

Electroplating of Metal Matrix Composites by Codeposition of Suspended Particles

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I. INTRODUCTION

It is well known that insoluble substances present in an electroplating bath codeposit with the metal and become incorporated in the deposits.¹ In conventional electroplating processes various bath purification methods, like continuous filtering and anode bagging, are employed to avoid incorporation of insoluble anode debris (oxide, alloying elements), airborne dust and solid drag-out from pre-treatment baths. These incorporated substances generally have a strong adverse effect on the deposit properties. The advantages of second phase material incorporated in metallic deposits were realized only later.

In electrochemical composite plating inert particles are deliberately added to the plating bath to obtain metal matrix composite coatings. Figure 1 shows an example of metal matrix composite coating of electroless nickel-phosphorous in which silicon carbide particles are incorporated. The particle materials used should be inert to the bath in the

sense that they do not dissolve into the bath. Different types of particles with a variety of properties, for example pure metals, ceramics and polymers, can be used. Combined with the variety of metals, which can be electrodeposited, electrochemical composite deposition enables the production of a wide range of composite materials. Compared to the plain metal coatings the composite coatings have improved physical and (electro)chemical properties.

Electrochemical composite plating combines the advantages of metal electroplating with those of composite materials. It requires only minor adjustments of proven and economical viable electroplating technology. Ideally, addition of particles to a standard electroplating bath suffices. Particularly in the field of composite coatings it compares favorably to other methods to produce composite materials with a metallic matrix. The most widely used methods are powder metallurgy, metal spraying and internal oxidation or nitridation.²⁻⁴ Disadvantages of these techniques are that they need to be performed at high temperatures and often necessitate complicated and expensive equipment, which are not viable on industrial scale for numerous applications.

In recent years several excellent review papers on electrochemical composite plating have been published by Celis *et al.*⁵⁻⁸ The uses and mechanism of the composite plating process are the main topics discussed

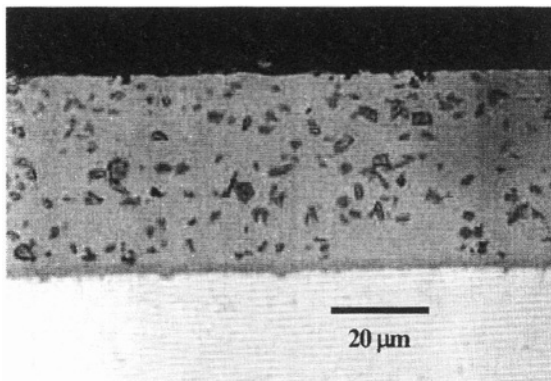


Figure 1. Cross-section of an electroless nickel-phosphorous coating on aluminium 6063-T6 with incorporated silicon carbide particles.

in these papers. Hovestad and Janssen⁹ published a review paper in 1995, which also includes the experimental facts reported in literature. The present chapter is an updated and extended revision of this earlier paper.

II. PROPERTIES AND APPLICATIONS

The first application of electrochemically deposited composites dates back to the beginning of this century. Sand particles held by a nickel matrix were utilized as anti-slip coatings on ship stairs. In 1928 Fink and Prince¹⁰ investigated the possibility of using electrochemical composite deposition to produce self-lubricating copper-graphite coatings for use in car engines. Apart from these early attempts until about forty years ago little research was done in the field of electrochemical composite plating. In the early sixties the interest in the technique grew and new applications of electrodeposited composites were found. Particularly, the use of Ni-SiC and Ni-PTFE coatings in the automotive industry has accelerated the research in the last 15 to 20 years. The increasing demand for new materials having precisely defined properties offers a promising perspective for further applications of electrodeposited composites.

