to-electrode configuration is dramatically changed. Instead of an increase in the HER rate a retardation is observed (Fig. 4.22b). When a buffer is present in the electrolyte and the deposition is carried out at -1480 mV_{MSE} the water decomposition (Eq. 2.34) may have a very significant contribution to the side reactions current (Fig. 4.14 in Chapter 4.1.1.3). On the other hand, Zech and Landolt \[140\] proposed that the water decomposition reaction is unaffected by the buffer addition, only the HER is modified. In the potential range close to the onset of the water decomposition more
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protons are released what leads to a higher HER contribution. This, in turn, results in a more positive potential of the onset of water reduction [140]. The retardation of the HER current enhancement with parallel magnetic field is unexpected and not yet understood. Nevertheless, the buffer effect on the HER and the influence of the parallel magnetic field are obvious. This is shown in Fig. 4.23, where the HER current density changes with magnetic field in the parallel-to-electrode configuration obtained at -1480 mV_{MSE} from CoFe(B) and CoFe(C) electrolytes are compared.

From Fig. 4.23 it becomes apparent that the current density consumed by the hydrogen evolution is strongly increased by the addition of the buffer (about 5 times) irrespective of a magnetic field. The reason is that the boric acid is very weakly dissociated. The dissociation at used pH and the concentration of boric acid proceed according to the reaction Eq. (4.8) with a pK equal to 7 (pK=-logK, where K is a dissociation constant)[139].

\[ 3H_3BO_3 \leftrightarrow B_3O_3(OH)_4^+ + H^+ + 2H_2O \]  \hspace{1cm} (4.8)

The H^+ ions are consumed by the HER (4.4) and their concentration in the diffusion layer is lower than in the bulk. The boric acid concentration (which is present in the electrolyte mainly as a molecular one [139,140]) in the diffusion layer is almost equal to the bulk one. When the concentration of hydrogen ions in the diffusion layer is depleted due to the HER, the reaction (4.8) shifts its equilibrium in the direction of products releasing H^+ ions. This in turn increases
the HER rate and its current density. Of course the above explanation is strongly simplified due to additional effects which may take part in the buffering action as, for example, the formation of a complex of the dissociated boric acid with a metal ion [145,146], which increases the buffer capacity or the adsorption of the boric acid at the electrode surface [111]. Similar results, i.e. an increased HER partial current density with addiction of boric acid, were found, for example, during the Ni [10] and the NiFe alloy [10,146] deposition.

The increase of the limiting HER current density with a parallel magnetic field obtained from the electrolyte without boric acid (CoFe(B)) and its linear dependence of the magnetic flux density in double logarithmic coordinates clearly shows the classical MHD effect dependence \((i \propto B^n)\). A reduced HER current density with magnetic field in the parallel-to-electrode configuration obtained in the buffered electrolyte appears also as a linear one in double logarithmic coordinates (Fig. 4.23). This suggests that the retardation in the HER rate is an answer of the system to the additional convection induced by the Lorentz force. But in this case it is more likely that the chemistry of the electrolyte in the diffusion layer is affected rather than the electrochemical reaction rate. An increased mass transport would be expected to affect the electrochemical reaction in the opposite direction and an increased reaction rate should be observed. In the limiting case, if the buffer would counteract any hydrogen concentration fluctuations within the diffusion layer, no influence of the additional convection would be expected as reported by Zhuang [147]. This influence is still unclear and further investigations are necessary to get more insight into it. Nevertheless, the retardation of the HER rate in the parallel-to-electrode magnetic field observed with buffered electrolytes could be caused by the following phenomena:

- the electrolyte chemistry within the diffusion layer is affected.
and thus the surface chemistry is changed, i.e. altered adsorption behaviour (different adsorbed species and/or the ratio between them and/or their surface coverage).

When a magnetic field is applied in the perpendicular-to-electrode configuration, irrespective of the electrolyte chemistry, the HER current enhancement is increased with the field (Figs. 4.21, 4.22). On the other hand, the current enhancement for the metal deposition in this magnetic field-to-electrode configuration is retarded or not affected at all (Figs. 4.19, 4.20). In this configuration the influence of the Lorentz force is expected to be minimized due to the parallel orientation of the electric and magnetic field lines. In many cases it was stated that the Lorentz force influence may be neglected [19,79,86]. It was shown by numerical simulations and by particle image velocimetry (PIV) measurements that, even if a magnetic field is aligned parallel to the electric field in the bulk of electrolyte, close to the electrode surface edge effects play a significant role and a Lorentz force driven convection might be predominant [142]. And indeed, considering the alloy deposit surface obtained at 5 T from the CoFe(A) electrolyte (Fig. 4.24a – in this case the field was applied vertically) the influence of edge effects is obvious. The deposition is favoured close to the electrode edge, which indicates a high value of the Lorentz force (MHD effect), which leads to a rotational flow.

![Fig. 4.24. Optical micrographs of CoFe deposits: (a) deposited in the cell shown in Fig. 3.1a at $B=5T$, (b) deposited in the cell shown in Fig. 3.1b at $B=10T$; CoFe(A) electrolyte (table 3.1).](image)

![Fig. 4.25. Current enhancement changes with magnetic flux density calculated for the metal deposition reaction and the HER; -1480 mV$_{\text{MSE}}$, perpendicular-to-electrode configuration, Co and CoFe (A) electrolytes (table 3.1).](image)
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primary current distribution and allows to neglect the edge effects [126]. This can be seen on the CoFe deposit surface obtained at 10 T from the CoFe(A) electrolyte (Fig. 4.24b), where even with a twice as high flux density as for the other cell (Fig. 4.24a) the deposit is uniform over the whole area, no edge effect influence is observed.

As for the other cell geometry (Fig. 3.1a), the current enhancement parameters were calculated. In Fig. 4.25 exemplary current enhancement vs. magnetic flux density dependencies calculated for the Co (a) and the CoFe(A) electrolyte (b) in the edge free cell (Fig. 3.1b) are shown. It is clearly visible, that the HER rate is increased in the perpendicular magnetic field whereas the metal deposition reaction is slightly retarded. This confirms the magnetic field impact on the HER. An increased desorption of hydrogen can be concluded from the morphology of the CoFe deposits. Deposits obtained without magnetic field appear black with large holes, which remained after the formation of H$_2$ bubbles (Fig. 4.26a). When the deposition is carried out in a perpendicular field of 1T, the deposits appear more uniform and no large “H$_2$ holes” were observed (Fig. 4.26b). To prove the hypothesis of an increased desorption rate of the hydrogen in the perpendicular-to-electrode magnetic field direct microscopic observation of the electrode surface during the deposition were performed by the shadowgraph technique. These investigations were performed only for the Co electrolyte. Investigations involving Fe containing electrolytes should be performed with a membrane between the anodic and the cathodic part of the cell to suppress the expected contamination of the electrolyte with the Fe$^{3+}$ ions [117,20]. The use of a cubic cell (Fig. 3.4), necessary for the optical inspection, excludes the application of a membrane.

In Fig. 4.27 shadowgraphs of the electrode surface obtained during the Co deposition without a magnetic field at potential $E_2$ (table 4.1) are shown. In the left column (Fig. 4.27a-d) the raw images and in the right column (Fig. 4.27e-h) the differential images after subtraction of the image (a) are shown. The subtraction was performed so that the electrolyte appears as grey, the unchanged area as white and the changes are represented by a black colour. From Fig. 4.27 the hydrogen bubbles formed at the electrode surface are clearly visible. Moreover, from Fig. 4.27e-f

![Fig. 4.26. Optical micrographs of CoFe layers deposited without (a) and in the perpendicular-to-electrode field ($B=1T$) (b) in the edge free cell (Fig. 3.1b); CoFe(A) electrolyte.](image-url)
it can be concluded that the bubbles are in a stagnant regime [68], i.e. they are fixed at the electrode and only a growth of the bubbles with time is observed (increasing black area around the white bubble). Only a small fraction of the bubbles is desorbed from the electrode surface (Fig. 4.27 – indicated with arrows), but most of them remain at the surface until the end of deposition (within the duration of the experiment of ~6 min).

Fig. 4.27. Shadowgraphs of the electrode surface obtained during the deposition of Co at -1480 mV$_{MSE}$ without a magnetic field (a-d) and corresponding ones after subtraction of the image (a) showing the increase of the bubble size (e-h). Shadowgraphs are shown in a time sequence as follows: 100 s (a,e), 200 s (b,f), 275 s (c,g) and 316 s (d,h) of deposition.

To clarify the stagnant regime of the bubbles during the deposition without a magnetic field a picture of the electrode surface after the experiment has been taken and compared with the shadowgraph obtained at the end of the process (Fig. 4.28b). From Fig. 4.28b it is clear that the bubbles are fixed at the electrode (indicated with circles). A similar observation was made for the deposition of a CoFe alloy, where the electrode surface after the deposition shows a characteristic hole pattern caused by the hydrogen bubbles (Fig. 4.26a). Since the shadowgraph operates in
transmission mode, it cannot distinguish between bubbles appearing at different depths. Furthermore, when bubbles overlap, only the biggest one is visible.

However, comparing the shadowgraph with the surface image in Fig. 4.28a, it is obvious that the bubbles observed during the deposition fit perfectly to the bubble pattern on the electrode. This proves the stagnant regime of the bubble formation. Moreover, the bubbles are formed all over the electrode surface and not preferentially at the edges.

In Fig. 4.29 a set of shadowgraphs obtained during Co deposition in the perpendicular-to-electrode magnetic field (650 mT) is shown. The magnetic flux density of 650 mT was the limit of the permanent magnet arrangement used to generate the magnetic field (Fig. 3.6c). The same subtraction procedure as for the images obtained without a field was employed.

In the left column (Fig. 4.29a-f) raw images and in the right column (Fig. 4.29g-k) images after subtraction of the image (a) are shown.

It is clear that the bubbles formed in the field are much smaller (indicated with arrows), except a single large one (Fig. 4.29a-f) which got stuck at the cell wall and could not be removed. This is clearly visible after the subtraction, where negligible or no growth of this bubble with time is observed (Fig. 4.29g-k). Despite the reduced bubble size, the HER regime is also shifted and stagnant bubbles are no longer observed. A desorption of bubbles from the electrode surface could be easily observed on a sequence of shadowgraphs. The bubbles which were observed at the electrode surface are desorbed and move rapidly (~20 mm s$^{-1}$) in the bulk electrolyte (Fig. 4.29 – indicated by arrows). This proves that a magnetic field in the perpendicular-to-electrode configuration is able to enhance the desorption of hydrogen, and most notably, at a drastically reduced bubble size.
Fig. 4.29. Shadowgraphs of the electrode surface obtained during the deposition of Co at -1480 mV\textsubscript{MSE} in the perpendicular-to-electrode field (a-f) and corresponding ones after subtraction of (a) showing the evolution of bubbles (g-k). Shadowgraphs are shown in a time sequence as follows: 269.8 s (a), 276.0 s (b,g), 277.0 s (c,h), 277.4 s (d,i), 281.6 s (e,j) and 281.8 s (f,k) of deposition.
The origin of the phenomenon is seen in a special type of a micro-\textit{MHD} effect [66]. When a H$_2$ bubble is formed at the electrode surface, in its vicinity the current distribution is distorted. The current lines are no longer perfectly normal to the electrode surface, but there is also a parallel-to-electrode component (Fig. 4.30). As a consequence an azimuthally directed Lorentz force is induced which drives a swirling flow around the bubble [92]. This is a situation resembling the classical Bödewadt problem in fluid mechanics ([148] and references therein). The resulting imbalance between centrifugal force and radial pressure difference in the velocity boundary layer at the electrode generates a secondary flow in a plane perpendicular to the electrode. It is directed radially inwards, moves over the bubble surface and finally rises above it. The shear stress, thereby imposed along the interface, provokes an additional pulling force at the liquid-gas interface. Furthermore, the lighter fluid of the concentration boundary layer is advected across the bubble surface. This modified buoyancy force together with the additional pulling force arising from the shear stress are probably the main mechanisms for the accelerated bubble desorption [98].

The HER accompanying metal deposition reaction may lead to a significant interface \(p\text{H}\) change [10,100,140]. The electrolyte \(p\text{H}\) value is a very important factor in the electrodeposition which may affect the deposit properties such as morphology [2,149,150], chemical [103,105,149] and phase composition of the alloys [24,150], and crystal structure [143,144]. Therefore, interface \(p\text{H}\) value measurements were performed in order to determine its dependence of magnetic field in the experimental setup shown in Fig. 3.3. In Fig. 4.31 exemplary CVs (a,c) and corresponding interface \(p\text{H}\) value changes (b,d) obtained without and with the superposed magnetic field (\(B=1\text{T}\)) for pure 0.1 M Na$_2$SO$_4$ and CoFe(B) alloy electrolyte, respectively, are shown. In the cathodic sweeps of the CVs (Fig. 4.31a,c) the first peak occurs independently from the deposition system with maximum at a potential of about -1200 mV$_{\text{MSE}}$ and is related to the HER which can be seen in the CV obtained from the pure Na$_2$SO$_4$ solution (Fig. 4.31a).
onset potential of this peak occurs at about \(-1000\) mV\(_{\text{MSE}}\) which correlates well with the beginning of the pH increase (Fig. 4.31b,d). It is clear that a superposed magnetic field increases the peak current. This is due to the MHD effect acting in the electrolyte.

The interfacial pH value is also affected by the magnetic field (Fig. 4.31b,d). A parallel-to-electrode magnetic field decreases the interface pH value, except at high overpotentials. In the case of high overpotentials, the HER and the water decomposition become predominant and the additional convection induced by the Lorentz force is not strong enough to reduce the pH. In the pH-potential (pH(E)) loops a hysteresis is visible which is much narrower with the superposed magnetic field. Additionally it can be seen from the pH(E) plots (Fig. 4.31b,d) that the interface
pH value at the end of the potential back scan recovers faster with the magnetic field applied and practically reaches the starting value.

When there is no magnetic field present, the interfacial pH at the end of the CV back scan is higher and does not reach the initial one. At high overpotentials during the deposition (Fig. 4.31b,d) it is possible that a spontaneous hydroxide formation might occur [135] which block the pores of the net and the pH measurements get impossible (working electrode – Fig. 3.3). The lower pH value at the end of the back scan and the narrower hysteresis in the CVs with the superposed magnetic field is also caused by the MHD effect which helps to remove the hydroxyl species from the electrode surface and to compensate faster the consumed protons. As a result, a lower extend in the interfacial pH value is observed. A similar effect was also observed during Co deposition by Uhlemann et al. [100]. When the interfacial pH value at the end of the cathodic scan for the pure Na$_2$SO$_4$ electrolyte is compared with that for the electrolytes containing Co and/or Fe ions, it can be seen that overall pH value at the interface is higher for the Na$_2$SO$_4$ electrolyte, irrespective of the magnetic field (Fig. 4.32). The reason for this is that in the Na$_2$SO$_4$ electrolyte there are no hydroxides formed at the surface (Eq. 2.35,2.36), which buffer the depletion of hydrogen ions. This leads to the higher pH increase in the Na$_2$SO$_4$ electrolyte [105]. A similar effect was also observed by Deligianni and Romankiw [10] during nickel deposition.

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Fig. 4.32. Interface pH($E$) curves obtained without (a) and with the superposition of the magnetic field ($B=1T$) (b). $dE/dt=20$ mVs$^{-1}$, first scans of CVs, cathodic slopes only.
In Fig. 4.33 the interface pH value vs. the magnetic flux density (pH(B)) dependencies at different potentials are shown (table 4.1 – additionally for the Na$_2$SO$_4$ electrolyte the potentials were chosen as indicated in Fig. 4.31a). A reduction of the interfacial pH value in the parallel-to-electrode magnetic field is apparent. This effect might be explained by the increased mass transport of the hydrogen ions towards the electrode surface caused by the additional convection induced by the Lorentz force (MHD effect). Moreover, the additional convection induced by the Lorentz force increases the hydroxyl ions flux away from the electrode surface which also reduces the pH value in front of the electrode.

