

Pulsed deposition of metals from aqueous solutions and the possible similarities to AC corrosion

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ABSTRACT

Electrodeposition of metals, such as nickel, copper, zinc and chromium, from aqueous solutions is an old and widely used technique within the field of surface treatment – and thus also in corrosion protection. Pulsed deposition of metals, or pulse plating, is a more recent attempt to improve the processes and to tailor the properties of the deposited metal. In this paper pulse plating is utilized for very different purposes, ranging from electroforming of nickel for rocket engines to deposition of soft magnetic alloys for microfluidic applications. The deposition, in all cases, takes place during cathodic pulses ranging in time from 10 to 100 ms. In order to modify the diffusion layer, and to improve the material distribution, anodic pulses are also applied – leading to dissolution of a fraction of the deposited metal in each cycle.

Compared to corrosion, and in particular AC corrosion, pulse plating does hold some similarities. Although the activity of the metals ions in the soil surrounding a pipe line is not as high as in an electrolyte for nickel plating, the frequency of the pulse plating cycle can be compared to AC frequencies and the local changes in pH and concentration of ions will also follow the same patterns.

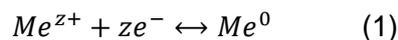
This paper will explain the advantages and challenges of pulse plating – through a number of examples – and then try to compare the electrochemical mechanisms involved to those found in AC corrosion. This will also include speculations into using a pulsed cathodic protection level that is “in phase” with the imposed alternating current – as a way to minimize AC corrosion on pipe lines operating close to AC power.

1 INTRODUCTION

Electrochemical deposition (ECD) is a term used for all types of electrochemical reactions leading to deposition of material. As such it includes electroplating and electroless plating, but also other processes such as electrophoretic polymer processes and conversion coatings such as anodizing of aluminium.

This paper will focus on the use of ECD for deposition of pure metals and metallic alloys, with or without pulse plating being applied, and the parameters and observations found here are compared to those found in corrosion scenarios – and particularly AC corrosion in pipelines under cathodic protection.

The two most important sub-groups of ECD, electroplating and electroless plating, are both based on the same electrochemical reaction:



In case of electroplating the part to be plated (called the cathode) is submerged in the electrolyte and connected to a power supply. Another electrode (called the anode) is also submerged in the electrolyte and connected to the power supply, thereby completing the electrical circuit.

On the surface of the cathode, reaction (1) moves from left to right, while on the anode, the reaction is reversed. In an ideal process the amount of metal deposited on the cathode is equalled by the same amount of metal being dissolved at the anode. However, in many practical processes this is not completely true, but a good electroplating bath can still be used for years with a minimum of maintenance.

In the electrolyte it is relatively easy to control where the deposition will take place, since the electrical resistance of the various cathode surface areas will determine the amount of available electrons for deposition and growth. For instance by applying a photoresist or other types of masking, deposition of metallic structures is possible with exceptionally good resolution (primarily governed by the resolution of the lithography process). Masking has a similar function, as compared to the organic coatings used for protection of pipelines against corrosion, which is to prevent the electrochemical reactions from taking place at certain areas of the surface.

1.1 Basic considerations of electroplating

In the following some basic consideration of electroplating will be discussed, using nickel (Ni) plating as a typical example.

The first useful nickel plating bath was proposed by C.P. Watts in 1916 [1]. This bath is still used extensively since it is relatively easy to establish - both from an economical and a practical point of view. The Watts Ni bath is operated at temperatures from 30 to 60 °C, usually with air agitation and at a pH ranging from 3.5 to 5.0. The current density is typically between 2 and 7 A/dm² – corresponding to a range from 20 to 70 mA/cm².

The appearance of deposits from the basic Watts Ni bath is not very good. The deposits are coarse and can have pitting holes in the high current density regions (corners, edges, etc.). The pitting holes are made by small hydrogen bobbles that have stayed on the surface long enough to prevent deposition in that point.

The bobbles are formed because the potential is close the hydrogen reduction line in the Pourbaix diagram – and a small fraction of the current will be used to reduce H⁺ ions in the electrolyte to hydrogen gas.

This, usually undesired, side reaction must be taken into account when the deposition rate is calculated.

The amount of coulombs delivered by the power supply is calculated as (I is the current in amperes and t the total plating time in seconds):

$$Q = I \cdot t \quad (2)$$

The theoretical amount of Ni deposited by the charge Q is calculated as (F is 96487 C/mole, $z=2$ for Ni and $M_{Ni}=58.71$ g/mole):

$$m_{theory} = \frac{Q \cdot M}{z \cdot F} = t \frac{I \cdot 58.71 \frac{g}{mole}}{2 \cdot 96487 \frac{C}{mole}} \quad (3)$$

If the current is 1.0 A and the metal is Ni we get 0.304 mg deposited Ni per second (at 100% current efficiency). The current efficiency (θ) is simply calculated as the difference between the theoretical and the actual (measured by weight, m_{Ni}) amount of Ni deposited.

$$\theta = \frac{m_{Ni}}{m_{theory}} 100\% \quad (4)$$

Since most Ni electroplating processes exhibits a relatively high current efficiency of 96% to almost 100%, one should expect the pitting problem to be very small. For some applications however, due to the geometry and the resulting high local current densities, the problem will be present.

Generally the current efficiency for acidic electrolytes is almost 100% (except for Cr plating which is from 6-30%) and for alkaline baths around 60-80% [2]. For the group of acidic baths, to which the Watts Ni baths belong, the current efficiency is highest (closest to 100%) at relatively high current densities. For the group of alkaline baths the tendency is the opposite [2]. Consequently one must be careful not to use very low current densities (from 0.5 A/dm² and below) in the acidic baths (or very high in the alkaline baths) as the current efficiency will be significantly reduced.