Applications of electrodeposited composites are generally determined by properties exhibited by the particles. The metal matrix merely serves as a dispersing medium for the particles. Frequently used particle materials like SiC, Al_2O_3 and diamond can be applied as a single coating on a metal substrate by vacuum deposition techniques, but it is difficult to deposit uniform and cohesive coatings and to coat complex shaped products. The difference in physical properties, like the coefficient of thermal expansion, between ceramics and metals often requires one or more intermediate layers are required to obtain a good adhesion to the metallic substrate. In a metal matrix composite the metal provides the adhesion to the substrate and keeps the particles together. The applications of electrochemically deposited composites can be divided into three main categories: Dispersion hardening, wear resistance and electrochemical activity.

1. Dispersion Hardening

Electrochemically deposited composites containing particles of refractory compounds, like oxides,^{4,11-16} nitrides,^{15,17,18} carbides^{14,15,19-23} or borides²⁴

are dispersion hardened compared to the plain metal as evidenced by improved mechanical properties. The micro hardness, ultimate tensile strength and yield strength are considerable higher and the elongation percentage is reduced. For example, the micro hardness of a composite of Ni with 2.4 vol% Al_2O_3 particles is a factor of 1.5 higher than that of pure Ni.¹⁹ Note that the hardness of the composites is still of the same order as that of the metal and that the particle materials are very much harder.¹⁶ The incorporation of soft materials, like MoS_2 , graphite¹⁴ or PTFE²⁵ has the reverse effect on the mechanical properties, that is it reduces hardness and strength.

Dispersion hardening or strengthening of a material means an increased resistance to deformation. The movement of dislocations in the metal facilitates metal deformation. Incorporated particles block the dislocation movement and thus strengthen the metal.^{4,11,12,21} Grain refinement of the metal due to the codeposition of particles has also been thought to contribute to the hardening effect, but this is not supported by experimental evidence. For several composites it was found^{4,12,13,26} that the grain structure of the metal matrix was not altered by the codeposition of particles.

In most investigation^{4,11,15-18,20,22,23} enhanced hardening was observed with an increase in the volume fraction incorporated particles,^{4,11,20} a decrease in particle size^{4,11} and a reduction in particle agglomeration.⁴ A linear relationship between the composite hardness and the square root of the volume fraction incorporated particles has been reported.^{4,22} The effect of composite deposition conditions, like particle bath concentration, current density or pH, on the dispersion strengthening can all be related to changes in the particle composite content.^{4,15-18,22,23,25} Hence the effectiveness of the dislocation movement blockage increases with decreasing (effective) interparticle distance.^{4,15} A high volume fraction of small particles finely dispersed through the metal matrix will therefore yield optimal hardening. It should be mentioned that there is no unlimited increase in dispersion strengthening with the volume fraction incorporated particles.^{13,14} Brown and Gow¹³ found a maximum ultimate tensile strength and hardness for Fe- Al_2O_3 composite at approximately 10 vol% Al_2O_3 .

A heat treatment of as-plated composites is sometimes^{5,19} considered necessary to achieve maximum hardening. Reported investigations^{4,11,12,23} do not show a significant improvement in the mechanical properties of annealed composites, but composites do retain their strength up to higher

temperatures. This makes the composites suitable for high-temperature applications. Nickel loses its mechanical strength when annealed above 700 K, whereas the strength of Ni-Al₂O₃ composites is lost above 1300 K.¹² Just as the strengthening, the strength retention of composites can be attributed to the blockage of dislocation movement by incorporated particles.¹² The loss of strength of a metal at high temperatures is due to the recrystallization of the metal, which is accompanied by the annihilation of dislocations. Verelst *et al.*¹¹ showed that grain refinement during recrystallization and some unknown process are also involved.

Dispersion hardened composites are mainly applied as free-standing structures, like bearings, die cavities or nozzles²¹ and not as coatings. Electrodeposition is therefore not the most suitable preparation method for dispersion hardened composites. In specialized applications, like the electroforming of hollow balls with high thermostructural stability as described by Verelst *et al.*,¹¹ electrochemical composite plating is a useful alternative. The potential use of electroformed parts in microtechnology and the increasing availability of nano-sized particles might lead to a renewed interest into electrodeposited dispersion hardened composites in the future.