Considering absolute surface pH values (Fig. 4.33), it is very likely that spontaneous hydroxide formation occurs, what is clearly visible in the hydroxide solubility diagrams shown in Fig. 4.34, where the starting conditions and the directions of changes during the deposition are indicated. When the potential step is applied, the diffusion layer is formed and grows until the limiting current is reached. After that the mass transport control dominates the deposition and the concentration of the electroactive species at the electrode surface is close to 0.

As a consequence the interface pH value (when HER is diffusion controlled) reaches a very high extend in comparison to bulk. Again if one focuses at the pH values where the hydroxide
products are stable (Fig. 4.34) and compares them with the values obtained during the experiment (Fig. 4.33), it is very probable that hydroxides are formed and might be incorporated in the deposited layer. The situation becomes very dramatic in the case of the deposition with the highest applied potential – $E_3$, i.e. on the end of the CV deposition peak, where a $pH$ value of about 12 is reached (Fig. 4.31a,c).

In the alloy deposition systems even the potential of the CV peak maximum gives a relatively large increase in the surface $pH$ value (Fig. 4.32b). This is obvious when one takes a look at the deposit quality obtained from CoFe(B) electrolyte at potential $E_2$ (deposited in the cell geometry shown in Fig. 3.1a). The deposits obtained without superposition of the magnetic field appear black and those obtained in the 1T parallel magnetic field are bright (Fig. 4.35). For the deposition from the CoFe(A) electrolyte using the same cell geometry (Fig. 3.1a) no precipitates are observed after deposition at potential $E_2$. For the Ni deposition system onto the RDE from the chloride electrolyte Deligianni and Romankiw [10] also observed that deposits obtained at high overpotentials and without rotation of the disc appeared black. But when the electrode rotated (1600 rpm), the deposits had a shiny and metallic appearance. It seems that the precipitation depends on the Fe concentration in the electrolyte ($pH$ values at the interface are very similar for the Fe concentrations), which suggests that the surface is successively covered by iron hydroxides such as Fe(OH)$_2$, FeOH$^+$ or even polymeric hydrolyzed species like Fe$_2$(OH)$_3^{3+}$. Such a high interfacial $pH$ value during the CoFe alloy deposition from unbuffered electrolytes may indicate that the deposition proceeds according to the model suggested by Dahms and Croll [104] which assumes precipitation of the metal hydroxides.

**Fig. 4.34.** Influence of $pH$ on the solubility of Fe(OH)$_2$ (a) and Co(OH)$_2$ (b) with the indication of the deposition starting conditions and the direction of changes. (Calculated from [135].)
Considering the alloy electrolytes containing boric acid (table 3.1), it was shown that the HER rate is reduced for the magnetic field applied in the parallel-to-electrode configuration (Fig. 4.22b and 4.23). This observation suggests that the interface pH value should be increased in the magnetic field compared to that without field, i.e. the lower the interface pH value the higher the HER rate. And indeed, if one takes a look at Fig. 4.35b, where the interface pH values obtained at potential $E_2$ (table 4.1) from the CoFe(B) and CoFe(C) electrolytes are compared it becomes apparent that a magnetic field applied in the parallel-to-electrode configuration increases the interface pH value. Also the buffering effect of the boric acid is clear which reduces the interface pH value by a factor of 2.5 at 0 T. The influence of a magnetic field is smaller for the CoFe(C) than for the CoFe(B) electrolyte, what indicates that it is suppressed by the presence of the buffer. Nevertheless, the limiting current density, irrespective of the buffer addition, is increased in the parallel magnetic field (Fig. 4.35a) indicating that the induced changes have a hydrodynamic origin, i.e. MHD effect. A similar effect of a parallel magnetic field on the interface pH value was concluded by Chounchane et al. [24] during a ZnNi alloy deposition from an electrolyte containing boric acid.

Fig. 4.35. The limiting current density vs. magnetic flux density plots (a) and corresponding interface pH values (b) obtained in CoFe(B) and CoFe(C) electrolytes (table 3.1); $E_2$, parallel-to-electrode magnetic field.
4.1.3. **Conclusions regarding the Influence of a Magnetic Field on the Mass Transport**

**Magnetic field applied in the parallel-to-electrode configuration:**

- The limiting current densities and deposited masses are increased with a magnetic field, irrespective of the applied potential and electrochemical system (table 3.1) studied;
- The metal deposition reaction rates, for all investigated potentials and electrochemical systems, are increased with the magnetic flux density, i.e. higher steady state deposition rates are observed;
- When deposition is carried out from an electrolyte without boric acid the HER rate is increased in the magnetic field;
- Addition of boric acid to the electrolyte leads to a higher HER rate, which is reduced with the magnetic flux density;
- The interface pH value is lower in the field for unbuffered electrolytes
- Addition of boric acid reduces the interface pH value when compared with the unbuffered electrolytes, but it is increased with the magnetic flux density;

The observed effects in this field configuration are induced by the Lorentz force driven convection, i.e. the MHD effect, which increases the mass transport of the electroactive species towards and away from the electrode surface.

**Magnetic field applied in the perpendicular-to-electrode configuration:**

- No influence of the magnetic field on the metal deposition reaction, irrespective of the applied potential and electrochemical system, was observed;
- The HER rate is greatly improved with magnetic flux density due to a faster desorption of hydrogen bubbles from the electrode surface through the influence of a micro-MHD effect induced in the bubble vicinity;
- A qualitative model has been developed in order to explain the improved desorption rate of hydrogen from the electrode surface supported by in-situ microscopic observations.
4.2. **INFLUENCE OF A MAGNETIC FIELD ON THE NUCLEATION AND GROWTH PROCESSES**

As it was shown in Chapter 4.1.1 neither a significant effect on the current density nor on the deposited mass in the early stages of the deposition was observed in the perpendicular-to-electrode configuration. Therefore, the further analysis of the \( i(t) \) transients will be reduced only to the parallel-to-electrode configuration.

When analysing the early stages of the potentiostatic polarisation, irrespective of the investigated electrochemical system (table 3.1), turns out that after applying the potential step the current density increases sharply and then a current decay is observed (Fig. 4.2, 4.7, 4.15 and 4.16a,c). Such an initial shape of the \( i(t) \) transients is often explained by the double layer (DL) charging [34,151]. However, in the present studies, experiments were supported by an in-situ EQCM mass measurement. Based on the results shown in Fig. 4.2, 4.7, 4.15 and 4.16b,d it is obvious, that a mass increase occurs even at those very short deposition times. A similar behaviour of the Fe-group metal deposition onto Au substrates was also observed by Lachenwitzer and Magnussen [152]. This suggests, that this part of the \( i(t) \) transients is not only related to DL charging phenomena but also to the nucleation and growth of a new phase on a foreign substrate. This deposition step seems to be unaffected by a superposed magnetic field. The amount of mass deposited at very short times is not of high accuracy because of the time delay of the EQCM device itself, which is in the range of tens of milliseconds. When compared with the acquisition rate of the potentiostate (50 ms), it might be more than 50% time delay for the first two points.

Due to a low precision of the first points of the \( m(t) \) transients, this nucleation and growth step will not be analyzed in detail to prevent misinterpretation. Nevertheless, the mass deposited in this time range, irrespective of the electrolyte, is equivalent to a few monolayers (MLs). It was observed by Gündel et al. [44], using in-situ STM investigations, that the overpotential deposition (OPD) of iron proceeds via a layer-by-layer growth up to a thickness of 4–5 ML on Au(111) electrodes. A similar observation, i.e. two successive MLs formation, during the OPD of Co was made by Krause et al. [46]. A formation of one or more monolayers followed by a 3D nucleation and growth was proposed by Abyaneh and Fleischmann [153] during Ni deposition. A 2D nucleation step precedent to the 3D one was also concluded from the analysis of the \( i(t) \) transients during the initial stages of Ag deposition by Palomar-Pardavé and coworkers [56]. It seems that
this part of the transient, irrespective of the applied potential and electrochemical system, may be linked to the first ML formation or a successive layer-by-layer growth in 2D mode [154].

The nucleation and growth studies are commonly performed throughout the chronoamperograms (CAs) analysis. The CAs have a characteristic feature – the maximum in the $i(t)$ plot. Nucleation studies are mainly based on the rising part of this peak as well as its maximum position analysis [33,49,155].

Another problem is that the HER accompanying the metal deposition reaction may and will affect the $i(t)$ transient shape significantly. This was observed in many studies for example during Co [35] and Fe [36] electrocrystallization. To avoid this problem a further analysis will be performed with transients without the HER contribution. The partial current densities were calculated throughout the graphical differentiation of the $m(t)$ transients (Eq. 4.1), but, now the whole transients are considered not to be only the steady state condition as it was done before. In Fig. 4.36 the total, HER and Co partial current densities are shown. It is apparent that the HER strongly obscures the chronoa mperometric response of the system, the current density maximum is barely (if at all) visible in the total current density plot but appears clearly in the Co partial one (indicated by an arrow). It was also observed that the shape of the $i(t)$ transients at the very beginning of the deposition, obtained with the same parameters, may significantly vary from one to the other experiment [38]. Because of that, an analysis of a single, independent transient may lead to a misinterpretation of the results. For this purpose it was proposed [38] to use transients which are average values of many measurements. This procedure was adapted to the present studies and all transients were averaged over at least four independent measurements. Nevertheless, the reproducibility of the experiments was very good, as it is clearly visible in Fig. 4.37, where the exemplary $m(t)$ transients measured with one set of parameters are shown.

![Fig. 4.36. $i(t)$ transients with separated partial current densities for Co and HER; $0T$, $E_2$.](image_url)
The maxima in the $i(t)$ transients occur at relatively long times (Fig. 4.2, 4.7, 4.15 and 4.16a,c – indicated by arrows), especially for the lowest applied potential (inset of Fig. 4.38 – indicated by an arrow). To minimize the contribution of the current from the previous layer growth (2D) on the first $i(t)$ peak position, the time of the onset of nucleation ($t_0$) was estimated. This estimation was performed by means of a $m(t)$ transients analysis. A linear fit to a steady state deposition rate of the previous layer was made. A nucleation of another layer was assumed to start from a point where a deviation from the linearity was observed. According to Scharifker and Mostany [59], irrespective of the growth mode, at the very beginning of the potential step, the $i(t)$ transient can be described by a simple power function of time. Based on this a power function was fitted to the part of the $m(t)$ where the deviation from the linearity was observed. $t_0$ was
found at the crossover of the linear and the power fits. A determination procedure of $t_0$ is shown exemplarily for Fe, in Fig. 4.38. The thickness of the layer grown under 2D layer-by-layer growth has been estimated to ~5 MLs.

In the following sections the analysis of the nucleation and early stages of growth will be performed for pure metals and alloys separately with all precautions discussed in this section. The $i(t)$ transients will be analyzed on a basis of different available theoretical models and the morphology evolution during the early stages of growth will be discussed with the help of microscopic techniques.

4.2.1. Cobalt

In Figs. 4.39a–b $i(t)$ transients obtained for Co at different magnetic flux densities in the parallel-to-electrode configuration and at different potentials are shown. It is obvious that the limiting current density is increased with the magnetic flux density regardless of the applied potential. The $i(t)$ transients exhibit a clear maximum followed by a decay. The shape of the transients after a decay, at a very low concentration of metal ions in the electrolyte, is characteristic for the nucleation processes followed by the 3D diffusion controlled growth [33]. The transients obtained at the highest potential (-1600 mV$_{\text{MSE}}$) are not shown. This is due to the fact that these transients do not exhibit a maximum (or the maximum appears at very short times, below the resolution of the EQCM) what excludes them from a further analysis.

The most established parameter influencing the nucleation behaviour is the overpotential [33,35,38,39,43] and will be analyzed in a first place. From Fig. 4.40 it is obvious that the applied potential affects the $i(t)$ maximum position, i.e. it is shifted to shorter times, and the maximum current density is increased (steeper dependency) with increasing overpotential. This is an expected behaviour and it means that the steady state nucleation rate ($AN_0$) increases with the potential which is the driving force for these processes [49,50,156].

In order to get more detailed information on this influence, the experimental transients were analyzed by a model proposed by Mirkin and Nilov [61] and independently by Heerman and Tarallo [53]. The nomenclature introduced by Heerman and Tarallo will be used (Eq. 2.21) and referred to as HT. The Levenberg–Marquart algorithm was used to fit Eq. (2.21) to the experimental results (OriginLab software), with $A$, $N_0$ and $D$ as fitting parameters, but the time
was corrected by the onset of nucleation (estimated as shown in the previous section) and expressed as $t-t_0$.

**Fig. 4.39.** Co partial current density vs. time transients obtained without and with a magnetic field in the parallel-to-electrode configuration at a potential of $-1400\text{mV}_\text{MSE}$ (a) and $-1480\text{mV}_\text{MSE}$ (b).

In Fig. 4.40 a comparison between the experimental and the best fits of Eq. (2.21) for transients obtained without a magnetic field are shown. Additionally a perfect Cottrell behaviour is illustrated (also corrected by $t_0$). The qualitative description of the experiments by the HT model is very good and the calculated dependences lie very close to the experimental ones. From the fits, the nucleation parameters were calculated (table 4.2) with a diffusion coefficient of $6.1\times10^{-6} \text{cm}^2\text{s}^{-1}$ which is in a fairly good agreement with values found in the literature [35,157]. Taking into consideration values shown in table 4.2 it is clear, as expected, that the steady state nucleation rate is increased by the applied potential. This
change is due to an increase in the nucleation rate constant \( A \) while the number of nuclei at saturation \( N_0 \) remains nearly the same for both potentials. A similar effect of the potential on the nucleation of Co was also observed by Palomar-Padavé et al. [35].

An investigation of the influence of the parallel magnetic field on the nucleation is much more complicated. This is due to the fact that most of the models are developed for quiescent condition. At long times reduces to a Cottrell equation [33,53]. A magnetic field applied in this configuration induces additional convection, i.e. the MHD effect, and a deviation from this behaviour is expected. Nevertheless, considering the \( i(t) \) transients (Fig. 4.39), it is clear that there is no significant change in the shape of the rising part of the \( i(t) \) maximum with magnetic field, irrespective of the applied potential. This strongly suggests that the nucleation of Co proceeds with the same nucleation rate, regardless of the magnetic field. A slight shift of the \( i(t) \) peak maximum, obtained at -1400 mV\( \text{MSE} \) (Fig. 4.39a), towards longer times and its higher current density is a reason of the higher growth rates observed in the parallel magnetic field. An additional Lorentz force driven convection increases the limiting current density on the right hand side of the \( i(t) \) maximum. This, in turn, leads to a higher maximum current density and longer times at which it is observed in a magnetic field.

**Table 4.2.** Co nucleation parameters, HT model, \( B=0\text{T} \).

<table>
<thead>
<tr>
<th>( E ) ( \text{mV}_{\text{MSE}} )</th>
<th>( A ) ( \text{s}^{-1} )</th>
<th>( N_0 ) ( 10^{-6} \text{ cm}^{-2} )</th>
<th>( AN_0 ) ( 10^{-5} \text{ cm}^{-2}\text{s}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>-1400</td>
<td>0.053</td>
<td>2.65</td>
<td>0.14</td>
</tr>
<tr>
<td>-1480</td>
<td>3.517</td>
<td>2.96</td>
<td>10.4</td>
</tr>
</tbody>
</table>

![Fig. 4.41. Reduced Co partial current–reduced time dependences obtained without and with magnetic field in parallel-to-electrode configuration at a potential of -1400 mV\( \text{MSE} \) (a) and -1480 mV\( \text{MSE} \) (b).](image-url)
It was suggested by Scharifker and Hills [33] that one can distinguish if the nucleation and growth processes proceed via the limiting cases, i.e. instantaneous or progressive, by comparing the experimental results with the theoretical dependencies (Eqs. 2.17 and 2.18) in reduced coordinates. In Fig. 4.41 the experimental transients and the theoretical ones, in reduced coordinates, are compared. It is apparent that a parallel magnetic field does not introduce any significant changes to the nucleation processes (left hand side of the maximum). Only some scattering at the lowest applied potential (Fig. 4.41a) can be observed, but the curves calculated from results obtained without magnetic field and with a magnetic flux density of 1T practically cover each other at times up to the maximum. The right hand side of the maximum is mainly governed by the growth of the previously formed nuclei, but due to convection induced by a magnetic field, a deviation from the Cottrell behaviour is expected, therefore, this part of the transients is not considered for a further analysis. Moreover, it was shown by Heerman and Tarallo [60] that, at large values of the $N_0/A$ ratio, i.e. progressive nucleation, the curves after the maximum are affected by $N_0/A$ value but not the rising parts. Nevertheless, the most important information regarding the nucleation ($A$ and $N_0$) is covered by the rising part of the maximum [33]. Therefore, in most cases it is enough to analyze only this part of the transients [39,43,158].