Whereas there is very little that can be done about the current efficiency (except to avoid extreme current densities) something can be done about the pitting problem. Most commercial plating baths use wetting agents to reduce the surface tension - thereby making it more difficult for the bobbles to attach themselves to the cathode surface. The wetting agents are typically "soap"-like organic chemicals with a long carbon chain connected to a polar group such as sodium lauryl-sulphate, CH₃(CH₂)₁₁SO₄Na.

When the current efficiency (θ), the plateable area (A) and the density (δ) are known, it is possible to calculate the thickness of the deposit (x_{Ni}) at a given time (t):

$$x_{Ni} = t \cdot \theta \frac{I \cdot M}{z \cdot F \cdot A \cdot \delta} \quad (5)$$

As a rule of thumb for Ni electroplating, we get a deposition rate of 0.5 μ m/min. at a current density of 2.5 A/dm² (which is a very typical current density for Watts Ni baths). The plating rate can be scaled perfectly linearly within a large current density range. Some special Ni electrolytes can reach deposition rates of 5 μ m/min. or more, but generally rates from 0.2 to 1.5 μ m per minute are normal.

1.2 Suitable conditions for electroplating

Deposition of metals using electrochemical deposition (ECD) requires an electrolyte. The electrolyte must fulfil a number of demands specific for the metal involved:

1. suitable salts of the metal can be dissolved in the electrolyte, at a reasonable temperature and in sufficient concentrations,
2. the electrolyte must be a relatively good electrical conductor in order to get an even distribution of the material and to avoid extensive heating of the bath,
3. the pH-value of the bath and the concentration of complexing agents should be kept within a certain range so that reduction of the metal occurs before reduction of hydrogen.

For some metals all these demands cannot be fulfilled using a water based electrolyte. Elements such as Ti and Al can only be deposited from organic electrolytes, while other metals such as Mg, Nb, Ta, and W can be plated from molten salt electrolytes (at 700°C and above). For obvious reasons these electrolytes are both difficult to use and expensive.

2 PULSE PLATING

Electrodeposition by means of pulsating current (or potential) offers the possibility to change the properties of the deposit, just like the addition of certain organic compounds to the electrolyte. The advantage is, that the pulse patterns or waveforms can be changed easily while the additives are difficult, if not impossible, to remove from an electrolyte once added. Furthermore, some of the improvements that pulse plating delivers are not possible by adding organic or other additives to the solution. This is especially true when pulse reversal plating (fig. 1) is applied.

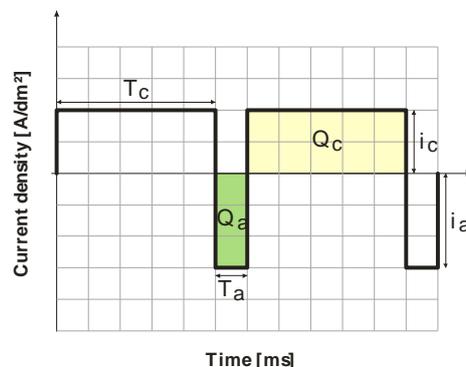


Fig. 1: Current versus time diagram for pulse reversal plating. Typical values for pulse reversal plating of Ni are; $T_c = 100 \text{ ms}$, $T_a = 20 \text{ ms}$, $i_c = 4 \text{ A/dm}^2$ and $i_a = 6 \text{ A/dm}^2$ [3]. In order to get a deposit, the cathodic charge (Q_c) must be larger than the anodic charge (Q_a), otherwise corrosion of the substrate will be the result.

Using uni-polar pulsed current (on/off plating) it is possible to reduce the size of the deposited crystals, thereby improving hardness and tensile strength of the deposit and reducing the number of pores [4-5]. This is only true however, when relatively high frequencies (above 100 Hz) are used - lower frequencies usually have little effect [6]. For some metals, such as Au, on/off plating will change the crystal growth pattern [7], leading to porosity and hardness improvement that are not obtainable using additives. Pulse reversal plating makes it possible to improve the material distribution, by dissolving "unwanted" crystals during the anodic periods. This type of pulse plating also has a dramatic influence on the texture of the film [4] and is known to be able to reduce internal stress of the deposits [3].

2.1 Plateable alloys

Perhaps even more useful and interesting than the pure metals are the numerous alloys that can be plated from aqueous solutions (fig. 2). The special rules that apply for alloy plating, such as the importance of agitation [8], diffusion and limiting current density for both metals, are excellently described by Brenner [9] and will not be discussed here.

One of the most important soft magnetic materials is PermAlloy (79% Ni and 21% Fe) which can be plated from sulphate based electrolytes [10], with better current efficiency from citrate electrolytes [11] or for special application from chloride electrolytes [8]. PermAlloy deposition is discussed in more detail in section 3.2.

Classic solderable alloys such as PbSn (90% Pb) and SnPb can be deposited [9]. Recently a number of lead-free alloys such as SnAg [12], SnAgCu (the so-called SAC solder), AuSn [13] and SnZn have been studied intensively.