2. Wear Resistance

Particularly in the field of wear resistant coatings appear the advantages of electrochemical composite plating. The actually realized industrial applications of composite coatings are found in this field.^{2,3,5,6} Incorporation of particles of either hard or low-friction materials strongly enhances the wear resistance of a metal coating. A coating of electrodeposited composite can considerably extend the lifetime of surfaces of tools, engine parts and machine parts that are in moving contact. Gages, dowel pins, saw blades, wood chisels and stamping mandrels coated with Ni-SiC last up to 10 times as long as tools made of hard chrome plated tool steel.²¹ The effectiveness and lifetime of dentist drills is considerably enhanced by Ni-diamond coatings. Abrasion resistant Ni-SiC coatings are employed as cylinder lining or on piston rings in motor blocks of aluminum alloys^{22,27} and coatings of Ni-PTFE are applied among others to reduce the wear of threads and low water adhesion coatings in condenser pipes.

(i) *Abrasion Resistance*

Coatings of composites containing particles of hard materials, like BN,¹⁷ diamond,^{20,28} WC,²¹ SiC,^{21,22,27,29} Al₂O₃,^{21,26,30} and TiC²³ were shown to have much higher resistance to abrasive wear than plain metal coatings. Composites of Ni-3vol%TiC have a factor of 4 lower weight loss than Ni in a cyclic Taber wear test.²³ Similar to the dispersion hardened composites wear resistant coatings require a high concentration of small particles.^{17,23,27,30} A high and uniform surface coverage of particles provides a large contact area and the smaller the particle size the more difficult they are removed during abrasion. However, investigations³⁰ on Cr- and CrNi- Al₂O₃ coatings indicate that a too high amount of incorporated particles should be avoided, because the composites become brittle. In general a particle volume fraction of 0.1 can be considered optimal. Composite coatings containing hard particles require careful and extensive grinding and polishing. Hard particles sticking out from the composite surface can dramatically increase the wear of opposite surfaces.

(ii) *Lubrication*

Another way of reducing the wear of metal surfaces in moving contact is through augmented lubrication. Nickel-SiC coatings have a factor 2 to 3 higher lubricated wear resistance than Ni, because the protruding SiC particles retain an oil film on the composite surface.²² Otherwise, particles of low friction materials like PTFE,^{19,25,31} graphite²⁹, BN or MoS₂²⁹ included in a metal coating are used to reduce the friction between sliding metal surfaces.

Electrodeposited Cu-graphite coatings show a substantial lower coefficient of friction and rate of wear than Cu/Sn alloys or sintered bronze PTFE composites.²⁹ In frictional contact Ni-PTFE composites act as self-lubricating coatings, which slowly erode away thus releasing incorporated particles, which are smeared out over the surface.²⁵ In a similar manner a recent development³² in electrochemical composite plating allows wet lubrication of metal surfaces. Microcapsules containing a liquid lubricant are incorporated in a metal. During use the microcapsules gradually wear away, thereby releasing the liquid lubricant. Since, electrochemical composite plating is practically the only method where liquids can be incorporated in metals, it opens up a new range of potential applications.⁵

3. Electrochemical Activity

A prerequisite for any application of a metal is a sufficient resistance to corrosive attack under operating conditions. Since a good resistance against corrosion does not naturally accompany favorable functional properties of a material, protective coatings are routinely applied. Certain composite coatings are suited for corrosion protective coatings of, among others, automotive body panels.³³ The improved corrosion resistance is achieved either directly by the composite itself or indirectly, that is as part of multiple-component coating system. In the first case corrosion resistance of the composite is due to the dispersed phase changing the electrochemical activity of the metal matrix. Otherwise composites containing (electro)chemically active particles could be used as catalytic electrodes in, for example, fuel cells.