Looking at the overall mechanism of the nucleation and growth is seems that it lies closer to the progressive limiting case at the lowest potential (Fig. 4.41a) and is shifted towards the instantaneous one at -1480 mV$_{MSE}$ (Fig. 4.41b). This is consistent with the result obtained by the HT model fits where the nucleation rate constant is increased with the potential (table 4.2). But from these values it can be concluded that the nucleation at $E_2$ is still far away from the instantaneous limiting case which is observed when $At \geq 20$ [60].

### 4.2.2. Iron

In Figs. 4.42a–c $i(t)$ transients obtained for Fe at different magnetic flux densities in the parallel-to-electrode configuration and at different potentials are shown. The limiting current density is increased with the magnetic flux density due to the MHD effect acting in the electrolyte, irrespective of the applied potential. The shape of the $i(t)$ transients, as in the Co case, exhibits a maximum followed by a decay, which is characteristic for the nucleation processes followed by a 3D diffusion controlled growth [33]. In the case of the first two applied potentials, i.e. -1500 and -1550 mV$_{MSE}$ (Fig. 4.42a,b), the current density of the first peak maximum (I) is
RESULTS

affected by a magnetic field, i.e. the peak current density is decreased and shifted to shorter times with a magnetic field. This is caused by the convective effect induced by the Lorentz force what was proved by independent RDE experiments (Fig. 4.8). Moreover, when the magnetic flux density is sufficiently high, a second \(i(t)\) peak (II) is observed at a longer time. The position of the second peak maximum also depends on the magnetic flux density (II – Fig. 4.42a,b). This is more pronounced for the lowest applied potential, i.e. the maximum current density is increased and the peak position is shifted to a longer time (Fig. 4.42a).

![Image](image.png)

**Fig. 4.42.** Fe partial current density vs. time transients obtained without and with a magnetic field in the parallel-to-electrode configuration at a potential of -1500 mV<sub>MSE</sub> (a), -1550 mV<sub>MSE</sub> (b) and -1650 mV<sub>MSE</sub> (c).

In the case of the highest applied potential no significant influence of magnetic field on the \(i(t)\) peak maximum position was noticed (Fig. 4.42c). Moreover, at -1650 mV<sub>MSE</sub> no current flow is observed above about 40 s of deposition without the field superposition. This effect can be explained by an increase of the interfacial pH value due to the parallel HER, which reaches a high extend compared to the bulk electrolyte, and is sufficient for a spontaneous hydroxide formation (for details see Chapter 4.1.2). The precipitated hydroxides successively block the electrode surface and, finally, the deposition is prevented. When a magnetic field is applied during the deposition, the Lorentz force induces an additional convection (MHD effect), which removes part of the precipitates from the electrode surface and allows a further deposition (Fig. 4.42c) [101].

The experimental transients obtained at chosen potentials without superposition of a magnetic field were analysed by a non-linear fitting procedure to the HT model (Eq. 2.21) (Fig. 4.43a-c), the same way as it was done for Co. As visible in Fig. 4.43 and already explained before, the
deposition is prevented at -1650 mV_{MSE}, above 40 s. Because of that the fitting procedure was performed within a time range below 6 s and the diffusion coefficient was adopted from the lower potentials (4.7×10^{-6} cm^2 s^{-1}), which is in good agreement with literature data [1,105,107]. From Fig. 4.43 it is apparent that the HT model fits closely to the experimental transient and provides a good qualitative description of the experiment. The nucleation parameters were calculated from the best fits and are listed in table 4.3. The values from table 4.3 show the expected trend, i.e. an increased nucleation rate with the potential is observed. Compared to the lower potential cases the nucleation parameters calculated for the highest potential are dramatically changed. The most pronounced influence is revealed for the A parameter, i.e. a strong increase of A is observed (about 50 times). This suggests that the nucleation mode shifts towards the instantaneous limiting case, but does not reach its limit (A_{t_{max}}≈6).

Figures 4.44a–c show the reduced partial Fe current density vs. the reduced time dependencies calculated for the first peak (I) from the i(t) transients obtained with different magnetic flux densities and applied potentials. The deposition at a potential of -1500 mV_{MSE} and -1550 mV_{MSE} can be assigned as the progressive case (Fig. 4.44a,b). When a magnetic field is applied in the parallel-to-electrode configuration during the deposition at -1550 mV_{MSE} it seems that the nucleation and growth mechanism shifts slightly in the direction of the instantaneous limiting case (Fig. 4.44b). As already mentioned for the i(t) transients obtained at -1500 mV_{MSE} and -1550 mV_{MSE} (II – Fig. 4.42a,b), in the reduced

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**Table 4.3.** Fe nucleation parameters, HT model, B=0T.

<table>
<thead>
<tr>
<th>E mV_{MSE}</th>
<th>A s^{-1}</th>
<th>N_0 10^{-6} cm^{-2}</th>
<th>AN_0 10^{-6} cm^{-2}s^{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>-1500</td>
<td>0.11</td>
<td>2.31</td>
<td>0.25</td>
</tr>
<tr>
<td>-1550</td>
<td>0.16</td>
<td>4.12</td>
<td>0.66</td>
</tr>
<tr>
<td>-1650</td>
<td>6.84</td>
<td>5.86</td>
<td>40.08</td>
</tr>
</tbody>
</table>

---

**Fig. 4.43.** Comparison of the experimental transients with the ones calculated according to (Eq. 2.21) and the Cottrell behaviour; 0T.
coordinates transients, at sufficiently high magnetic flux density, a second nucleation and growth step can be observed (Fig. 4.44a,b – (II) indicated by arrows). Additionally, it can be seen from the dimensionless plots calculated at low magnetic flux densities, that, after reaching the maximum, the experimental transients lie below the theoretical curves (Fig. 4.44a,b). This has been commonly observed in nucleation studies [36,37,48,151]. In many cases it was linked to the HER [36,37,48], but this is not the case, because the Fe partial currents were calculated from the $m(t)$ transients. A deviation can also be induced by the natural convection contributing to the mass transport, which cannot be neglected since the electrode is arranged vertically (Fig. 3.1). No influence of the superposed magnetic field on the nucleation and growth mechanism at $-1650 \text{ mV}_\text{MSE}$ was found. At this potential it fits best to the instantaneous mode (Fig. 4.44c), what is in agreement with the nucleation parameters calculated by the HT model (table 4.3). But a deviation from the theoretical behaviour is observed at times below the maximum. This is probably due to the contribution of the previous layer growth, whose current is still significant and, therefore, the experimental points lie above the theoretical lines [26].

![Fig. 4.44. Reduced Fe partial current–reduced time dependencies obtained without and with magnetic field in parallel-to-electrode configuration at a potential of -1500 mV$_\text{MSE}$ (a), -1550 mV$_\text{MSE}$ (b) and -1650 mV$_\text{MSE}$ (c).](image)

The rising part of the $i(t)$ maximum is the most relevant for the determination of the nucleation parameters, especially when no clear maximum is observed [39,43,158]. Moreover, the HT model is convection-free. At long times it reduces to the Cottrell behaviour and should not be used to describe convective effects such as the MHD effect. Fortunately, at the first two potentials the rising part of the $i(t)$ transients is affected by the parallel magnetic field (Fig. 4.42a,b). To omit problems with a deviation from the Cottrell behaviour at long deposition times only the
rising part of the maximum will be considered as proposed by Hyde et al. [159]. They claimed that at small values of $\Delta t$ the Scharifker-Mostany (SM) expression [59] can be simplified to (Eq. 4.9). From (Eq. 4.9) it is apparent that the $i(t)$ transient at the rising part of the maximum should straighten out with time to a power of 1.5. Unfortunately, with this reduced version of the SM model it is impossible to separate $A$ and $N_0$ parameters, but at least the steady state nucleation rate, $j_0=AN_0$, can be analysed [43,39,158].

Moreover, this analysis can only be performed for the progressive nucleation or at very short times, otherwise Eq. (4.9) has no physical meaning, i.e. in the instantaneous case, parameter $A$ is equal to 0 immediately after nuclei formation. In Fig. 4.45 exemplary $i(t^{1.5})$ dependencies with linear fits to the rising parts obtained at -1500 mV$_{MSE}$ with different magnetic flux densities are shown. The linearity in a relatively wide time range of the rising part of the maximum is apparent. From the slopes of the linear fits a calculation of the nucleation rates becomes possible. As a first test, a comparison of the nucleation rate constants obtained by the HT model (Eq. 2.21) and by linear fit of Eq. (4.9) calculated at different potentials without a magnetic field has been performed (Fig. 4.46a). The potential in Fig. 4.46a is represented by an overpotential ($\eta$), calculated as the difference between the applied potential and the onset potential of the mass increase (-1325 mV$_{MSE}$) from the $m(E)$ plots (Fig. 4.4b,d). A discrepancy, about one order of magnitude, between the results obtained by calculations from different approaches is apparent. However the steady state nucleation rate vs. the overpotential dependency is qualitatively the same, i.e. the nucleation rate is increased by the potential. Large differences between different
nucleation and growth models have been commonly observed [38,160]. But it is more important to look at the general trend of changes induced by the investigated parameters rather than the absolute values [38]. Since the nucleation rate axis in Fig. 4.46a is logarithmic and its dependency on the overpotential is fairly linear. Linearity is expected and consistent with the atomistic theory of electrolytic nucleation [156,161].

In Fig. 4.46b the steady state nucleation rate vs. magnetic flux density dependencies obtained at -1500 mV_{MSE} and -1550 mV_{MSE} are shown. It is apparent that, as a general trend, the steady state nucleation rate is reduced in the parallel to the electrode magnetic field, irrespective of the applied potential. This will be discussed in detail in chapter 4.2.4. Nevertheless, the changes introduced by a magnetic field in the parallel-to-electrode configuration are of hydrodynamic origin and have to be discussed with respect to the MHD effect.
4.2.3. Cobalt-Iron Alloys

In Fig. 4.47 $i(t)$ transients are shown, which were obtained for the CoFe(A) (a,b) and for the CoFe(B) (c,d) electrolyte (unbuffered – table 3.1) at different potentials and magnetic flux densities applied in the parallel-to-electrode configuration.

![Graphs showing $i(t)$ transients for CoFe(A) and CoFe(B) electrolytes](image)

**Fig. 4.47.** CoFe alloy partial $i(t)$ transients obtained without and with magnetic field in the parallel-to-electrode configuration at a potential of -1400 mV<sub>MSE</sub> (a,c) and -1480 mV<sub>MSE</sub> (b,d) for CoFe(A) (a,b) and CoFe(B) (c,d) electrolytes (table 3.1).

The limiting current density, as already observed for Co and Fe, increases with the magnetic flux density due to the $MHD$ effect. No clear maximum in the $i(t)$ transients, irrespective of the
RESULTS

electrolyte composition, was observed at -1600 mV_{MSE}, therefore, these transients are not shown. The shape of the \( i(t) \) transients at -1400 mV_{MSE} and -1480 mV_{MSE}, as in the single metal cases, exhibit a maximum followed by a decay, characteristic for the nucleation processes and the 3D diffusion controlled growth [33]. Irrespective of the electrolyte composition and the applied potential, the peak current density of the first maximum (I) is affected by a magnetic field, i.e. the peak current density is decreased and shifted to shorter time with a magnetic field. This effect, as already discussed in previous sections, is of convective origin, i.e. the MHD effect acting in the electrolyte. The magnitude of this effect is electrolyte composition as well as potential dependent and the weakest influence of the magnetic field is observed at -1480 mV_{MSE} for the CoFe(B) electrolyte (Fig. 4.47d). The current density at the peak maximum also depends on the electrolyte composition, i.e. it is proportional to the electroactive species concentration. The \( i(t) \) maximum position is shifted to shorter time with the increase of \( \text{Fe}^{2+} \) concentration in the electrolyte as well. As in the Fe case, when the magnetic flux density is sufficiently high a second \( i(t) \) peak (II) can be observed at longer time, but only at the lowest applied potential (Fig. 4.47a,c), although this is not so clear as for Fe (Fig. 4.42a,b).

The first step in the nucleation and growth analysis will be to determine the potential influence. A new approach has to be developed which allows the modelling of the alloy systems. As a starting point the mathematical expression of Heerman-Tarallo (HT) will be used (Eq. 2.21). However, it has to be re-expressed for a two elements system. To make this possible a few simplified assumptions will be introduced. The alloy formation from the beginning of the process and nuclei with a chemical composition equal to a dense layer will be assumed. The assumption of alloy formation starting from a critical cluster was proposed by Milchev and Lacmann [162]. Moreover the chemical composition will be held constant with time. This is supported by AES depth profile analysis where no differences in the chemical composition with thickness were noticed (for details see Chapter 4.3.1). Due to a fixed chemical composition in time the current density can be expressed as follows:

\[
i(t) = i_{c_{0}}(t) + i_{p}(t)
\]

Now the expressions of the extended current density for each metal, assuming that it is deposited separately with equal \( A \) and \( N_{0} \) parameters, can be written as:

\[
i_{M_{e}}^{\text{ext}}(t) = \frac{zFD_{M_{e}}^{0.5}c_{M_{e}}^{*}}{\pi^{0.5}t^{0.5}} \Phi \left[ 1 - \exp \left[-\frac{\pi D_{M_{e}}N_{0}}{1 - t}\right] \right]
\]

(4.11)

where the \( M_{e} \) subscript stands for Co or Fe.
This allows to write the expression for the alloy formation, assuming the partial currents for pure metals during the alloy deposition proportional to the chemical composition of the deposit:

\[ i_{\text{CoFe}}(t) = x_{\text{Co}} \cdot i_{\text{Co}}^\text{ext}(t) + (1 - x_{\text{Co}}) \cdot i_{\text{Fe}}^\text{ext}(t) \]  
(4.12)

where \( x_{\text{Co}} \) is the atomic fraction of Co in the deposit.

The total current density for the alloy nucleation and 3D diffusion controlled growth according to the HT model can be finally expressed as follows:

\[ i(t) = \frac{zF}{\sqrt{\pi \cdot t}} \cdot \frac{\Phi}{\Theta} \cdot \left\{ x_{\text{Co}} \cdot c_{\text{Co}}^* \cdot \sqrt{D_{\text{Co}}} \cdot \left[ 1 - \exp\left[ -\pi k_{\text{Co}} N_0 D_{\text{Co}} t \Theta \right] \right] + (1 - x_{\text{Co}}) \cdot c_{\text{Fe}}^* \cdot \sqrt{D_{\text{Fe}}} \cdot \left[ 1 - \exp\left[ -\pi k_{\text{Fe}} N_0 D_{\text{Fe}} t \Theta \right] \right] \right\} \]  
(4.13)

where symbols have the same meaning as in the original HT expression (Eq. 2.21).