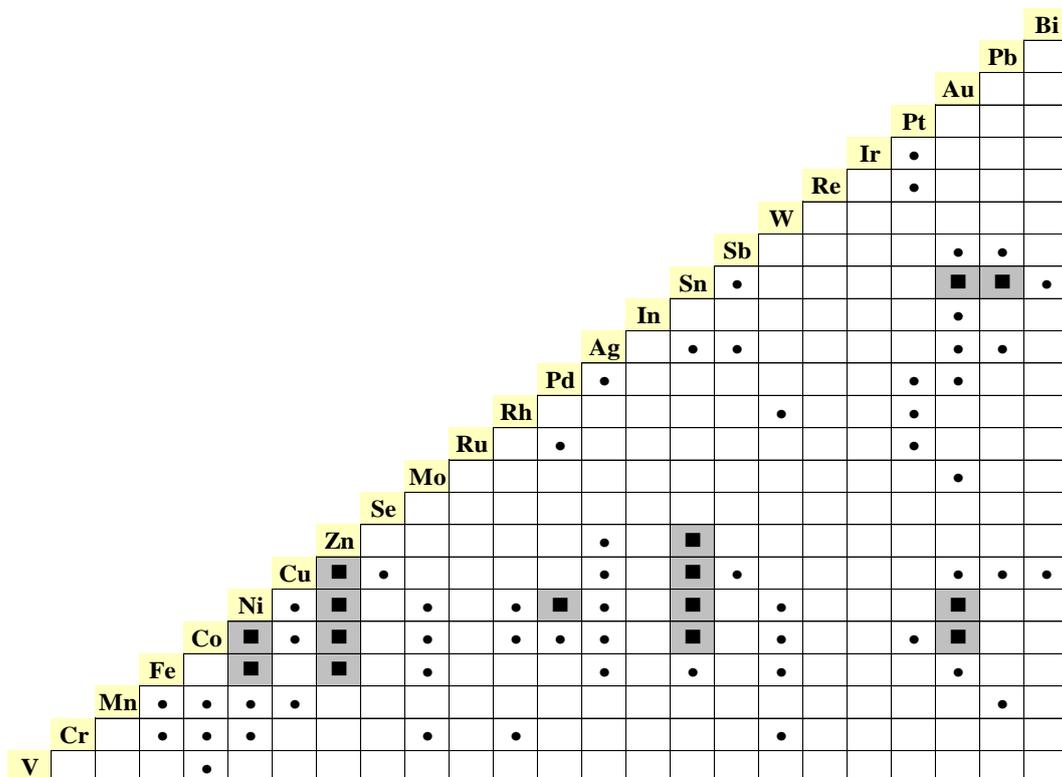


Fig. 2: Binary alloys (•) that can be deposited from aqueous solutions. A box on a grey background (■) indicates that the alloy deposition process is commercially available (adapted from [9]).

CuNi alloys such as Monel (30% Cu) or konstantan (60% Cu) are stable in various corrosive environments. Konstantan is also known to have a temperature independent (high) electric resistance. The CuNi alloys can be deposited from several different electrolytes [9]. Brass (CuZn) and bronze (CuSn) are fairly easy to deposit [9], while stainless steel (FeNiCr) can be very difficult to electroplate with an acceptable result.

The most important use of alloy plating however, is perhaps the possibility to improve the mechanical properties of metals such as Ni, Au and Cu. The hardness and wear resistance of Cu is increased 75% by alloying with 0.2-0.4% of Sb [10]. The hardness of electroplated Ni can be almost tripled (560 HV) using Co (30-40%) as the alloying element [14]. Temperature resistant alloys such as CoW (59/31) maintain a hardness of almost 700 HV at 600°C [15] and also NiW (12% W) provides a hard deposit with substantial thermal stability [16].

3 APPLICATION EXAMPLES

To demonstrate the versatility of electroplating, and also the use of pulse plating, a few very different applications are briefly discussed below.

3.1 Rocket engine combustion chamber

Mainly due to the extreme conditions within the field of rocket engines, many combustion chambers are actually made by electroforming [17]. Electroforming provides a seamless, thick and uniform chamber wall, which can resist the enormous pressure inside the combustion chamber. The alternative would be to weld the chamber similarly to the process use for large diameter pipes or tubes, but the mechanical weakness near the welding line means that electroforming is still the preferred method of manufacturing for many types of rockets.

Electroforming also makes it possible to include a complex system of cooling channels inside the chamber wall. The cooling channels are machined in a copper substrate, filled with conducting wax, over plated with several centimetres of nickel and finally emptied by melting the wax. By pumping the fuel (such as liquid oxygen and hydrogen) through the cooling channels, the inside surface of the chamber can be kept at a sufficiently low temperature to avoid melting or softening of the metal.

The EADS Astrium Company, that produces the engines for most of the European Space programme, have started to utilise pulse plating of nickel for electroforming of the combustion chamber of the Vulcain 2 and other rocket engines. As the chambers are rather large, 12.000 litres of nickel electrolyte is available in one tank. The thickness of the deposited nickel is up to 5 centimetres.



Fig. 3: Ariane 5 rocket engine combustion chamber made by electroforming (features on the top and bottom are welded to the chamber). Picture reproduced with permission from EADS Astrium.

The main reason for using pulse reversal plating are the good mechanical properties combined with a much more uniform material distribution leading to faster production time a less waste of nickel due to mechanical machining of the outer surface.

3.2 Pulse plating of soft-magnetic alloys for microfluidics

Electroplating of nickel-iron alloys has been known for many years. IBM filed some of the first patents aiming at deposition of soft magnetic films around 1970 [18-19]. At that time the preferred plating bath for electrodeposition of nickel-iron alloys, and particularly the Ni79Fe21 or PermAlloy, consisted of simple mixtures of the sulphate or chloride salts of nickel and iron. The typical bath would furthermore contain boric acid as a pH buffer and a few organic additives such as lauryl sulphate (wetting agent) and saccharin (stress reducer). Especially when chloride salts are used, the internal stresses in the deposits are very high and must be reduced using efficient stress reducing additives. Unfortunately, the use of the so-called sulphur containing additives results in small amounts of sulphur being co-deposited (up to a few percent). Even small amounts of sulphur will influence the corrosion resistance [20], as well as both the mechanical and the magnetic properties, in a negative way.

In order to reduce the internal stress, or to avoid the use of sulphur containing stress reducing additives, some authors have reported PermAlloy plating processes based on sulphamate rather than sulphate (and chloride) [21].