(i) Corrosion Resistance

Composites of Ni and Al_2O_3 ,^{33,34} Cr_2O_3 ,¹⁵ SiC ,¹⁵ Si_3Ni_4 ,¹⁵ TiO_2 ³³ and SiO_2 ³³ show decreased corrosion rates under certain conditions compared to Ni. The dissolution rate of Ni-6 vol% Si_3Ni_4 is a factor 3 lower than that of Ni in $100 \text{ mol m}^{-3} \text{H}_2\text{SO}_4$.¹⁵ The electrochemical mechanism responsible for this reduced corrosion has not yet been elucidated. The effects of composite composition and the type of corrosive environment on the corrosion resistant of a composite are not straightforward. For some composites^{33,35} the corrosion rate decreases with particle content, whereas for others^{17,33} the opposite is observed. Ramesh Babu *et al.*³⁶ reported that at pH 3 in a NaCl solution a Ni- V_2O_5 composites corrodes faster than Ni, but at pH 6.5 the corrosion rate is similar. The electrochemical activity of the particles, the presence of a metal/particle interface and changes in the metal matrix structure due to particle codeposition seem to be the main factors contributing to the corrosion resistance of composites.

Enhanced oxidation resistance was also found at elevated temperatures for Co- Cr_3C_2 ,³⁵ Ni- Cr_2O_3 ¹⁵ and Ni- Si_3Ni_4 ¹⁵ composites. In contrast Ni-SiC¹⁵ and Ni-TiC²³ composites have a higher hot oxidation rate than nickel. During hot oxidation porous metal oxide scales are formed at the metal-air interface. At elevated temperature interdiffusion between the particles and the metal in composites affects the formation of these scales. The break down of TiC particles in Ni-TiC composites accelerates corrosion by favoring the formation of nickel oxide.²³ In

$\text{Co-Cr}_3\text{C}_2$ ³⁵ composites the carbide particles supply chromium to a mixed cobalt/chromium oxide scale, which improves corrosion protection. If these composites are heat-treated in the absence of oxygen, a homogeneous cobalt-chromium alloy is formed showing an even better corrosion resistance than conventional cobalt-chromium alloys.³⁵ Similarly, Stainless steel type anti-corrosion coatings are obtained by subjecting Ni-Cr³⁷ or Fe/Ni-Cr³⁸ composites to a homogenizing heat-treatment.

Takahashi *et al.*³⁹ used SiO_2 particles to obtain Zn/Cr- SiO_2 coatings exhibiting excellent corrosion resistance. The SiO_2 particles themselves hardly affect the corrosion rate, but they promote codeposition of chromium, which reduces the susceptibility to corrosion. Tomaszewski *et al.*³⁴ reported enhanced corrosion protection by nickel composites, with various submicrometer particles, covered by a thin chromium finish. The fine dispersion of particles in the nickel matrix makes the composite porous and this porosity is retained in the thin chromium layer. Numerous tiny chromium cathodes surrounded by numerous tiny Ni anodes are formed, which reduces the net corrosion current. Finally, a composite coating can be used to reduce corrosion by enhancing the adhesion of a protective lacquer to a metal substrate.⁵ On the metal substrate the composite, a primer and the lacquer are successively applied. The metal matrix provides the adhesion to the substrate and holds the particles. Functional groups of the primer adhere to the lacquer and the particles.

(ii) *Electrocatalysis*

In chloralkali cells, electro-organic oxidation processes and batteries there is a need for electrodes with a high electroactive area. Relatively new is the use of electrochemical composite plating in the preparation of these electrocatalytically active electrodes.^{40,41} Powder of the electroactive material is kept together by the metal matrix, which serves as the current collector. A Ni-LaNiO₃ composite⁴¹ was found to be an effective and stable electrocatalyst for hydrogen evolution. Compared to sintered or electrodeposited Ni the polarization curve in alkaline solutions is shifted to lower potentials. If this due to an increase in surface area or an electrocatalytic effect of the LaNiO₃ is not clear. Keddam *et al.*⁴⁰ prepared Ni-Ni(OH)₂ composites to investigate the electrochemical activity of Ni(OH)₂ particles used in Ni-Cd battery. Since here the particles and not the composite are the object of study, it was verified that the activity of a

Ni-NiOH₂ composite electrode is fully determined by the NiOH₂ particles. These two examples show that composites can be suitable electrocatalytic electrodes. Though it is clear that more research has to be done to find out the full potential of electrochemical composite deposition in the preparation of electroactive electrodes.