The diffusion coefficients as determined for pure metals were used. The atomic ratio in the deposit was determined by ICP-OES analysis (for details see Chapter 4.3.1) and the metal ions concentration is given in table 3.1. The fitting procedure was performed with a function expressed by Eq. (4.14).

\[ i(t) = \frac{1}{\sqrt{t}} \cdot \frac{\Phi}{\Theta} \cdot \left\{ x_{\text{Co}} \cdot P_1 \cdot \left[ 1 - \exp\left[ -P_2 t \Theta \right] \right] + (1 - x_{\text{Co}}) \cdot P_3 \cdot \left[ 1 - \exp\left[ -P_4 t \Theta \right] \right] \right\} \]  
(4.14)

Where:

\[ P_1 = zF c_{\text{Co}}^* \cdot \sqrt{D_{\text{Co}} \pi}, \ P_3 = zF c_{\text{Fe}}^* \cdot \sqrt{D_{\text{Fe}} \pi}, \ P_2 = \pi k_{\text{Co}} N_0 D_{\text{Co}} \cdot \pi k_{\text{Fe}} N_0 D_{\text{Fe}}, \ P_4 = \pi k_{\text{Fe}} N_0 D_{\text{Fe}} \]

Eq. (4.14) was then fitted to the experimental data with \( \Theta \) (implemented into \( \Theta \) and \( \Phi \)), \( P_2, P_4\) as fitting parameters. To prevent differences in the \( N_0 \) parameter calculated from \( P_2 \) and \( P_4 \), what would be unphysical, a linear constraint was implemented into the fitting procedure as shown in Eq. (4.15). Also the time was re-expressed to \( t-t_0 \), as for Co and Fe.

\[ \frac{P_2}{P_4} = \frac{k_{\text{Co}} D_{\text{Co}}}{k_{\text{Fe}} D_{\text{Fe}}} = \text{const.} \]  
(4.15)

In Fig. 4.48 a comparison between the experimental results and the best fits of Eq. (4.14) for transients obtained without a magnetic field, from unbuffered alloy electrolytes and the Cottrell behaviour is shown. The modified case of HT model closely fits to the experimental results providing a good qualitative description.
The calculated nucleation parameters are listed in table 4.4. As expected, the steady state nucleation rate is increased with the potential irrespective of the electrolyte composition. The $A$ and $N_0$ parameters increase with increasing concentration of the electroactive species ($\text{Fe}^{2+}$). This is also expected since the nucleation is a probabilistic process where the probability of finding a nucleus is proportional to both the potential and the concentration of the electroactive species [163].

<table>
<thead>
<tr>
<th>$E_{\text{MSE}}$</th>
<th>$A$</th>
<th>$N_0 \times 10^5$</th>
<th>$A N_0 \times 10^6$</th>
<th>$A$</th>
<th>$N_0 \times 10^6$</th>
<th>$A N_0 \times 10^6$</th>
<th>$A$</th>
<th>$N_0 \times 10^6$</th>
<th>$A N_0 \times 10^6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>-1400 mV</td>
<td>0.03</td>
<td>5.95</td>
<td>0.2</td>
<td>-1480 mV</td>
<td>0.10</td>
<td>19.00</td>
<td>1.9</td>
<td>-</td>
<td>0.12</td>
</tr>
<tr>
<td></td>
<td>0.12</td>
<td>1.17</td>
<td>1.4</td>
<td>-1480 mV</td>
<td>0.17</td>
<td>6.57</td>
<td>11.4</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

The influence of a magnetic field on the nucleation and the early growth stages will be analysed by the Scharifker-Mostany (SM) model considering only the rising $i(t)$ maximum part re-expressed to the alloy case (Eq. 4.16), and taking into account the same simplifications as for the HT model.
\[ i(t) = zF \pi \left[ x_{Co} \cdot D_{Co}^{3/2} \left( \frac{2M_{Co}C_{Co}^*}{\rho_{Co}} \right)^{1/2} + (1 - x_{Co}) \cdot D_{Fe}^{3/2} \left( \frac{2M_{Fe}C_{Fe}^*}{\rho_{Fe}} \right)^{1/2} \right] \cdot N_0 A \cdot t^{1/2} \] (4.16)

In Fig. 4.49 the steady state nucleation rate vs. the magnetic flux density dependencies obtained for unbuffered electrolytes at -1400 mV_{MSE} (a) and -1480 mV_{MSE} (b) are shown.

![Fig. 4.49. AN_0(B) dependencies calculated by the reduced form of the SM model (Eq. 4.16) for transients obtained at -1400 mV_{MSE} and -1480 mV_{MSE} (a,b), respectively; parallel-to-electrode configuration, unbuffered electrolytes.](image)

From Fig. 4.49, similar to the Fe case, a general trend of changes of the AN_0 parameter with a magnetic field superimposed in the parallel-to-electrode configuration can be observed, i.e. the steady state nucleation rate is reduced with the magnetic flux density. The magnitude of this influence is clearly potential and electrolyte composition dependent and almost vanishes at -1480 mV_{MSE} for the CoFe(B) electrolyte, as expected from the i(t) transients shape (Fig. 4.47d).

It is also expected that an addition of buffer may affect the nucleation and the growth behaviour (Figs. 4.15 and 4.16). In Fig. 4.50a a comparison between partial CoFe i(t) transients calculated from m(t) plots at -1480 mV_{MSE} for CoFe(B) and CoFe(C) electrolytes (the only difference is an addition of H_3BO_3 – table 3.1) is shown. The influence of the boric acid addition on the i(t) shape is obvious, i.e. a reduction in both i_{max} and t_{max} and an enhancement in the limiting current density are observed. The shift in the i(t) maximum position clearly indicates that the nucleation and the growth phenomena have to be affected by the buffer addition. In Fig. 4.50a the i(t) transients and in Fig. 4.50b the reduced coordinates transients are compared with the
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Theoretical plots (Eq. 2.17 and 2.18). The deposition from the CoFe(B) electrolyte lies closer to the progressive mode while after addition of the buffer (CoFe(C)) the mode shifts towards the instantaneous case. This influence is quite similar to the one induced by the parallel magnetic field superposition for Fe deposition at -1550 mV_{MSE} (Fig. 4.44b). What, in turn, suggests that the steady state nucleation rate should be retarded after the buffer addition. And indeed, if one has a closer look at the nucleation parameters calculated by the HT model (Eq. 4.14) for CoFe(B) and CoFe(C) electrolytes, it becomes obvious that the steady state nucleation rate is reduced by the boric acid (by a factor of about 2 – table 4.4). This is mainly due to a retardation in the $A$ parameter, while only a slight decline of the $N_0$ is noticed. A similar influence of a gelatine addition during the deposition of zinc onto HOPG was observed [164], i.e. a reduced nucleation rate constant. This influence has been explained by an adsorption of the gelatine at defects and edges which act as the active sites [164]. As proposed by Horkans [111], boric acid adsorbs at the electrode surface. This may act as a surfactant and similar effects as with the gelatine should be observed. It was also proposed that boric acid can form complexes with metal ions [145,146], which possibly adsorb at the electrode surface as well. Also a shift from an instantaneous to a progressive mode in absence of the $t$-octylphenoxyethoxy ethanol surfactant for the deposition of tin has been observed [165]. This is again a similar effect as for the boric acid and suggests that the adsorption plays a significant role. But the real interface chemistry is very complex and beyond the scope of this work.

**Fig. 4.50.** CoFe alloy partial $i(t)$ transients obtained without and with boric acid addition in linear (a) and in reduced current-reduced time coordinates (b); no magnetic field, CoFe(B) and CoFe(C) electrolytes (table 3.1), -1480 mV_{MSE}. 

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In Fig. 4.51a the $i(t)$ transients obtained for the CoFe(C) electrolyte in the parallel to the electrode magnetic field are shown. As expected, an enhancement of the limiting current density with magnetic flux density is observed. The $i(t)$ maximum shape and position is affected by a magnetic field in this configuration as well, i.e. the maximum is observed at longer times and its current density is retarded by a magnetic field.

![Fig. 4.51. CoFe alloy partial $i(t)$ transients obtained without and with a magnetic field superimposed in the parallel-to-electrode configuration (a) and corresponding $AN_0(B)$ dependency (b); -1480mV$_{MSE}$, CoFe(C) electrolyte.](image)

These changes are quite similar to the ones observed for the unbuffered electrolytes (Fig. 4.47). No significant influence of a magnetic field for the CoFe(D) and the CoFe(E) electrolyte was observed. Therefore, it will not be considered for the further analysis. An analysis of a magnetic field impact on the nucleation and the growth processes has been carried out, in analogy to the unbuffered electrolytes, by fitting the rising part of the $i(t)$ maximum to Eq. (4.16). The influence of the parallel magnetic field on the steady state nucleation rate calculated for the CoFe(C) electrolyte is shown in Fig 4.51b. From this figure it is apparent that the parallel magnetic field reduces the steady state nucleation rate, as already observed for unbuffered alloy electrolytes (Fig. 4.49) and for Fe (Fig. 4.46b). This dependency is a clear answer of the system, irrespective of its chemistry, to the MIHD and will be discussed in more detail in the next section.
4.2.4. Summary and Conclusions Regarding the Influence of a Magnetic Field on the Nucleation and Growth Processes

As shown in previous sections the deposition of metals and alloys under the investigated conditions, after a 2D (epitaxial) layer formation (Fig. 4.52a), proceeds via nucleation and further 3D diffusion controlled growth, irrespective of the electrochemical system. A magnetic field applied in the parallel-to-electrode configuration during the deposition significantly affects the nucleation and growth behaviour. This influence is apparent in the partial $i(t)$ transients, where a shift of the first $i(t)$ maximum with magnetic field is observed (I – Figs. 4.42, 4.47 and 4.51a). The most astonishing impact of the parallel magnetic field is visible in the steady state nucleation rate, which is reduced by the field (Figs. 4.46b, 4.49 and 4.51b). Additionally a slight shift of the nucleation mechanism from progressive, without a field, towards the instantaneous case, in the field, has been observed (Fig. 4.44b). At long deposition times it is apparent that the growth processes are affected by a magnetic field, irrespective of the deposition parameters ($MHD$ effect).

At the beginning of the potential step two processes occur simultaneously, i.e. nucleation and growth. Both of them are competitive, so when the growth rate is increased the nucleation rate has to be retarded. This can explain the decrease of the $i(t)$ peak current density in the magnetic field. In the case of the deposition without an applied magnetic field, progressive nucleation occurs which corresponds to a fast growth of the nuclei on many active sites (Fig. 4.52b). The nuclei appear at the electrode surface with a constant rate, the nucleation and the growth processes occur simultaneously (Fig. 4.52c), what means that the nuclei are at different age and size. The total current density over the whole geometric electrode area is high due to the large number of nuclei per unit surface ($N(t)=N_0A(t)$), i.e. the area of the electrode active for deposition is large.

When a magnetic field is applied in the parallel-to-electrode configuration the number of initially formed nuclei ($t \rightarrow 0$ s) seems to be unaffected (Fig. 4.52d), but the growth rate of the nuclei is increased. The nuclei formed in the beginning of this step develop spherical diffusion zones (Fig. 4.52d) which may overlap. The thickness of the diffusion layer of each nucleus is reduced due to the $MHD$ effect and, thus, the growth rate of the nuclei is enhanced (Fig. 4.52e). A surface area active for deposition is determined by the total surface of the nuclei. The growth occurs quickly on a relatively small number of active sites that are formed in the early stage of the rising part of
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the \(i(t)\) maximum. The current density to a separated metal nucleus is high but the total current to all the nuclei is relatively low because of the small active surface area (nuclei are formed at the beginning of this step followed by a 3D growth with a constant rate). The growth rate of the nuclei is increased and, as a consequence, \(N_0\) is retarded. This in turn reduces the \(AN_0\) product. The electrode area active for deposition is lower than without a magnetic field. As a consequence, the current density related to the whole geometric electrode area is reduced. The retardation of \(AN_0\) is proportional to the magnetic flux density (Figs. 4.46b, 4.49 and 4.51b) and is related to the increased mass transport to the nuclei due to the MHD effect acting in the electrolyte [85]. This is the reason for a slight shift in the nucleation mechanism towards the instantaneous mode with a magnetic field observed in the reduced coordinate plots (Fig. 4.44b).

Fig. 4.52. A schematic representation of the parallel to the electrode magnetic field influence on the nucleation and the early stages of 3D diffusion controlled growth.
The above interpretation is consistent with the results obtained at the highest applied potential for the Fe deposition, i.e. -1650 mV_{MSE} (Fig. 4.42c). At this potential nucleation proceeds via an almost instantaneous mode and no influence of a magnetic field has been noticed (Fig. 4.44c). All the nuclei are formed at the very beginning of the rising part of the $i(t)$ peak ($A_{t-o_0}>>1$) and then grow with a constant rate. A magnetic field increases the growth rate but it can not affect $A$ because all the nuclei are formed initially and after that no further nucleation occurs ($A=0$). Matsushima and co-workers [25] have found a similar influence of a magnetic field studying the initial stages of Cu deposition. On the contrary, Ispas et al. [27] have found that a parallel magnetic field applied during Ni deposition increases the nucleation rate. However, the proposed mechanism is valid only when the nucleation processes are relatively slow, i.e. the $i(t)$ maximum appears at long times (tens of seconds). When these processes are fast, i.e. the $i(t)$ maximum appears at short times (ms), this effect can not be observed since the convection induced by the Lorentz force needs some time to set in. Thus no influence of a magnetic field would be observed.

Above the maximum in the current density-time plot, the nuclei spherical diffusion zones overlap and a Cottrell behaviour is expected, which corresponds to a planar diffusion to the electrode surface. A deviation from this behaviour is expected when convection operates within the cell. This is clearly observed when the MHD effect is induced which is a convective one (Fig. 4.44). But also with a vertical electrode arrangement a natural convection is expected to play a significant role.

It has also been noticed that, with a sufficiently high magnetic flux density in this configuration, a second nucleation peak can be observed (II – Fig. 4.42a,b and 4.47a,b) indicating another nucleation step. The position of this peak is also affected by the parallel magnetic field, however, the deconvolution of the nucleation parameters is not straightforward.

It is necessary to add few words of criticism to the applied models. All of the applied models are based on the nucleation “law” developed by Fleischmann and Thirsk [51] \(N(t)=N_0[1-\exp(-At)]\), further modified by Markov and Stoycheva [166] to allow a potential dependence of $N_0$. This assumes a uniform distribution of the activity of all sites on the electrode surface, which implies a so-called “frozen” energetic state of the surface, i.e. the number of active sites is fixed after applying the potential step. This was criticized by Deutscher and Fletcher [52] stating, that the $N_0$ value is a physical property of the substrate and cannot be affected by the potential. They introduced the so-called “nucleation rate dispersion”, which basically describes a distribution of
the sites activity, i.e. different sites are activated at different potentials. Also Milchev [167,168] proposed an approach to model nucleation taking into consideration the dynamics of the sites activation. On the other hand, Wijenberg et al. [163] concluded that real surfaces are characterised by so many defects and imperfections that it can be assumed as homogeneous for nucleation.

Moreover, a good qualitative description of the experiment by a model does not necessarily mean that the absolute values are correct and those should be confronted with a direct measurement [38]. However in most cases the general trend of changes with the investigated parameters is more important than the absolute values. Also the usage of reduced coordinate plots, if possible, should be avoided. It was shown by a numerical simulation [58] that a deviation from a diffusion control (slow charge transfer) may have a similar qualitative influence as a slow nucleation and an instantaneous nucleation may appear as a progressive one.