The mechanism of nickel-iron alloy plating belongs to the so-called anomalous type [9] which means that the iron is plated preferentially although it is not the most noble metal of the two. The degree of anomalous deposition depends on bath temperature [9] but also on pH and the use of pH-buffers [8]. A bath without pH-buffer is less anomalous in behaviour as compared to a bath with 0.4 M of boric acid [8]. According to the literature [9], but also the experience obtained within the present work, simple sulphate or chloride based PermAlloy baths, should be operated in a pH range from 3 to 5. Much below 3 the current efficiency will drop to unacceptable values, see also fig. 5, and above 5 the formation of Fe(III)-based precipitates will slowly destroy the electrolyte. Adding a suitable complexing agent for Fe(III) postpones the formation of ferric compounds. Venkatesetty [11] reports that the addition of citrate (to an otherwise simple sulphate bath) will increase the period in which good deposits can be obtained from a few hours to more than 25 hours. Depending on the complexing agent, it may also have the effect that the iron to "total metal" concentration ratio can be increased from 2 percent to 4 percent or more – while still depositing the desired PermAlloy composition. As most baths use pure nickel anodes, having a relatively high iron concentration in the bath will make the bath easier to operate and less susceptible to small concentration changes.

Electroplated PermAlloy has several applications in MEMS technology. PermAlloy is widely used when some form of magnetic actuation is required, such as magnetically actuated valves or flux guides in electromagnet applications [22]. In recent years magnetic manipulation in microfluidic systems has emerged as a promising technology for bio-separation in lab-on-a-chip systems. A receptor molecule (DNA, RNA, proteins, cells, antigens etc.) is bound on the surfaces on magnetic beads or particles. These beads or particles are attracted to regions of large magnetic field, and thus if they are suspended in a solution containing target molecules for the receptor molecules, the target molecules can be separated from the solution by application of a spatially varying magnetic field. Both active systems with on-chip electromagnets and passive systems with on-chip soft magnetic structures have been realized using electroplated PermAlloy [22].

Table 1: Recipe for the PermAlloy electrolyte. The pH-value was adjusted to 3.0 using sodium hydroxide. The bath was operated at 35 °C.

Compound	Formula	Concentration (M)
Nickel sulfate	$\text{NiSO}_4 \cdot 6 \text{H}_2\text{O}$	0.2000
Nickel chloride	$\text{NiCl}_2 \cdot 6 \text{H}_2\text{O}$	0.2000
Iron Sulfate	$\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$	0.0293
Boric acid	H_3BO_3	0.5000
5-sulfosalicylic acid	$\text{HO}_3\text{S} \cdot \text{C}_6\text{H}_3\text{OH} \cdot \text{COOH}$	0.0350
Naphthalene tri-sulfonic acid (sodium salt)	$(\text{NaO}_3\text{S})_3\text{C}_{10}\text{H}_8$	0.0070

The main stability problem associated with alloy plating baths containing iron, is the oxidation of Fe(II) to Fe(III) and the following formation of strong hydroxide complexes (see Table 2) leading to precipitation of Fe(OH)₃. The complexing agent 5-sulfosalicylic acid is one of very few candidates for a compound forming complexes with Fe(III) that are stronger than the hydroxides. In Table 2 the formation constants of oxalate, which is usually regarded as a strong complexing agent for Fe(III), is clearly weaker than 5-sulfosalicylic acid.

Metal ion	Ligand	log K ₁	log K ₂	log K ₃
Fe ²⁺	OH ⁻	5.56	9.77	9.67
Fe ³⁺	OH ⁻	11.87	21.17	29.67
Ni ²⁺	OH ⁻	4.97	8.55	11.33
Fe ²⁺	HO ₃ S·C ₆ H ₃ OH·COOH	5.90		
Fe ³⁺	HO ₃ S·C ₆ H ₃ OH·COOH	14.64	25.18	32.12
Ni ²⁺	HO ₃ S·C ₆ H ₃ OH·COOH	6.42	10.24	
Fe ²⁺	C ₂ O ₄ ²⁻	2.9	4.52	5.22
Fe ³⁺	C ₂ O ₄ ²⁻	9.4	16.2	20.2
Ni ²⁺	C ₂ O ₄ ²⁻	5.3	7.64	~8.5

The use of 5-sulfosalicylic acid, and a few other related compounds, in iron alloy plating baths was patented in 1978 [24]. Besides the capabilities as complexing agent, other advantages of 5-sulfosalicylic acid include a very strong red colour (absorbance at 480 nm) of the complexes with Fe(III) and that 5-sulfosalicylic acid is a stable molecule which is not destroyed in the electrolyte and does not seem to cause co-deposition of sulphur or carbon. Initially 2 litres of bath were mixed using the recipe of Table 1. The bath was split into two 1litre bottles, one was used as the plating bath and the other was used for reference.