III. PROCESS PARAMETERS

The amount of incorporated particles is the parameter characterizing a metal matrix composite. As discussed in the previous section it largely determines the composite properties. In order to obtain a composite exhibiting certain properties, the effect of process parameters on the particle composite content has therefore to be known. Apart from the practical significance knowledge of these effects is also a prerequisite for the understanding of the mechanism underlying particle codeposition.

Through the years it has been found that numerous process parameters directly or indirectly affect the particle composite content. These parameters can be divided into three main categories:

- 1) particle properties:
 - particle material
 - particle size
 - particle shape
- 2) bath composition:
 - constituents
 - pH
 - additives
 - aging
- 3) deposition variables:
 - particle bath concentration
 - current density
 - electrolyte agitation
 - temperature

A straightforward effect of a single parameter on the particle composite content can not always be given, because the influence of several parameters is interrelated. The fact that some parameters have been investigated extensively, whereas others were hardly examined even

adds to this difficulty. If possible a general effect of a certain parameter will be given, else the various effects reported will be discussed.

The mechanism of particle incorporation is treated extensively in the next section, but a generalized mechanism is given here to better comprehend the effects of the process parameters. Particle incorporation in a metal matrix is a two step process, involving particle mass transfer from the bulk of the suspension to the electrode surface followed by a particle-electrode interaction leading to particle incorporation. It can easily be understood that electrolyte agitation, viscosity, particle bath concentration, particle density etc affect particle mass transfer. The particle-electrode interaction depends on the particle surface properties, which are determined by the particle type and bath composition, pH etc., and the metal surface composition, which depends on the electroplating process parameters, like pH, current density and bath constituents. The particle-electrode interaction is in competition with particle removal from the electrode surface by the suspension hydrodynamics.

1. Particle Properties

The particle properties are the least controllable process parameters. The choice of particle material is limited by the desired composite properties. The chosen particle material and (commercial) availability again restrict particle shape and size. Consequently the particle properties set the limits for the attainable particle composite contents.

(i) Particle Material

Comparison of different particle materials is very difficult, because generally particle shape and size will also vary, but it is clear that differences in particle density and surface composition will affect particle incorporation. Greco and Baldauf⁴ noticed that three times as much TiO_2 is incorporated in a Ni matrix as Al_2O_3 under the same deposition conditions. Moreover, SiC ⁴² and Al_2O_3 ^{43,44} particles of different crystal structure yield composites with different particle content. The apparent impossibility of incorporating Al_2O_3 particles in Cr⁴⁵ and $\gamma\text{-Al}_2\text{O}_3$ in Cu⁴³ was overcome by changing the particles surface composition by means of dry grinding and calcining respectively.⁴⁶ Similarly, for Ni-SiC composites⁴² it was shown that the surface composition of the particles

that is the SiO/SiC ratio at the surface plays determines the particle codeposition.

Due to their hydrophobic character BN particles strongly aggregate in electrolyte solutions as is shown for an electroless Ni(P) bath in Figure 2.¹⁰⁷ Particle aggregation results in low particle incorporation in the Ni(P) coating. Particle codeposition is inhibited either by a reduction in particle bath content, because of particle flotation accompanied by strong foaming on top of the plating bath or dominant particle removal by hydrodynamics at the composite surface due the large size of the aggregates. Addition of a surfactant (see Section III.2.iii) facilitates suspension of BN particles and increases the composite particle content from around 1 to 15 vol%. However, Fig. 2 shows that also an oxide modification of the BN-particle surface can prevent particle aggregation and result in a Ni(P) composite