In spite of these controversies, the influence of a magnetic field on nucleation and the early growth stages can be summarised as follows:

- Irrespective of the magnetic field strength and relative to the electrode surface orientation, two nucleation steps can be observed: (i) the first one is a successive layer-by-layer growth with a 2D mode (possibly epitaxial) and (ii) the second one is assigned as nucleation and 3D diffusion controlled growth;
- No influence of a magnetic field, regardless of its flux density and relative to the electrode configuration on the first 2D nucleation step has been noticed;
- The second 3D step is affected by a magnetic field applied in the parallel-to-electrode configuration, this results in a retardation of the steady state nucleation rate;
- A qualitative model has been proposed in order to explain the impact of a parallel to the electrode magnetic field on the nucleation behaviour of the 3D step based on the Lorentz force driven convection (MHD effect);
- Additional nucleation and growth steps at sufficiently high magnetic flux densities applied in the parallel-to-electrode configuration have been reported, which can also be affected by a magnetic field;
- No influence of a magnetic field on nucleation and the early growth stages in the perpendicular-to-electrode configuration has been observed.
4.3. INFLUENCE OF A MAGNETIC FIELD ON THE PROPERTIES OF DEPOSITED LAYERS

There are many examples that a superposition of a magnetic field during the deposition of metals and alloys could introduce significant changes to the deposit’s properties such as: chemical composition [16,169], morphology [15-20,23,83,91,93,94,170], phase composition [24] and texture [21,23,170], magnetic properties [14,16,93], etc. In the following sections the influence of a magnetic field on the deposited layer properties will be discussed in detail with respect to its strength and relative-to-electrode configuration.

4.3.1. Chemical Composition of Cobalt-Iron Alloys

In order to clarify whether a magnetic field has any influence on the chemical composition of CoFe alloy layers, what has been observed by others [16,169], the chemical composition was determined by ICP-OES after dissolution of the layer in concentrated HCl. In Fig.4.53a exemplary dependencies of the Fe content in CoFe layers deposited at -1480 mV\text{MSE} vs. magnetic flux density and magnetic field-to-electrode configurations are shown.

![Fig. 4.53. Fe content in the deposited CoFe layers vs. magnetic flux density and configuration for electrolytes CoFe(A) and CoFe(D) (table 3.1) (a) and Fe\textsuperscript{2+} concentration (b); -1480 mV\text{MSE}.](image)

From Fig. 4.53a some fluctuations of the chemical composition with magnetic field are observed. But in general it can be concluded that the magnetic field has no influence on the chemical
composition under the chosen experimental conditions, which was also confirmed by EDX and AES measurements. This behaviour is expected since both Co as well as Fe are in the mass transport control regime [20,79]. A magnetic field influence on the electrochemical reaction is related mainly to convective phenomena. Therefore both elements are affected simultaneously. A similar effect was observed by Ispas et al. [19] during the deposition of NiFe alloys in a uniform magnetic field, i.e. only a weak influence of a magnetic field on the alloy composition was reported. The above interpretation is a simplification of a real alloy deposition mechanism, which may be much more complicated due to complex interactions between the elements [103].

Table 4.5. Fe content in the deposited CoFe layers including standard deviations (SD).

<table>
<thead>
<tr>
<th>Electrolyte: CoFe(A)</th>
<th>CoFe(B)</th>
<th>CoFe(C)</th>
<th>CoFe(D)</th>
<th>CoFe(E)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$E_{\text{MSE}}$ mV</td>
<td>Fe at. %</td>
<td>SD</td>
<td>Fe at. %</td>
<td>SD</td>
</tr>
<tr>
<td>-1400</td>
<td>24.5</td>
<td>1.4</td>
<td>37.9</td>
<td>3.6</td>
</tr>
<tr>
<td>-1480</td>
<td>22.9</td>
<td>2.3</td>
<td>39.9</td>
<td>4.3</td>
</tr>
<tr>
<td>-1600</td>
<td>31.9</td>
<td>3.1</td>
<td>62.2</td>
<td>16.5</td>
</tr>
</tbody>
</table>

In Fig.4.53b the influence of the Fe$^{2+}$ concentration on the chemical composition of deposits is shown. The Fe$^{2+}$ concentration was chosen to represent the electrolyte chemistry because the Co$^{2+}$ concentration was held constant (table 3.1). It is apparent from Fig.4.53b that the Fe content in the deposited layer is, as expected, proportional to its concentration in the electrolyte, irrespective of the buffer addition. Additionally it has been observed that the boric acid addition to the electrolyte does not significantly change the deposit composition. The chemical composition of the deposits together with used deposition parameters is listed in table 4.5. It is apparent that the layers deposited at more negative potentials from unbuffered electrolytes (table 3.1) have a higher Fe content. This effect is more pronounced for the CoFe(B) electrolyte where the Fe$^{2+}$ concentration is higher. This is not a normal situation because the alloy deposition is mass transport controlled and a composition shift with the applied potential is not expected [103]. The reason is an anomalous behaviour of the alloy deposition observed at high potentials, as shown in chapter 4.1.1.3 (Fig. 4.18). There is a very high standard deviation in the Fe content at -1600 mV$_{\text{MSE}}$ obtained for the CoFe(B) electrolyte, the reason is a very high interface pH value (see Chapter 4.1.2) which leads to hydroxide precipitation and poor reproducibility. It was also observed that the anomalous behaviour depends on the electrolyte composition, i.e. a more anomalous behaviour at higher Fe$^{2+}$ concentrations is observed.
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Depth profiles of ~100 nm thick layers were measured with AES in order to clarify changes of oxygen incorporation into the layer and changes of the chemical composition with layer thickness. In Fig. 4.54 exemplary depth profiles of the layers deposited at -1480 mV_{MSE} from electrolyte CoFe(A) without and with superposition of a magnetic field in both relative to the electrode configurations are compared. From Fig. 4.54 it is clear that the chemical composition of the layer is uniform over its thickness, irrespective of the deposition parameters, up to the limit of the AES technique (few nm). The same observation is also valid for deposits obtained with other sets of deposition conditions. The interior of the CoFe layer contains only a very low amount of O and C except for the deposit obtained in the perpendicular to the electrode magnetic field configuration (inset of Fig. 4.54c), where the O and C signals have been found for the whole depth profile have been found. The reason of the O and C contamination is seen in the specific columnar morphology (for details see Chapter 4.3.2). Due to the columnar layer growth, where the columns are separated from each other, the metal in contact with air oxidizes, including the columns side walls, and the resulting oxygen signal is significant.

Fig. 4.54. The AES depth profiles of the CoFe layers deposited without (a), in the parallel (b) and in the perpendicular to the electrode magnetic field (c) (B=1 T); CoFe(A), -1480 mV_{MSE}.
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in the whole film depth. The carbon contamination is most probably of the same origin, i.e. atmospheric contamination. The AES investigation can be summarized as follows: the deposited layers have a uniform chemical composition in depth and no oxygen incorporation into the layers has been observed (according to the device resolution).

4.3.2. Morphology

4.3.2.1. Cobalt and Iron

SEM, AFM and TEM investigations were performed for deposited Co and Fe layers of ~100 nm thicknesses. Figure 4.55 shows SEM and AFM images of the Co layers with corresponding section analysis obtained at -1480 mV\textsubscript{MSE} without and with a magnetic field ($B=1$ T) superimposed in both relative-to-electrode configurations.

![Fig. 4.55. SEM micrographs and corresponding AFM images with line section analysis of layers (~100 nm) deposited without superposition of a magnetic field (a,d,g), in parallel- (b,e,h) and in perpendicular- (c,f,i) to-electrode configuration ($B=1$ T); Co, -1480 mV\textsubscript{MSE}, $R_{\text{rms}}$ determined from a 2 $\mu$m $\times$ 2 $\mu$m surface area.](image-url)
The layer morphology, regardless of the magnetic field characterizes a polyhedral grain shape (Fig. 4.55a-c). It is apparent that a magnetic field applied during the deposition influences the morphology of the deposit. The layer deposited without a magnetic field develops a diverse morphology and the porosity can easily be seen (Fig. 4.55a). In contrast, the layer deposited in a parallel magnetic field appears compact and the grain size is reduced when compared to the layer obtained without a field (Fig. 4.55b,e,h). On the contrary, a perpendicular-to-electrode magnetic field increases the grain size (Fig. 4.55c,f,i). The layer deposited in this field configuration appears compact and smooth.

Because of the weak influence of a magnetic field, irrespective of its configuration, on the layer morphology a scaling analysis was performed. This analysis was shown to be a successful and sensitive method to describe the morphological changes with the deposition parameters [94,97,171]. The principles of this method are based on the roughening of self-affine surfaces which obey the following dependence (Eq. 4.17) [96]:

\[ w(l,t) = l^\alpha f \left( \frac{t}{l^{\beta-\alpha}} \right) \]  

(4.17)

where \( w(l,t) \) is the surface width (root mean square height – \( R_{\text{ms}} \)), \( \alpha \) is the roughness (Hurst) exponent, \( \beta \) is the growth exponent, \( l \) is the spatial size and \( t \) is the deposition time.

Two regions of \( w \) can be distinguished. For small values of \( l \) the \( w \) is independent of \( t \) and scales as \( l^\alpha \). On the other hand, for large values of \( l \) the \( w \) is independent of \( l \) and scales as \( t^\beta \). For a given value of \( t \) a change between these two limiting behaviours occurs at a spatial length equal to a critical length \( l_c \). Eq. (4.17) can then be rewritten as follows:

\[ w(l,t) = \begin{cases} 
  l^\alpha & \text{for } l < l_c \\
  t^\beta & \text{for } l > l_c 
\end{cases} \]  

(4.18)

This is the normal case, but it was also observed [97] that even for small values of \( l \) the \( w \) depends on \( t \), i.e. an anomalous scaling is observed. The anomalous case is beyond the scope of this work, as no time series were investigated. In Fig. 4.56a the \( R_{\text{ms}} \) vs. \( l \) dependencies obtained for Co deposition at -1480 mV_{MSE} without and with a magnetic field (\( B=1 \) T) superposed in both magnetic field-to-electrode configurations are shown. Based on the plots shown in Fig. 4.56a, and on a linear fitting to distinguished regions, a change in the \( \alpha \) exponent was revealed (table 4.6). It is apparent that a magnetic field applied in the parallel-to-electrode configuration reduces
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the $\alpha$ exponent. In contrast, the perpendicular magnetic field increases the $\alpha$ exponent when compared to the one obtained without field (table 4.6). The influence of a parallel magnetic field is not as strong as in the perpendicular configuration, although the roughness of the layer deposited in a parallel field is significantly higher (Fig 4.55g,h,i and Fig.4.56a).

The reduced $\alpha$ exponent found in the parallel field is due to the Lorentz force driven convection which suggests less kinetic roughening of the surface. This observation is in agreement with results obtained by Osafo-Acquaah et al. [171] for Cu deposition under controlled fluid flow conditions. On the other hand, when the deposition is carried out in the perpendicular to the electrode magnetic field, the roughness exponent is strongly increased (by a factor of 1.4 – table 4.6). This in turn implies that the kinetic roughening of the surface is increased in this field configuration. It might be expected, regarding $\alpha$ exponent values obtained without and with a magnetic field, that for longer deposition times (thicker layers) the roughness in the parallel field would be reduced and in the perpendicular field increased, when compared to the one obtained for a layer deposited without a field (of the same thickness). This

![Fig. 4.56. Rms vs. scanned region size (spatial length) obtained with AFM on Co (a) and Fe (b) layers (~100 nm thick) deposited at $E_2$ (table 4.1) without and with a magnetic field ($B=1$ T) of different relative to the electrode orientation.](image)

<table>
<thead>
<tr>
<th>$B$-field</th>
<th>Co $\alpha$</th>
<th>Co $l_c$</th>
<th>Fe $\alpha$</th>
<th>Fe $l_c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 T</td>
<td>0.29</td>
<td>1.02</td>
<td>0.25</td>
<td>1.04</td>
</tr>
<tr>
<td>1 T (//)</td>
<td>0.24</td>
<td>0.92</td>
<td>0.19</td>
<td>1.36</td>
</tr>
<tr>
<td>1 T (⊥)</td>
<td>0.40</td>
<td>0.90</td>
<td>0.34</td>
<td>1.40</td>
</tr>
</tbody>
</table>

Table 4.6. Values of the roughness exponent $\alpha$ and the critical length $l_c$ obtained without and with a magnetic field for Co and Fe layers deposited at $E_2$ (~100 nm thick).
effect was shown by Matsushima et al. [94] for Fe and Tabakovic et al. [18] for NiCu deposition in the parallel to the electrode magnetic field. Considering the values of the critical spatial length obtained without and with a magnetic field, no significant change is found (table 4.6).

In Fig. 4.57 SEM and AFM images of the Fe layers with corresponding section analysis obtained at -1550 mV_{MSE} without and with a magnetic field (B=1 T) superposed in both relative-to-electrode configurations are shown.

It is apparent that the deposits obtained without and in the parallel to the electrode magnetic field exhibit a “leaf”-like morphology. A magnetic field applied in the parallel configuration reduces the grain size and the roughness of the deposit (Fig. 4.57b,e,h) compared to the without a field case (Fig. 4.57a,d,g). The deposits obtained in the parallel magnetic field are more compact with a smaller porosity. A magnetic field superposed in the perpendicular-to-electrode configuration
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dramatically affects the layer morphology, a columnar morphology is revealed. The layer deposited in the perpendicular to electrode magnetic field characterises, contrary to non-magnetic field and the parallel magnetic field cases, a polyhedral grain shape, the most diverse morphology (Fig. 4.57c,f) and the highest roughness (Fig. 4.57i). A scaling analysis was performed in the same way as for Co, in order to quantify the morphological changes induced by a magnetic field. The results are listed in table 4.6. The influence of a magnetic field is qualitatively the same as already observed for Co, i.e. the roughness exponent is reduced in the parallel and increased in the perpendicular to the electrode magnetic field. However, contrary to the Co case the critical length is increased in a magnetic field, irrespective of the relative to the electrode configuration. A reduced roughness exponent in the parallel to the electrode magnetic field was also reported by Matsushima et al. [94] for Fe deposition. They concluded that due to the MHD convection the growth mode changes from surface diffusion to a step growth. Therefore, a smoothing effect is observed.

In order to get more insight into the morphological changes induced by magnetic field cross sections of the layers, prepared by FIB, were investigated. In Fig. 4.58 SEM images of the cross sections of Fe layers deposited at -1550 mV_{MSE} without and with a magnetic field superposed in both relative to the electrode configurations are shown. It is apparent that the thicknesses of the layers are equal (~100 nm). The deposits obtained in the perpendicular magnetic field are characterised by a columnar morphology (Fig. 4.58c), i.e. the grains tend to grow as separate columns in the magnetic field direction (perpendicular to the electrode surface). Moreover, this characteristic growth mode is observed from the beginning of the deposition, i.e. starting from the interface (Fig. 4.59a).
The columnar growth mode of the layers deposited in the perpendicular to the electrode magnetic field was confirmed by TEM investigations (Fig. 4.59b). Additionally, a polycrystalline structure of columns has been revealed. This morphology obtained in a perpendicular field is diametrically opposed to those obtained without (Fig. 4.58a) and in the parallel magnetic field (Fig. 4.58b). It is also visible that the deposits obtained in the parallel magnetic field are more compact and smoother than those obtained without the superposition of a magnetic field (Fig. 4.58a,b). Also the higher porosity of the layer deposited without a field is noticeable (Fig. 4.57a and 4.58a). These findings correlate well with the roughness exponents obtained by the scaling analysis (table 4.6).

4.3.2.2. Cobalt-Iron Alloys

In Fig. 4.60 exemplary SEM and AFM images of the CoFe layers (~100 nm) with corresponding section analysis obtained from the CoFe(A) electrolyte at -1480 mV_{MSE} without and with a magnetic field (B=1 T) superposed in both relative-to-electrode configurations are shown. It is apparent that a magnetic field applied during the deposition, as already reported for Co and Fe, influences the morphology of the deposited CoFe layers. The layer deposited without a magnetic field has a diverse morphology with large polyhedral grains (Fig. 4.60a,d). A parallel-to-electrode magnetic field reduces the grain size and the layer roughness significantly, the resulting layer is very homogeneous (Fig. 4.60b,e,h). This finding is similar to results obtained for the Fe deposition and is clearly induced by an MHD stirring of the electrolyte. On the contrary, when the magnetic field is applied in the perpendicular-to-electrode configuration the deposited layer is very diverse with a tendency of columnar grain growth along the magnetic field direction (Fig. 4.60c,f,i), as already reported for Fe (Fig. 4.57c,f,i). This in turn results in the highest roughness observed for a layer deposited in this field configuration (Fig. 4.60i).
RESULTS

In Fig. 4.60 SEM micrographs and corresponding AFM images with line section analysis of layers (~100 nm) deposited without superposition of magnetic field (a,d,g), in parallel (b,e,h) and in perpendicular- (c,f,i) to-electrode configuration ($B=1$ T); CoFe(A) electrolyte, -1480 mV$_{MSE}$. $Rms$ determined from a 2 $\mu$m $\times$ 2 $\mu$m surface area.