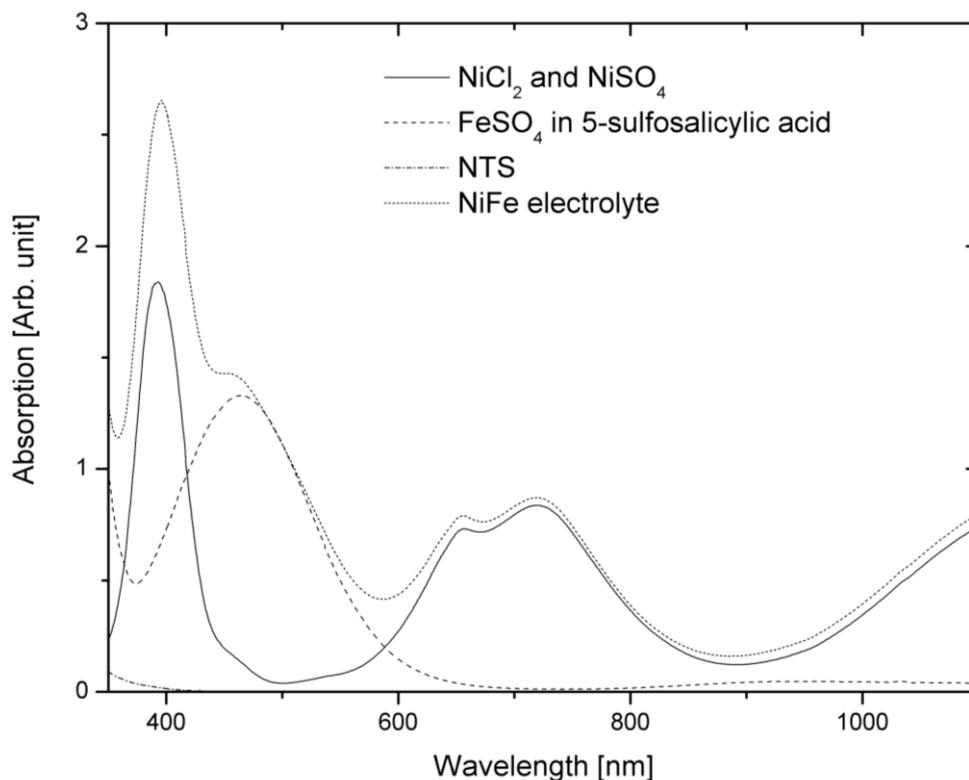


Fig. 4: Spectrophotometric data for the components of the Permalloy electrolyte. The data for the individual components add up to give the data for the finished electrolyte.

These two baths were used to study of the development of the electrolyte over time. Once a week for eight weeks, PermAlloy was electroplated onto a 3 x 3 cm² copper plate for 30 minutes using pulse reversal plating with the cathodic pulse being 60 ms of 4 A/dm² and the anodic pulse being 20 ms of 6 A/dm² corresponding to an average current density of 1.5 A/dm². Absorbance, as well as pH, was recorded in the plating bath before and after each deposition. At the same time similar data were also measured for the reference bath.

Two other baths were mixed to establish the connection between spectrophotometric data and the concentration of Fe(III) and Fe(II) ions in solution. 800 ml of bath was mixed using the recipe of Table 1 without the iron sulphate. This was split into two 400 ml portions, and 0.0293 M FeSO₄ was added to one portion, and 0.01465 M Fe₂(SO₄)₃ was added to the other, such that the amount of Fe ions was the same in the two solutions. This gave two baths; one containing Fe(II) ions only, the regular bath, and one containing Fe(III) ions only. These two baths were then mixed in various ratios to determine the absorbance at 480 nm as a function of Fe(III)-content.

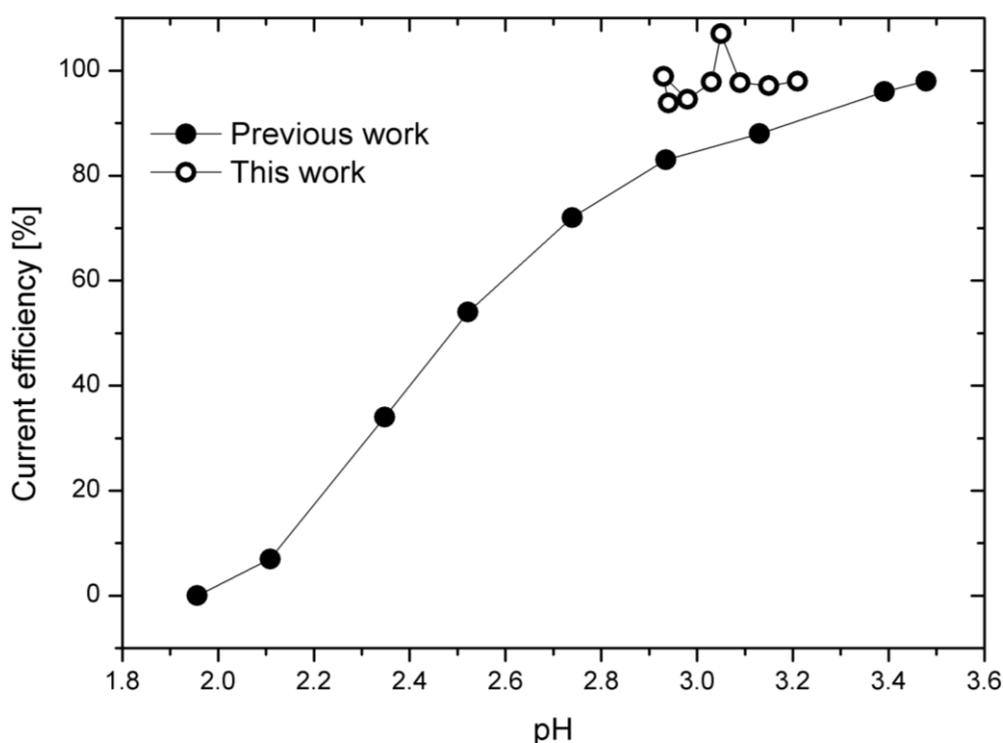


Fig. 5: Current efficiency as a function of pH. Results from this work are compared to previous work [25] using almost identical electrolytes.

The current efficiency was measured by weighing the samples before and after the electroplating using a Sartorius BP61 scale with a maximum precision of ± 0.1 mg. The Fe (and Ni) content in the deposits was determined semi-quantitatively with energy dispersive X-Ray spectrometry (EDX, Oxford Scientific) in a JEOL Scanning electron microscope (SEM, JSM-5900).

There is a relatively good correlation between the results obtained in [25] and the new ones. The only differences between the experiments are a higher chloride content in the new bath (called "This work" in Fig. 5). It is also noteworthy that absolute no deposit is obtained if the pH gets below 2 – and at higher pH-values the formation of iron hydroxides will also make deposition difficult.

It is seen in fig. 4 how the curves for the individual components add up to give the total curve for the bath. Also, that Fe sulphate with 5-sulfosalicylic acid has a distinct peak at 480 nm,

whereas Ni has several peaks at 393, 657 and 720 nm. This means that we can distinguish the Fe peak from the nickel peaks, and thus we can monitor the development of the different components.

The development of the spectrophotometric data was monitored over time. Fig. 6 displays that the Fe peak grows rapidly. Within 25 days it has grown to a state, where it completely dominates the entire spectrum. It is well-known that Fe(II) and Fe(III) absorb roughly at the same wavelength (in the complex with 5-sulfosalicylic acid), but Fe(III) absorbs much more strongly than Fe(II). Therefore the rise in the peak is interpreted as a sign that some Fe(II) ions have been oxidized to Fe(III). However, when the Fe peak at 480 nm is reduced after plating - this means that some of the Fe(III) ions are removed, deposited or more likely reduced to Fe(II), during the plating process.

In Figure 6 the data for the absorption at 480 nm and the pH-value of the plating bath before and after plating are compared with data for an unused reference bath. We see that the absorption grows steadily and that the plating bath grows slightly faster than the reference bath. This may be due to the fact that the plating bath was exposed more to air than the reference bath. It is also seen that the plating process consistently causes the absorption to drop – at least temporarily – which indicates that Fe(III) ions are reduced to Fe(II) ions during plating.

It is also seen in Fig. 6 that pH rises substantially during electrodeposition such that pH is enhanced just after plating, but during the time before the next experiment (around one week) pH drops back to a value that is only a little higher than before the previous experiment. On the other hand pH in the reference bath is consistently falling, even if the total change is small.

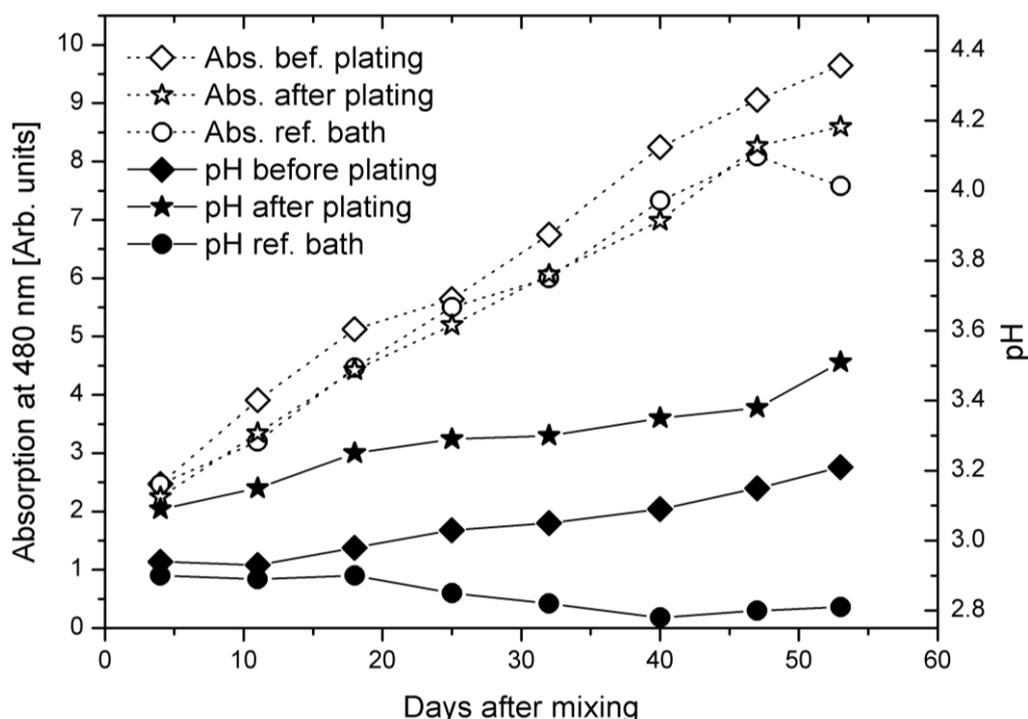
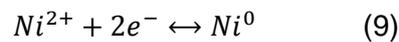
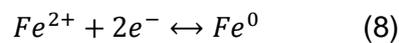
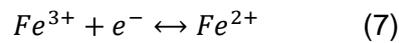
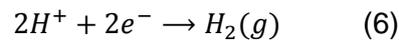
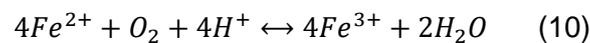


Fig. 6: Development of the characteristic spectrophotometric peak at 480 nm (left axis) and pH (right axis) as function of time. Data is shown before and after plating as well as for the unused reference bath. A total of 8 plating experiments were conducted.

During the electrodeposition, although pulse reversal plating is applied and thus makes many reactions possible, the dominating or resulting electrochemical reactions are:



Reactions 6 and 7 are directly responsible for the current efficiency being in the range from 94-98% (see Fig. 5), whereas reactions 8 and 9 are the ones leading to the actual deposit. After electrodeposition, when the solution is resting in a closed PE bottle, the following reaction is anticipated:



Following this oxidation, we expect a protolysation-like process to take place. The exact role of 5-sulfosalicylic acid and the complexes formed during and after electrodeposition, as compared to the protolysation reactions when water is acting as a ligand is somewhat unclear.

Reaction 10 explains why we see the general rise in absorption at 480 nm and thus in Fe(III) content over time. There is not enough 5-sulfosalicylic acid in the bath to form complexes with all the metal ions, but it will most likely form complexes with Fe(III) preferentially.

4 PULSE PLATING COMPARED TO AC CORROSION

In the field of corrosion, and particularly AC corrosion of cathodically protected pipelines, several similarities to pulse plating can be drawn. The pipeline is made of steel, and although the surface of the pipeline has an organic coating for protection against corrosion, there will always be coating defects which allow direct access to the steel. The pipelines are often cathodically protected using a rectifier and an anode buried in the soil, to keep the pipeline in the immune area for steel. However, pipelines placed near high voltage transmission lines are exposed to AC corrosion, because the alternating current induces quite different potential and currents in the system.