In Fig. 4.61 TEM micrographs of the layer cross sections deposited from the CoFe(A) electrolyte at -1480 mV$_{MSE}$ without and with a magnetic field applied in both relative-to-electrode configurations are shown. The roughness of the layer deposited in the perpendicular field (Fig. 4.61c) is significantly higher than for the other cases. The grain size is increased under this condition as well. Moreover, the diversity of the layer obtained in the perpendicular field is the highest one and the polycrystalline columns are separated from each other, as already observed for Fe. A columnar growth mode of the grains was also confirmed by SEM investigations of the cross sections (FIB cuts – not shown).

In Fig. 4.62 exemplary SEM and AFM images of the CoFe layers (~100 nm) with corresponding section analysis deposited from the CoFe(E) electrolyte (containing boric acid) at -1480 mV$_{MSE}$ without and with a magnetic field ($B=1$ T) superposed in both relative-to-electrode configurations are shown.
RESULTS

It was found that, irrespective of the electrolyte composition, an addition of boric acid reduces the grain size and the roughness significantly. This also affects the grain shape. The influence of a magnetic field on the deposit morphology, regardless of the relative to the electrode orientation, is marginal after the addition of boric acid. These changes are not as significant as those observed with an unbuffered electrolyte (Fig. 4.60).

Characteristic features are large holes left after the evolution of hydrogen bubbles, which have been observed for the layers deposited without a field (Fig. 4.62a,d). Those were suppressed in a magnetic field (Fig. 4.62b,c,e,f), irrespective of its configuration, suggesting that a magnetic field supports the desorption of hydrogen from the electrode surface (for details see chapter 4.1.2). This effect has been divided into macroscopic and microscopic MHD flow induced by a Lorentz force, i.e. a predominant macroscopic flow in the parallel- and micro- MHD in the perpendicular-to-electrode configuration. Diao et al. [99] have reported that an increased HER was observed because of an easier coalescence of hydrogen bubbles due to MHD stirring of the electrolyte and in turn a decrease in the overpotential of the hydrogen formation.

**Table 4.7.** *Rms* roughness of the deposited CoFe layers measured over a 2 µm × 2 µm area (~100 nm thick).

<table>
<thead>
<tr>
<th>B-field</th>
<th>CoFe(A) -1400 mV_{MSE}</th>
<th>CoFe(B) -1400 mV_{MSE}</th>
<th>CoFe(C)</th>
<th>CoFe(D) -1400 mV_{MSE}</th>
<th>CoFe(E)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Rms</td>
<td>SD</td>
<td>Rms</td>
<td>SD</td>
<td>Rms</td>
</tr>
<tr>
<td>0 T</td>
<td>11.6</td>
<td>0.9</td>
<td>18.7</td>
<td>1.0</td>
<td>8.2</td>
</tr>
<tr>
<td>1 T (</td>
<td></td>
<td>)</td>
<td>11.4</td>
<td>0.3</td>
<td>9.1</td>
</tr>
<tr>
<td>1 T (⊥)</td>
<td>10.6</td>
<td>1.2</td>
<td>19.9</td>
<td>1.7</td>
<td>8.0</td>
</tr>
</tbody>
</table>
In Table 4.7 the roughness of the CoFe layers deposited from different electrolytes is listed. There is no $R_{\text{rms}}$ value given for the layer deposited from the CoFe(B) electrolyte at -1480 mV$_{\text{MSE}}$. This is because the surface of the deposit obtained at this potential appeared black due to a very high interfacial $p\text{H}$ value (see chapter 4.1.2) resulting in a precipitation of hydroxides, which disqualifies the layer from any further morphological or magnetic investigations. As it is visible from Table 4.7 a magnetic field impact on the morphology depends also strongly on the applied potential, i.e. the higher the potential the stronger the observed changes.

Based on the $R_{\text{rms}}$ vs. $l$ dependencies obtained for CoFe layers (not shown) deposited at -1480 mV$_{\text{MSE}}$ the scaling parameters were calculated and are listed in Table 4.8. It is apparent that a magnetic field applied in the parallel-to-electrode configuration reduces the $\alpha$ exponent, as
already observed for Co and Fe. In contrast, the perpendicular magnetic field increases $\alpha$ when compared to the non-magnetic field deposits. Only the layer deposited from the CoFe(A) electrolyte, where $\alpha$ obtained for the layer deposited without a field displays a different dependency. No clear dependence of $l_c$ with a magnetic field has been found. Additionally, the $\alpha$ exponents obtained from the buffered electrolytes are reduced as compared with those obtained with unbuffered electrolytes. This suggests that an addition of boric acid has the expected smoothing impact on the deposit. This also correlates well with the $R_{rms}$ values obtained from corresponding layers (table 4.7). The influence of a magnetic field on the scaling parameters will be discussed in the following chapter together with pure metals deposits.

### 4.3.2.3. Summary

As shown in previous sections, a magnetic field superposed during the deposition of Fe group metals and alloys affects the resulting layer morphology. This influence can be discussed with respect to the relative to electrode orientation of a magnetic field.

In general a parallel-to-electrode magnetic field applied during the deposition results in a very homogeneous and compact layer. The deposits obtained in this field configuration exhibit a finer grain structure and, except for the buffered electrolytes, where the influence of a magnetic field is not so significant, a reduced $R_{rms}$ roughness compared to that obtained without a field is found. A scaling analysis revealed that in the parallel field the roughness exponent is reduced regardless of the chemical composition of the electrolyte. This can be explained by the MHD effect, which reduces the thickness of the diffusion layer and in turn improves a mass transfer towards the electrode surface. These results are in agreement with published studies, which focus on the magnetic field effects on electrodeposition [17,64,69,77,81-83]. A similar effect of a magnetic field has been observed by Matsushima et al. [94] for Fe deposition. Moreover, the

<table>
<thead>
<tr>
<th>$B$-field</th>
<th>CoFe(A)</th>
<th>CoFe(C)</th>
<th>CoFe(E)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 T</td>
<td>$\alpha$</td>
<td>$l_c$</td>
<td></td>
</tr>
<tr>
<td>0.50</td>
<td>0.59</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 T (/)</td>
<td>0.25</td>
<td>1.33</td>
<td></td>
</tr>
<tr>
<td>1 T ()</td>
<td>0.32</td>
<td>0.98</td>
<td></td>
</tr>
<tr>
<td>0.34</td>
<td>0.43</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.15</td>
<td>2.15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.10</td>
<td>1.13</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.18</td>
<td>0.40</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
hydrodynamic origin of the smoothing effect is supported by results obtained by Osafo-Acquaah et al. [171]. They have studied the influence of a well defined hydrodynamic condition on the Cu deposition by changing the electrolyte flow in the cell. A reduction of the roughness and the growth exponent as well as the saturated $R_{\text{rms}}$ roughness was reported for an increased flow. It was proposed that the deposition conducted without a forced convection results in a privileged growth at the surface peaks and rough deposits. With an increase in the flow rate the concentration gradient at the electrode surface is reduced, a surface peak growth mode is suppressed and the resulting deposits appear smoother [171]. However, a forced convection is of much higher magnitude than the one induced by a Lorentz force. Nevertheless, the observed changes in a parallel magnetic field have to be of the same nature as the ones reported under a forced convection.

In contrast, a superposition of a perpendicular to the electrode magnetic field results, in most cases, in less homogeneous, more porous, and rougher deposits. A scaling analysis performed from the layers deposited in this field configuration revealed that the roughness exponent is increased by the magnetic field. The most remarkable observation in this field configuration has been made for the layers deposited from Fe and CoFe(A) electrolytes (table 3.1) at $E_2$ (table 4.1), i.e. a dramatic change in the deposit morphology has been observed (Fig. 4.57c,f, 4.59, 4.60c,f and 4.61c). The resulting layer consists of polycrystalline columns, which are separated from each other and grow perpendicular to the electrode surface in the magnetic field direction. This effect is lost after addition of boric acid, which suggests that the HER is playing a significant role in the formation of this characteristic morphology. As shown in chapter 4.1.2 the HER rate is greatly improved in the perpendicular to the electrode magnetic field, while the metal reduction rate is nearly unaffected. This means that more active sites at the electrode surface are occupied by hydrogen and a smaller active surface area is available for the metal reduction and in turn the deposition rate (at a reduced active surface area) has to be increased. It is known that at relatively high deposition rates (high current densities) the deposition could proceed by a columnar growth mode [172]. Such a columnar growth was observed for example during the electrodeposition of Au [173]. That is one of the possible explanations, but many other effects may also have a very significant contribution. It was shown that a magnetic field applied during the deposition could texture the deposit [21-23], but this effect was not found in the present study (for details see chapter 4.3.3). The adsorption of hydrogen can also affect the resulting morphology. Li and co-workers have shown that hydrogen has different adsorption abilities at different Fe crystal planes.
This then leads to a privileged grow direction. It was proposed by Krause et al. [67] that the adsorption of hydrogen can affect the growth mode of electrodeposited Co and a shift in the structure from \textit{fcc} to \textit{hcp} has been reported. The columnar growth mode in a perpendicular magnetic field can induce stray fields above the columns. The stray fields then generate a field gradient force, which increases the deposition rate at the regions of a higher magnetic flux density by attracting the paramagnetic ions [28] and the columnar growth mode should be amplified. All of these effects can act simultaneously overlapping each other. Further investigations are necessary to clarify this very interesting phenomenon.
4.3.3. Structure and Texture

In Fig. 4.63a,b sections of the $\theta/2\theta$ plots obtained for Co layers deposited without and with a magnetic field ($B=1$ T) are shown. The $\theta/2\theta$ scans, irrespective of the magnetic field (a) and the applied potential (b) exhibit only one main reflex at the angle of about $52^\circ$, which lies between two possible Co planes, i.e. the (111) in the fcc lattice and the (002) in the hcp lattice. A relative assignment of the peak to the structure is not possible due to a very small difference in the $2\theta$ angles between them ($0.3^\circ$). Nevertheless, no significant influence neither of the magnetic field nor of the applied potential on the peak position and its broadening has been observed (Fig. 4.63a,b).

![Fig. 4.63. Sections of $\theta/2\theta$ scans of Co (a) and Fe (c) layers deposited without and with a superposed magnetic field in both relative to the electrode configurations ($B=1$ T) at $E_2$ potential, and sections of $\theta/2\theta$ scans of Co (b) and Fe (d) layers deposited at potentials $E_1$ and $E_2$ (table 4.1 – $B=0$ T).](image-url)
The estimated crystallite size according to the Debye-Scherrer formula (Eq. 3.6) [132] is about 17 nm. Slight differences in the peak maximum positions are most likely caused by a change in the internal stress state of the layer obtained without and with field (Fig. 4.63a). In order to clarify, if the deposited Co layers are cubic or hexagonal, the (200)$_{fcc}$ pole figures ($2\theta=60.6^\circ$) were measured and the first quarter of the pole figure is shown in Fig. 4.64a. In this figure the strongest maximum in the $\psi$ scan is observed at an angle of 54.7$^\circ$ giving a clear hint to the (111)$_{fcc}$ reflection. Moreover, no maxima in the $\Phi$ scan have been noticed clearly indicating the fibre texture, i.e. the (111)$_{fcc}$ grains randomly rotate around the <111> axis in the film plane. Another maximum in the $\psi$ scan observed at an angle of about 15.5$^\circ$ can probably be attributed to the growth of twins ($\psi=15.6^\circ$ (511)$_{fcc}$ peak) which have been revealed by TEM imaging (A in Fig. 4.65a). Additionally, in the pole figure centre a very weak increase in the intensity is noticeable which indicates that there is also a small amount of the (200)$_{fcc}$ component present. No maxima neither in the $\psi$ nor in the $\Phi$ scans of the (101)$_{hcp}$ pole have been noticed (not shown). This proves that the peaks observed in the $\theta/2\theta$ plots (Fig. 4.63a,b) are attributed to the (111)$_{fcc}$ plane.

![Fig. 4.64.](image)

Fig. 4.64. (200)$_{fcc}$ poles for a Co layer deposited at $E_2$ (a) and (110)$_{hcp}$ poles obtained for CoFe layers deposited from the CoFe(B) electrolyte at $E_1$ (b) and the CoFe(C) electrolyte at $E_2$ (c); $B=0$ T.

In Fig. 4.65b an exemplary SAD analysis is shown. The small points forming a ring result from the fine crystallites of cobalt whereas the large ones derive from the large Au substrate grains. The obtained SAD pattern has been compared with the theoretical one. It fits best to the $fcc$ Co structure (Fig. 4.65c). The large substrate reciprocal points lie on the rings what also supports the
fcc Co structure since the Au substrate has the fcc structure as well. Also the nanodiffraction on selected grains (inset in Fig. 4.65a) has shown that the Co deposits characterise the fcc structure irrespective of the magnetic field and the applied potential. However the hexagonal structure is not completely excluded. Krause et al. [67] studied the influence of a magnetic field on the Co electrocrystallization and found that there is a small amount of the hcp structure present in the deposit but only at the interface.

Fig. 4.65. TEM image of a Co layer with indicated twinned grain structure (A) (a) and the corresponding SAD pattern (b) compared to the calculated SAD pattern of the Co fcc lattice (c). The inset of (a) represents the nanodiffraction pattern of the grain indicated by an arrow showing the (110)\text{fcc} plane; \(B=0\text{T, } -1480 \text{ mV}_{\text{MSE}}\).

In Fig. 4.63c,d sections of the \(\theta/2\theta\) plots obtained for Fe layers deposited without and with a magnetic field (\(B=1\text{T}\)) are shown. The \(\theta/2\theta\) scans, irrespective of the magnetic field (c) and the applied potential (d), as reported for Co layers, exhibit only one main reflex at an angle of about 52.5°, which corresponds to the (110) plane in the bcc lattice. As expected no significant changes of the peak position with neither the magnetic field nor the applied potential have been observed. Only a slight shift, most likely stress related, can be noticed. The estimated crystalline size is about 25 nm. The XRD pole figures (not shown) reveal a fibre texture of the deposited Fe layers irrespective of the deposition parameters, i.e. Fe crystallites with the (110)\text{bcc} plane parallel to the film randomly rotate around the \(<110>\) axis. The much lower intensities in the \(\theta/2\theta\) scan obtained for the layer deposited in the perpendicular magnetic field (Fig. 4.63c) are most probably caused by a columnar structure of this deposit (Fig. 4.59) and, therefore, a reduced volume of the material is considered in the analysis.

In Fig. 4.66 exemplary sections of the \(\theta/2\theta\) plots obtained for CoFe layers deposited without and with a magnetic field (\(B=1 \text{T}\)) at -1400 mV\text{MSE} from the CoFe(B) electrolyte (a) and at
RESULTS

-1480 mV_{MSE} from the CoFe(D) electrolyte (b) are shown. The $\theta/2\theta$ scans, irrespective of the magnetic field, the applied potential, and the electrolyte composition exhibit only one main reflex at the angle of about 53°. This corresponds to the (110) plane in the bcc lattice. Only a very slight shift of the peak position with magnetic field is observed. The estimated crystallite size from Debye-Scherrer’s formula (Eq. 3.6), irrespective of the magnetic field, the applied potential, and the electrolyte composition, is about 20 nm.