Normally the high voltage transmission lines will carry three phases with a 50 Hz frequency. Depending on the distance between the individual lines and the pipeline, and several other factors, each of these lines will interfere and impose "pulses" of 10 ms cathodic followed by 10 ms of anodic potential (corresponding to a 50 Hz sinusoidal curve) on the potential already applied by the rectifier for cathodic protection.

With a constant cathodic protection, even with the imposed alternating potential, the overall result should be reduction of ions and not corrosion. Only the anode, buried in the soil and working as counter electrode for the cathodic protection of the pipeline should corrode. However, this is not the case... the situation seems similar to pulse reversal plating, but the result is different. The frequency, or the length of the individual pulses, in AC corrosion are very similar to the ones used in pulse plating of Ni or NiFe-alloys – as described above.

The main theory [26] regarding the mechanism behind AC corrosion of steel pipelines, is based on the formation of a passive film (mainly Fe_3O_4) during the anodic part of the half cycle – followed by a conversion of the passive layer into a porous layer of rust during the cathodic half cycle.

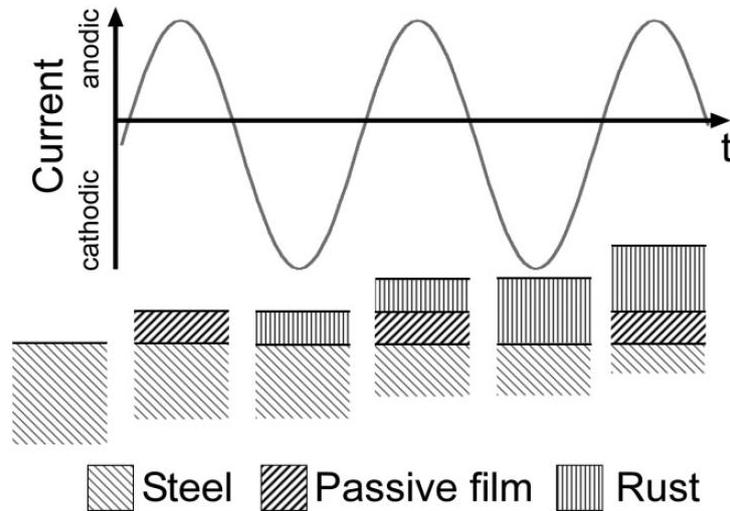


Fig. 7: Mechanism of AC corrosion of steel for cathodically protected pipelines with AC interference [26]

The formation of the passive layer is only possible during the anodic period in presence of water. Depending on the availability of oxygen in the soil, as well as other ions such as calcium and magnesium, several different compounds can form. Similar to pulse plating of NiFe, the oxidation of Fe(II) to Fe(III) plays a major role – particularly in terms of the amount of dissolved iron in the soil. As illustrated in table 2, $\text{Fe}(\text{OH})_3$ complexes are much stronger than $\text{Fe}(\text{OH})_2$ complexes, indicating that it will be easier to oxidize Fe(II) to Fe(III) during the anodic periods than to reduce Fe(III) to Fe(II) during the cathodic periods. This can, to some extent, explain why iron is not deposited on the steel pipe – although the pipeline is cathodically protected most of the time.

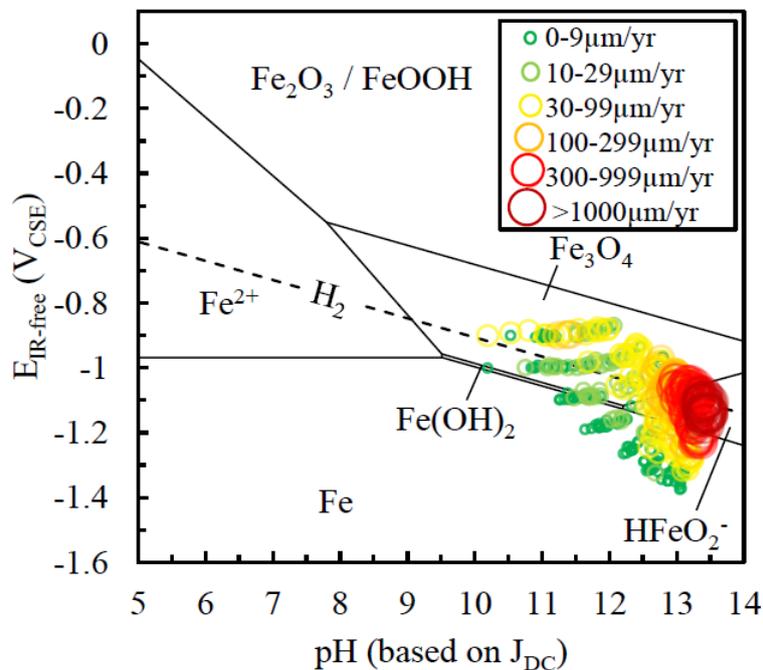


Fig. 8: Results from a series of corrosion experiments under potentiostatic cathodic protection, superimposed onto the Pourbaix diagram for iron [27]. The pH has been calculated based on the measure current (J_{DC}) at the set cathodic protection potential [27].

In Fig. 7 this is illustrated by showing the sinusoidal curve slightly moved into the cathodic region. The reason for the soil being alkaline near the coating defects of the pipeline is also created by the cathodic protection – following equation 6 above – leading to an alkalization of soil near coating defects.

The production of hydrogen gas, as a result of equation 6 during the cathodic periods, will lead to an alkalization of the soil in the vicinity of the coating defects. If the local pH increases beyond 12, iron could dissolve as HFeO_2^- as shown in the Pourbaix diagram of fig. 8. Corrosion experiments made by Olesen [27] have shown (see also fig. 8) that corrosion is particularly strong if the applied cathodic potential is high in combination with a strong AC interference level. In this case the soil pH could exceed 12 and the conditions near the coating defects will match those of the HFeO_2^- area of the Pourbaix diagram above.