![Fig. 4.66. Sections of $\theta/2\theta$ scans of CoFe layers deposited without and with a superposed magnetic field at -1400 mV_{MSE} from the CoFe(B) electrolyte (a) and at -1480 mV_{MSE} from the CoFe(D) electrolyte (b) with the corresponding (110)$_{bcc}$ pole figure sections (c,d), respectively.](image)

A reliable assignment of the peak to the phase is not possible as at least three different Co$_x$Fe$_{100-x}$ ($x=30, 50, 70$) bcc phases which have nearly the same (110) reflex position contribute and, as a result, line broadening occurs. Nevertheless, considering the differences in the (110)$_{bcc}$
interplanar distances \( (d_{110}) \) acquired from the XRD patterns of the CoFe layers with different chemical composition obtained from buffered electrolytes (table 3.1), it becomes apparent that, regardless of the magnetic field, \( d_{110} \) is increased with increasing Fe content in the deposit (Fig. 4.67a). A similar dependence is obtained by plotting \( d_{110} \) vs. Fe content in the CoFe alloy taken from the reference patterns (Fig. 4.67b). This strongly implies that, with increasing Fe content in the deposit, irrespective of the magnetic field, the deposited CoFe phase is shifted towards the one of the higher Fe content. However, the experimental \( d_{110} \) values are lower than the ones taken from the reference patterns, which suggests that the structure is compressed in the direction normal to the layer surface what in turn indicates a tensile stress in the layer.

![Fig. 4.67. \( d_{110} \) vs. Fe content in the CoFe layer deposited without and with magnetic field from buffered electrolytes (table 3.1) at -1480 mV_{MSE} (a) and taken from the reference patterns (b).](image)

In table 4.9 the \( d_{110} \) values obtained under the experimental conditions used are listed. A magnetic field applied during the deposition, regardless of its relative to the electrode configuration, increases the \( d_{110} \) of the layers deposited from buffered electrolytes. This indicates stress relief processes most probably due to an improved desorption of hydrogen (for details see chapter 4.1.2), which is known to have a very significant impact on the layer internal stress state development [175]. On the contrary almost no influence of the magnetic field on \( d_{110} \) for the layers deposited from unbuffered electrolytes is found. Only a retardation of the \( d_{110} \) value for the layer deposited from the CoFe(A) electrolyte at \( B=1 \ T \) in the perpendicular to the electrode magnetic field has been noticed, indicating a higher internal stress. This is supported by TEM
investigations which have revealed stacking-faults and grain boundaries in this layer (Fig. 4.68) [93].

Table 4.9. $d_{110}$ values obtained for CoFe layers deposited without and with a magnetic field at -1480 mV_MSE (~100 nm thick) from electrolytes of different chemical composition (table 3.1).

<table>
<thead>
<tr>
<th>$B$ -field</th>
<th>CoFe(A)</th>
<th>CoFe(B)</th>
<th>CoFe(C)</th>
<th>CoFe(D)</th>
<th>CoFe(E)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0T</td>
<td>2.005</td>
<td>2.007</td>
<td>2.000</td>
<td>2.005</td>
<td>2.010</td>
</tr>
<tr>
<td>1T(∥)</td>
<td>2.005</td>
<td>2.007</td>
<td>2.005</td>
<td>2.011</td>
<td>2.014</td>
</tr>
<tr>
<td>1T(⊥)</td>
<td>2.003</td>
<td>2.007</td>
<td>2.004</td>
<td>2.009</td>
<td>2.013</td>
</tr>
</tbody>
</table>

Comparing the $d_{110}$ values obtained for layers deposited from buffered and unbuffered electrolytes (table 4.9) it is apparent that the latter is characterised by smaller interplanar distances, although the Fe content in the deposit is higher (table 4.5) and therefore larger $d_{110}$ values are expected (Fig. 4.67b). This can be explained by higher internal stress in the layers deposited from buffered electrolytes caused by a simultaneous HER, the rate of which is far greater in the buffered electrolytes (about six times higher – Fig. 4.23). The magnetic field influence on the HER in the buffered electrolytes has also been found to be more pronounced than in the unbuffered ones. This is most probably the reason of a higher magnetic field influence on the $d_{110}$ parameter obtained for the layers deposited from buffered electrolytes, whereas this influence is hardly seen in the case of unbuffered electrolytes.

In order to determine the magnetic field influence on the texture of the deposits, pole figures were measured. The exemplary pole figure measured at $2\theta=53^\circ$ for the layers deposited without superposed magnetic field are shown in Fig. 4.64b,c. $\psi$-scans exhibit only one peak at ~60$^\circ$ giving a hint that there is only a (110) plane parallel to the film surface and no twinning processes are observed. $\Phi$-scans at $2\theta=53^\circ$ and $\psi=60^\circ$ show no local minima, and maxima irrespective of the magnetic field strength and orientation. This clearly indicates the $(110)_{bcc}$ fibre texture, irrespective of the electrolyte chemical composition (Fig. 4.64b,c). The superposition of a magnetic field regardless of its
relative-to-electrode configuration does not change the deposit’s texture significantly. This is clearly demonstrated in Fig. 4.66c,d where the exemplary pole figure sections ($\Phi = 0^\circ$) obtained without and with a magnetic field ($B=1$ T) are shown and no changes induced by a magnetic field superposition are noticed. A slight change of the peak maximum position with magnetic field is most probably caused by the different internal stress states of the layers. This is valid for thin layers, however the texture development may require thicker layers to introduce significant changes. This was shown by Li et al. [21] for the deposition of Fe under a magnetic field. They have shown that at the substrate/deposit interface the Fe deposit is characterised by a fibre texture, regardless of the magnetic field, while with the thickness a preferred texturing in the direction of a magnetic field was reported. Similar results have been reported by Matsushima at al. [22].
4.3.4. Magnetic properties

Different deposition parameters affect the magnetic properties of the layers [2,14,114,150,175]. This influence is mainly caused by the changes, which are induced to the layer morphology [14,93,150,176], structure, phase composition, and texture [2,114,150]. Moreover, the internal stress state of the films [2,14,93,114,150] plays a significant role due to magneto-elastic interactions. As shown in previous sections, the superposition of magnetic fields influences the morphology and the internal stress state of the layer, and thus it is expected that the magnetic properties are affected as well. In order to clarify this, magnetisation loops have been measured at room temperature by means of vibrating sample magnetometry (VSM) and magneto-optical Kerr effect (MOKE) magnetometry. The domain structure has been investigated by Kerr microscopy.

![Normalized in-plane VSM hysteresis loops](image)

Fig. 4.69. Normalized in-plane VSM hysteresis loops obtained for Fe (a) and CoFe (b) (CoFe(A) electrolyte) layers deposited at $E_2$ (table 4.1) without and with a magnetic field ($B=1$ T) superposed in both relative-to-electrode configurations, $\sim$100 nm thick layers.

Figure 4.69 shows exemplary hysteresis loops, measured by VSM with the magnetic field along the plane of the film, obtained for layers deposited from the Fe (a) and the CoFe(A) electrolyte (b) (table 3.1) at $E_2$ (table 4.1) without and with superposed magnetic field ($B=1$ T) in both relative-to-electrode configurations. From Fig. 4.69 it is apparent that a superposition of
magnetic fields significantly affects the magnetic properties of the deposit. Most pronounced effect on the layer coercivity ($H_c$) has been observed, but also the squareness ($J_r/J_s$ – where $J_r$ and $J_s$ stand for remanence and saturation polarization, respectively) is affected.

The layers obtained in the parallel field exhibit the lowest $H_c$. On the contrary the layers deposited in the perpendicular field configuration exhibit the highest $H_c$ and also display an increase in saturation field. These findings were also confirmed by the MOKE measurements (Fig. 4.70a). The magnetic properties of the deposits obtained for the used conditions are summarised in table 4.10 for the pure metals and in table 4.11 for the alloys.

From table 4.11 it is apparent that the $H_c$ of the layers deposited at -1400 mV$_{MSE}$, irrespective of the electrolyte composition, are almost unaffected by a magnetic field applied regardless its relative to the electrode configuration.

In contrast, the $H_c$ of the layers deposited at $E_2$ from Fe and CoFe(A) electrolytes are affected the most by the superposed magnetic field. A slight effect has also been observed for the layers deposited from the CoFe(C) electrolyte. This observation correlates well with the results of the roughness measurements (Fig. 4.57g,h,i and table 4.7 for Fe and alloys, respectively). The roughness of the layers deposited at $E_1$ is almost unaffected by a magnetic field applied during the deposition, but it is strongly influenced when deposition is carried out at $E_2$ (table 4.7).

<table>
<thead>
<tr>
<th>$B$ -field</th>
<th>Co</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>0T</td>
<td>5.4</td>
<td>14.3</td>
</tr>
<tr>
<td>1T(//)</td>
<td>6.2</td>
<td>6.2</td>
</tr>
<tr>
<td>1T(_)</td>
<td>4.2</td>
<td>19.6</td>
</tr>
</tbody>
</table>

Table 4.10. $H_c$ and squareness of the Co and Fe films deposited without and with a magnetic field at $E_2$ (table 4.1), ~100 nm thick.

<table>
<thead>
<tr>
<th>$B$ -field</th>
<th>CoFe(A)</th>
<th>CoFe(B)</th>
<th>CoFe(C)</th>
<th>CoFe(D)</th>
<th>CoFe(E)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0T</td>
<td>$H_c$</td>
<td>$J_r/J_s$</td>
<td>$H_c$</td>
<td>$J_r/J_s$</td>
<td>$H_c$</td>
</tr>
<tr>
<td></td>
<td>mT</td>
<td></td>
<td>mT</td>
<td></td>
<td>mT</td>
</tr>
<tr>
<td>0T</td>
<td>8.2</td>
<td>0.92</td>
<td>12.0</td>
<td>0.85</td>
<td>7.1</td>
</tr>
<tr>
<td>1T(//)</td>
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<td>0.85</td>
<td>4.2</td>
<td>0.84</td>
<td>7.0</td>
</tr>
<tr>
<td>1T(_)</td>
<td>8.3</td>
<td>0.81</td>
<td>21.3</td>
<td>0.86</td>
<td>6.4</td>
</tr>
</tbody>
</table>

* - ~70 nm , ** - ~60 nm

Table 4.11. $H_c$ and squareness of the CoFe films deposited without and with a magnetic field (~100 nm thick) from.

It is well known that an increase in the roughness of the magnetic layer leads to a decrease of its soft magnetic properties [121,177,178], e.g. an increase in $H_c$ [177,178]. This also explains the low coercivities $H_c$, which are obtained for layers deposited in the parallel field configuration.
RESULTS

(Fig. 4.69). No changes in the chemical composition, crystal structure, and texture with magnetic fields, irrespective of the deposition potential and the electrolyte chemistry are observed (for details see Chapters 4.3.2 and 4.3.3). On the other hand, no significant change in the roughness of the layers deposited at \(-1480\) mV\(_{\text{MSE}}\) from the CoFe(A) electrolyte without and in the perpendicular to electrode magnetic field is found (table 4.7). Nevertheless the value of \(H_c\) obtained from the layer deposited under the perpendicular field from the CoFe(A) electrolyte is higher by a factor of about two as compared to the one obtained without field (table 4.11, Figs. 4.69b and 4.70a). This fact might be related to the increase in film roughness. Moreover, the internal stress state together with changes in composition in the layers leads to varying magneto-elastic interactions that also add to the shown dependency.

In conclusion, the increase in \(H_c\) of the CoFe layers deposited at the presented conditions is caused by overlapping effects: the layer’s roughness, the internal stress state, and the chemical composition, e.g. magnetostriction and crystalline anisotropy, of the layer. A clear distinction between the contributions cannot be given easily. The above considerations regarding \(H_c\) are also reflected in the squareness parameter analysis (tables 4.10 and 4.11), where no influence of the superposed magnetic field was observed. Dieter et al. [121] analyzed the influence of the internal stress state on the magnetic properties of Co\(_{50}\)Fe\(_{50}\) layers deposited under different conditions. They found that stress does not influence the saturation and remanence polarisation significantly, but that the \(H_c\) is increased due to magneto-elastic interactions. Moreover a slight influence of the layer roughness on the magnetization loop squareness (in the easy magnetization axis) was reported [177]. The increase of \(H_c\), measured for the alloy layers deposited from the buffered electrolytes (table 3.1), corresponds well to the layer roughness (tables 4.10 and 4.11). Only the film deposited from the CoFe(D) electrolyte in parallel magnetic field and without field from the CoFe(E) electrolyte, where a huge change has been noticed (table 4.11), displays a different behaviour. The inspection of the cross sections prepared by FIB revealed a large deviation from the nominal thickness for these layers (not shown). The deposited layer thicknesses were found to be lower by a factor of nearly two (table 4.11 marked by *).

It is known that the \(H_c\) above a certain thickness depends on the layer thickness and can be described by the Néel dependence [14]:

\[
H_c = ct^n
\]

(4.19)

where \(c\) is a constant, \(t\) is the layer thickness and \(n\) is the so-called Néel exponent.
From Eq. (4.19) it is obvious that for thin films, even small changes in the thickness will significantly affect the $H_c$.

The saturation polarisation ($J_s$) of the deposited layers has been estimated from the saturation field by perpendicular to plane VSM measurements to be $J_s = 1.7$ T for Co and 2.0 T for Fe. Regarding the alloy layers, $J_s = 2.2$ T for films deposited from the CoFe(A) electrolyte and approx. 2.4 T for the rest of the films were obtained. In turn, this shows that the CoFe layers exhibit an ordered structure (CsCl [118]). The changes of $J_s$ correlate well with the changes in the composition, where a decrease in $J_s$ with decreasing Fe concentration is expected [2].

It has been observed that a superposition of a magnetic field during the electrodeposition can also induce an in-plane magnetic anisotropy to the alloy layers [14,16]. In order to clarify, if this is the case, in-plane hysteresis loops of the CoFe layers deposited in the parallel-to-electrode magnetic field were measured parallel ($0^\circ$) and perpendicular ($90^\circ$) to the superposed magnetic field. In Figure 4.70b shows the in-plane hysteresis loops for the layer deposited at -1480 mV$_{MSE}$ from the CoFe(A) electrolyte in the parallel to the electrode magnetic field ($B=1$ T) measured by MOKE at $0^\circ$ and $90^\circ$ with respect to the superposed magnetic field.

Fig. 4.70. Normalized in-plane MOKE hysteresis loops obtained for alloy layers deposited without and with a magnetic field ($B=1$ T) superposed in both relative-to-electrode configurations (a) and in-plane anisotropy of the layer deposited under a parallel magnetic filed (b); CoFe(A) electrolyte, -1480 mV$_{MSE}$, ~100 nm thick layers.

From the difference in the magnetisation loops shown in Fig. 4.70b, it is apparent that the magnetic properties of the layer are anisotropic. This anisotropic behaviour is most probably
linked to a preferred formation of atom couples in the direction of the superposed magnetic field, based on the so-called Néel mechanism [179]. In addition, a stress induced anisotropy could also play a role [121]. From structural investigations no magnetocrystalline anisotropy effects are expected in the multi-grain material as the layers have a clear (110) fibre texture. In Fig. 4.71 the surface domain patterns obtained by Kerr microscopy of the layer corresponding to the hysteresis loops from Fig. 4.70b are shown. From Fig. 4.71 it is apparent that the domain shape is quite the same irrespective of the measurement direction suggesting that the stress induced anisotropy is not very significant. In order to further clarify this, MOKE hysteresis loops of the layer deposited in the perpendicular to the electrode magnetic field (CoFe(A) electrolyte), which is characterised by the smallest $d_{110}$ among the films deposited from the CoFe(A) electrolyte at -1480 mV$_{MSE}$ (table 4.9), were measured (Fig. 4.72a). The angles in the legend of Fig. 4.72a are arbitrary and the notation 0° and 90° is used only for two different but oblique measurement directions as the layer was deposited in the perpendicular to the layer plane configuration. From Fig. 4.72a it is clear that the shape of the magnetization loops irrespective of the measurement directions is quite the same, and that no stress induced anisotropy is noticed. The domain shape is also unchanged, regardless of the measurement direction (Fig. 4.72b,c), but it is noticeable that the layer is characterised by a higher defect density, i.e. more rippled in-plane domains compared to the layer deposited in the parallel-to-electrode configuration (Fig. 4.71) have been observed.