5 CONCLUSION

Excessive cathodic protection should be avoided. High levels of cathodic protection can lead to alkalization of the soil, formation of hydrogen gas near coating defects could mechanically remove more coating (and make the defects larger) and the power consumption to maintain the cathodic protection will be larger than needed.

Having no cathodic protection, or a very modest protection, will also lead to AC corrosion. One solution could be, if a technically feasible solution can be found, to change the constant DC potential (or current) of the cathodic protection, into a pulsed cathodic protection. The pulsed protection should follow, using a sensor in the ground or another type of direct feedback loop, the alternating current from the high voltage transmission lines.

6 REFERENCES

- [1] C.P. Watts, Trans. Electrochem. Soc., Vol. 29, pp. 395 (1916)
- [2] P. Møller & L.P. Nielsen, "Advanced Surface Technology", ISBN 978-87-92765-17-B, Møller and Nielsen (2013)
- [3] P.T. Tang, H. Dylmer & P. Møller, "Nickel Coatings and Electroforming Using Pulse Reversal Plating", AESF SUR/FIN'95, pp. 529-536, Baltimore Jun. 26-29 (1995)
- [4] P.T. Tang, T. Watanabe, J.E.T. Andersen & G. Bech-Nielsen, "Improved corrosion resistance of pulse plated nickel through crystallisation control", J. of Applied Electrochem., Vol. 25, pp. 347-352 (1995)
- [5] W. Paatsch, "Galvanotechnik mit Strompulsen", Metalloberfläche, Vol. 40, No. 9, pp. 387-390 (1986)
- [6] P.T. Tang, P. Leisner & P. Møller, "Improvement of Nickel Deposit Characteristics by Pulse Plating", AESF SUR/FIN '93, pp. 249-256, Anaheim Jun. 21-24 (1993)
- [7] J.W. Dini, "Electrodeposition - The Materials Science of Coatings and Substrates", Noyes Publ. (1993)
- [8] J. Horkans, "Effect of Plating Parameters on Electrodeposited NiFe", J. Electrochem. Soc., Vol. 128, No. 1, pp. 45-49 (1981)
- [9] A. Brenner, "Electrodeposition of Alloys", Academic Press, New York (1963)
- [10] W.H. Safranek, "The Properties of Electrodeposited Metals and Alloys", AESF, Florida (1996)
- [11] H.V. Venkatesetty, "Electrodeposition of Thin Magnetic PermAlloy Films", J. Electrochem. Soc., Vol. 177, No. 3, pp. 403-407 (1970)
- [12] S. Arai & T. Watanabe, "The electroplating of Sn-Ag alloy for the use of Pb-free solder film", MRS Symposium, Tokyo May (1996)
- [13] A. He, B. Djurfors, S. Akhlaghi & D.G. Ivey, "Pulse Plating of Gold-Tin Alloys for Microelectronic and Optoelectronic Applications", proceedings of AESF Sur/Fin, Chicago, 9 pages, June 24-27 (2002)
- [14] P.T. Tang, "Pulse Reversal Plating of Nickel and Nickel Alloys for MEMS", Proceedings pp. 224-232, SUR/FIN 2001, Nashville, 25-28 June (2001)

- [15] G. Ekström (ed.), "Lärebok i Elektrolytisk och Kemisk Ytbehandling", (in Swedish) Ytforum Forlåg AB (1990)
- [16] I. Mizushima, P.T. Tang, H.N. Hansen & M.A.J. Somers, "Residual stress in Ni-W electrodeposits", *Electrochem. Acta*, Vol. 51, pp. 6128-6134 (2006)
- [17] K. Tajiri & T. Imamura, "Periodic Reverse Copper Electroforming from a Low Cu-content Acid Copper Sulfate Bath", *Plating & Surface Finishing*, Vol. 2, pp. 60-63 (2001)
- [18] J.V. Powers & L.T. Romankiw, US 3,652,442, March 28 (1972)
- [19] E.E. Castellani, J.V. Powers & L.T. Romankiw, US 4,102,756, Juli 25 (1978)
- [20] T. Osaka et al., "Influence of Crystalline Structure and Sulfur Inclusion on Corrosion Properties of Electrodeposited CoNiFe Soft Magnetic Films", *J. Electrochem. Soc.*, Vol. 146, No. 6, pp. 2092-2096 (1999)
- [21] A.F. Bogenschütz & U. Georg, "Galvanische Legierungsabscheidung and Analytik" (in German), Eugen G. Leuze Verlag, Saulgau (1982)
- [22] K. Smistrup, P.T. Tang, O. Hansen & M.F. Hansen, "Microelectromagnet for magnetic manipulation in lab-on-a-chip systems", *J. Magn. Magn. Mat.* Vol. 300, pp. 418-426 (2006)
- [23] J.G. Speight, "Lange's Handbook of Chemistry", McGraw-Hill, New York (2005)
- [24] R.J. Lash, "Electroplating Iron Group Metal Alloys", US 4,129,482 patent, Dec. 12 (1978)
- [25] K. Korsbæk & R. Rubæk, "Udvikling og karakterisering af magnetiske legeringer til mikromekaniske komponenter" (in Danish), master thesis at IPL, Technical University of Denmark (2004)
- [26] M. Büchler, "Alternating current corrosion of cathodically protected pipelines: Discussion of the involved processes and their consequences on the critical interference values", *Mat. & Corr.*, Vol. 63, No. 12, pp. 1181-1187 (2012)
- [27] A.J. Olesen, "AC Corrosion of Cathodically Protected Pipelines", Ph.D.-thesis, Technical University of Denmark, Dept. of Mech. Eng. (2018)