An induced in-plane magnetic anisotropy has also been observed for the CoFe layers deposited from buffered electrolytes. In Fig. 4.73 the hysteresis loops measured for the CoFe layer deposited from the CoFe(C) electrolyte (table 3.1) are shown. From the difference in coercivity and the decrease of squareness for the 90° case it is obvious that the layer exhibits an in-plane magnetic anisotropy and the easy axis of magnetisation is induced along the magnetic field superposed during the deposition. Moreover, when the loops measured by VSM (a) and MOKE...
(b) are compared, they show the same angular dependency, which indicates that the observed dependency is not related to local fluctuations of anisotropy.

**Fig. 4.72.** Normalized in-plane MOKE hysteresis loops obtained for alloy layers deposited from the CoFe(A) electrolyte at -1480 mV$_{MSE}$ in the perpendicular-to-electrode configuration ($B=1$ T) (a) and corresponding surface domain patterns obtained by Kerr microscopy at 0° and 90° (b,c), respectively.

**Fig. 4.73.** Normalized in-plane hysteresis loops obtained for alloy layers deposited from the CoFe(C) electrolyte at -1480 mV$_{MSE}$ in the parallel-to-electrode magnetic field ($B=1$ T) showing signatures of induced in-plane anisotropy measured by VSM (a) and MOKE (b), ~100 nm thick layers.
In table 4.12 the in-plane $H_c$ and $J_r/J_s$ parameters obtained for CoFe layers deposited in the parallel to the electrode magnetic field ($B=1$ T) from different electrolytes (table 3.1) measured in parallel and perpendicular direction with respect to the superposed magnetic field are listed. It is apparent that the induced in-plane magnetic anisotropy depends on the layer chemical composition, i.e. is inverse-proportional to the Fe content in the film and has not been observed for the layer deposited from the CoFe(E) electrolyte which exhibits the highest Fe content.

Table 4.12. $H_c$ and squareness of the CoFe layers deposited in the parallel-to-electrode magnetic field at -1480 mV_{MSE} from investigated electrolytes (table 3.1) measured by VSM at 0° and 90° with respect to the magnetic field applied during deposition.

<table>
<thead>
<tr>
<th></th>
<th>CoFe(A)*a</th>
<th>CoFe(B)*a</th>
<th>CoFe(C)</th>
<th>CoFe(D)</th>
<th>CoFe(E)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$H_c$ mT</td>
<td>$J_r/J_s$</td>
<td>$H_c$ mT</td>
<td>$J_r/J_s$</td>
<td>$H_c$ mT</td>
</tr>
<tr>
<td>0 deg</td>
<td>5.1</td>
<td>0.95</td>
<td>15.4</td>
<td>-0.97</td>
<td>11.6</td>
</tr>
<tr>
<td>90 deg</td>
<td>3.5</td>
<td>0.90</td>
<td>13.5</td>
<td></td>
<td>9.4</td>
</tr>
</tbody>
</table>

* - MOKE measurements
a - deposited at -1400 mV_{MSE}
4.3.5. Conclusions Regarding the Influence of a Magnetic Field on the Deposited Layer Properties

The magnetic field applied during the deposition of Fe-group metals and alloys significantly affects the deposited layer properties. This influence can be summarised as follows:

- The chemical composition of the deposited CoFe alloy layers, irrespective of the deposition parameters, is unchanged by magnetic fields;
- Oxygen contamination of the deposited layers was not found;
- A magnetic field affects the morphology of the deposits. The layers deposited under the influence of the parallel to the electrode magnetic field appear denser and more homogeneous than the ones obtained without a magnetic field. On the contrary, the layers deposited in the perpendicular to the electrode magnetic field appear more diverse and, in the case of the unbuffered electrolytes, rougher as compared to the no-magnetic field situation. In the case of the perpendicular configuration, the grains tend to orient perpendicular to the surface, i.e. the grains grow as separated columns in the field direction;
- A scaling analysis has revealed a smoothing effect of a parallel magnetic field manifested in a reduced value of the roughness exponent in comparison to the layers deposited without a magnetic field. On the contrary, the roughness exponent has increased for the layers obtained in the perpendicular-to-electrode magnetic field, i.e. a roughening effect of the perpendicular field is observed;
- An increased desorption of hydrogen reported under the influence of a magnetic field improves the deposit quality, no large holes left by hydrogen bubbles have been observed for layers deposited under a magnetic field, regardless of its relative to the electrode orientation;
- The magnetic field affects neither the crystal structure nor the texture. All layers irrespective of the deposition parameters develop a fibre texture;
- A magnetic field applied during the deposition of alloy layers from buffered electrolytes, irrespective of its relative to the electrode orientation, reduces the internal stress of the
layer. This effect is attributed to an improved desorption of hydrogen from the electrode surface, which is observed under the influence of magnetic fields;

- The magnetic properties of the deposits are found to be affected by a magnetic field applied during the deposition. These effects are caused by microstructural changes induced by the magnetic field, i.e. the roughness of the layer, the internal stress state, and the chemical composition of the layer;

- An in-plane magnetic anisotropy is observed in the alloy layers deposited under the parallel magnetic field, where, according to the XRD investigations, isotropic properties were expected. The origin of this phenomenon is seen in a preferential same atom couples formation in the magnetic field direction.
5. CONCLUSIONS AND REMARKS

The general aim of this work was to contribute to the fundamental understanding of the influence of homogeneous external magnetic fields on different steps of the electrodeposition of iron-group metals and alloys. A special attention was given to the initial stages of the electrocrystallisation and to the side reactions occurring simultaneously with a metal reduction together with their impact on the development of the layer properties.

The effect of a superposed magnetic field in the parallel and the perpendicular to the electrode surface orientation on the electrocrystallisation of Co, Fe and CoFe alloys was studied in acidic sulphate electrolytes at room temperature. It is clearly demonstrated that the superposition of homogeneous magnetic fields influences the electrochemical processes and the resulting layer properties significantly.

In the parallel to the electrode magnetic field the metal deposition rates, regardless of the electrolyte chemistry and the applied potential, increase with the magnetic flux density. This is caused by a Lorentz force driven convection, i.e. the MHD effect, which increases the mass transport of metal ions towards the electrode surface. This is supported by the current density vs. magnetic flux density dependencies, which irrespective of the investigated system obey the power dependence (Eq. 2.27) expected for the MHD convection. The mass transport of hydrogen ions towards and hydroxide species away from the electrode surface is increased by the MHD stirring. This results in an increased HER rate in unbuffered electrolytes, which, in turn, reduces the interface pH value. As a consequence the spontaneous hydroxide formation is suppressed and an improved deposit quality is observed. Moreover, the desorption of hydrogen in this magnetic field configuration is supported, i.e. no holes left by hydrogen bubbles in the deposit have been noticed.

On the contrary, when the deposition is carried out in a perpendicular to the electrode magnetic field, where the Lorentz force is expected to be negligible, no significant influence or a slight retardation of the metal deposition rate is noticed, irrespective of the electrolyte composition. But, surprisingly, in this magnetic field-to-electrode configuration the HER rate is remarkably increased. For the first time a qualitative model is proposed in order to explain this phenomenon [92]. The origin of this effect is seen in a special localized convection which arises close to the hydrogen bubble. In the vicinity of a bubble the current distribution is distorted. The current lines are no longer perfectly normal to the electrode surface, but there is also a parallel to the electrode
current component. As a consequence a Lorentz force is induced, in analogy to the micro-\textit{MHD} effect \cite{66}, which results in an improved desorption of hydrogen from the electrode surface. This was proved by direct in-situ microscopic investigations. Moreover, it is clearly demonstrated that a perpendicular magnetic field remarkably reduces the bubble size and the period of time when the bubble is fixed at the electrode surface is shortened \cite{98}. This leads to an increased mass transport of ions towards and away from the electrode surface and as a result a better quality of the deposit is achieved \cite{92}. This effect most probably reduces the interface pH value as well.

The nucleation and the very beginning of the layer growth are of particular importance for the thin film deposition, since the deposit properties are determined by these processes. Hence, a special attention has been given to analyse the influence of a magnetic field on the early electrocrystallisation steps. It was found that the nucleation behaviour can be altered by a magnetic field. The changes in the nucleation behaviour have been studied on the basis of theoretical models by an \textit{i(t)} transients analysis. Regardless of the electrolyte chemistry, the magnetic field strength, and its relative to the electrode orientation, similar features in the \textit{i(t)} transients have been observed. The nucleation and growth are characterised by a layer-by-layer mode. The first nucleation and growth step at the very beginning of the potential step has been attributed to the 2D (most probably epitaxial) layer formation (up to a few MLs), which was found unaffected by a magnetic field superposition. The 2D step is then followed by the next nucleation and growth step indicated by the occurrence of a maximum in the \textit{i(t)} transients. This is attributed to the nucleation and 3D diffusion controlled growth and is altered by a magnetic field applied in the parallel-to-electrode configuration. The analysis of the \textit{i(t)} maxima rising part reveals that the superposition of the parallel magnetic field leads to a retardation of the steady state nucleation rate ($AN_0$). A qualitative model was proposed in order to explain this unexpected phenomenon \cite{20}. The origin of the steady state nucleation rate retardation is explained on the basis of two competitive processes occurring simultaneously, i.e. nucleation and growth. The nucleation rate constant ($A$) remains unaffected by a magnetic field, i.e. the frequency of the site activation remains constant. Whilst, at the same time, a Lorentz force driven convection arises, i.e. the \textit{MHD} effect, increasing the electroactive species transport towards already existing nuclei, i.e. the growth rate is increased. This leads to an increase of the area covered by already existing nuclei and, more importantly, the surface fraction covered by the diffusion zones formed around the nuclei, where the probability to find a new nucleus is lower \cite{163}. The number of sites available for nucleation, considering slow nucleation processes as in this case, is lowered. This in
CONCLUSIONS

turn results in a retardation of the saturation nuclei density ($N_0$) and finally a reduced steady state nucleation rate is obtained. Moreover, at high magnetic flux densities applied in the parallel-to-electrode configuration a second 3D step can be observed manifested by an occurrence of the second $i(t)$ maximum which has been attributed to the nucleation and 3D growth under diffusion control and is altered by a magnetic field as well. The hydrodynamic origin of the introduced changes was proved by independent RDE investigations.

In contrast, the perpendicular to the electrode magnetic field does not change the nucleation behaviour, regardless of the electrolyte chemistry and the applied potential. However, in unbuffered electrolytes, the growth mode of the layer is remarkably changed, i.e. a columnar growth is observed.

The magnetic field impact on the electrochemical reaction rates, on the desorption of hydrogen from the electrode surface, and on the nucleation behaviour has strong consequences for the resulting layer characteristics. The most pronounced effect is noticed for the morphology of the layers. The quality of the layers deposited in a magnetic field, irrespective of its relative to the electrode orientation, is strongly improved. The reason of this is an enhanced desorption of hydrogen from the electrode surface. As a result large holes left by hydrogen bubbles observed for the layers deposited without a field disappear for the layers deposited under the influence of a magnetic field. Moreover, the interface pH value is reduced in the field and the hydroxide precipitation is inhibited. This leads to a further improvement of the quality of the layers, i.e. shiny mirror-like deposits are obtained with a field superposed, whereas the layers deposited without a field appear black.

The layers deposited under an influence of the parallel-to-electrode magnetic field appear denser and more homogeneous than the ones obtained without a magnetic field. On the contrary, the layers deposited in the perpendicular to the electrode magnetic field appeared more diverse and in the case of unbuffered electrolytes rougher compared to the non-magnetic field situation. The most remarkable effect has been observed for the layers deposited from the Fe and the CoFe(A) electrolyte at $E_2$ in a perpendicular magnetic field where the grains tend to grow as separated columns in the direction of the magnetic field. The origin of this fascinating phenomenon is still unclear and further investigations are essential in order to clarify this. Nevertheless, possible effects which could be responsible for this situation are discussed (Chapter 4.3.2.3).

A scaling analysis [96,97] has revealed, irrespective of the electrolyte composition, a smoothing effect of a parallel magnetic field manifested in a reduced value of the roughness
CONCLUSIONS

exponent in comparison to the layers deposited without a magnetic field. On the contrary, the roughness exponent has increased for the layers obtained in the perpendicular to the electrode magnetic field, i.e. a roughening effect of the perpendicular magnetic field is observed.

No magnetic field effects neither on the crystal structure nor on the texture of the deposits have been observed. All layers irrespective of the deposition parameters develop a fibre texture. Nevertheless, the internal stress state of the deposited layers is affected by a magnetic field. A magnetic field applied during the deposition of alloy layers from buffered electrolytes, irrespective of its relative to the electrode orientation, reduces the internal stress of the layer. This effect is attributed to an improved desorption of hydrogen from the electrode surface, which is observed under the influence of a magnetic field. In contrast, it was concluded, on the basis of HRTEM and XRD investigations, that the films deposited from the CoFe(A) electrolyte in the perpendicular magnetic field, where the columnar growth is observed, characterise higher tensile stress compared to the layers deposited without and in the parallel magnetic field. The chemical composition of the deposited CoFe alloy layers, irrespective of the deposition parameters, is unchanged by magnetic fields.

The magnetic properties of the deposits are found to be affected by a magnetic field applied during the deposition. These effects are caused by microstructural changes induced by the magnetic field, i.e. the roughness of the layer, the internal stress state, and the chemical composition of the deposit. A good correlation between the coercivity $H_c$ and the roughness is found. Moreover, an in-plane magnetic anisotropy is observed in the alloy layers deposited under the influence of the parallel to the electrode magnetic field, where, according to the XRD investigations, isotropic properties were expected. The origin of this phenomenon is seen in a preferential same atom couples formation in the magnetic field direction [179].

To summarize this work it can be stated that the superposition of magnetic fields and carefully chosen deposition parameters can significantly improve the deposited layer properties. The morphology can be smoothened or roughened in dependence of the application requirements. Moreover, the magnetic properties of the deposited soft magnetic layer can be tailored by magnetoelectrolysis. A magnetic anisotropy for the alloy deposits can be induced already at the deposition step what will reduce the manufacturing process complexity. The possible improvement of the hydrogen bubble removal from the electrode surface may be essential for the preparation of MEMS devices. The hydrogen bubble can block a trench or any other structure, prepared for example by lithographic techniques, and the deposition would be prevented.
Magnetoelectrolysis could suppress this unwanted situation. All of that makes the electrodeposition under the influence of a magnetic field a very promising alternative for the already existing, mainly physical, deposition technologies. This becomes possible mainly because of the modern permanent and superconductive magnets development, which can be implemented into the technology.
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Publications in refereed international journals:


**Conference proceedings:**


5. R. Sueptitz, **J. Koza**, M. Uhlemann, A. Gebert, L. Schultz: „Magnetic field effect on the anodic behaviour of a ferromagnetic electrode in acidic solutions”, Proceedings of the 6th


Contributions to international conferences and workshops (speaker is underlined):


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Erklärung

Hiermit versichere ich, dass ich die vorliegende Arbeit ohne unzulässige Hilfe Dritter und ohne Benutzung anderer als der angegebenen Hilfsmittel angefertigt habe; die aus fremden Quellen direkt oder indirekt übernommenen Gedanken sind als solche kenntlich gemacht.

Bei der Auswahl und Auswertung des Materials sowie bei der Herstellung des Manuskripts habe ich Unterstützungsleistungen von folgenden Personen erhalten:

Prof. Dr. Ludwig Schultz
Dr. Margitta Uhlemann
Dr. Annett Gebert


Die Arbeit wurde bisher weder im Inland noch im Ausland in gleicher oder ähnlicher Form einer anderen Prüfungsbehörde vorgelegt und ist auch noch nicht veröffentlicht worden.

Ich erkenne die Promotionsordnung der Fakultät Maschinenwesen der Technischen Universität Dresden an.

Jakub Adam Koza    Dresden, 22.01.2010