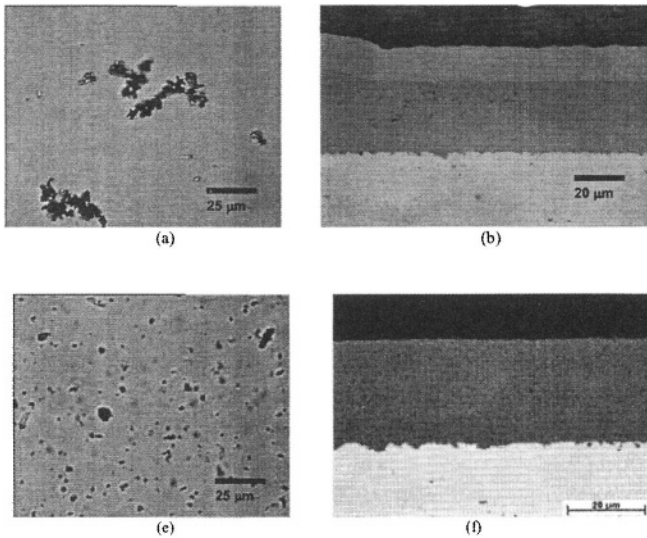


Figure 2. Optical microscope pictures of an electroless Ni(P) bath with suspended BN particles of 3 μm mean diameter (a,c) and a cross-section of the composite deposited from these baths (b,d); untreated (a,b) and oxide treated (c,d) particles.¹⁰⁷

with 15–20 vol% of finely distributed particles. The oxide modification changes the surface composition of the particle from mainly BN with about 3% B_2O_3 , to a high oxide content.

The discussed examples clearly point out that the different interaction of for example particle surface oxides compared to particle surface nitrides and carbides with the electrolyte and the metal surface significantly affects particle incorporation. Note that, although it is often observed, it should not be concluded from the presented examples that oxide or oxide-covered particles will always codeposit more easily than non-oxides. Changing the surface of the BN particles to a silicon oxide does not prevent aggregation or enhance codeposition.¹⁰⁷

Though it was stated that composite plating involves particles inert to the bath, particles do always interact with the electrolyte. Chemical and physical adsorption of electrolyte ions onto the particle occurs.⁴⁷ This adsorption and the initial particle surface composition determine the particle surface charge, which induces a double layer of electrolyte ions around the particle. In electrolytes double layers play a major role in the interactions between particles and between particles and the electrodes. According to the DLVO theory^{48,49} surfaces in electrolytes interact through the competitive action of attractive and repulsive forces. Overlap of double layers results in the electro-osmotic force, which is repulsive for surfaces of like charge and attractive for surfaces of unlike charge. In an electroplating bath the applied electrical field will also exert an electrophoretic force on the particle double layer.

In view of this Tomaszewski *et al.*⁵⁰ proposed that particles with a positive charge codeposit more easily, because they are attracted to the negatively charged cathode. It was noticed that in a sodium sulfate electrolyte negatively charged SiO_2 particles move much more difficult to the cathode than the positively charged Al_2O_3 particles. Lee and Wan⁵¹ quantified this by determining the ζ -potential, which is a measure for the double layer interactions. Corresponding to their respectively high and low particle composite content, the ζ -potential of α - Al_2O_3 is positive and that of γ - Al_2O_3 is negative in a dilute copper sulfate bath. In contrast measurements under practical conditions, that is in concentrated copper sulfate⁵² and chromium/nickel chloride⁵³ baths, yield a negative ζ -potential for α - Al_2O_3 particles due to strong anion adsorption. Despite the negative charge α - Al_2O_3 codeposit readily from these baths.

As will also be shown later for charged surfactants adsorbed on codepositing particles, it can be concluded that the particle material

influences the particle composite content through the particle surface composition, but that this is not determined by the particle charge. Other interaction forces, like the London-Van der Waals force or hydration force, dominate and are responsible for the effect of particle material on particle composite content as will be discussed further in the Section IV.

Apart from the surface composition the bulk properties of a particle material will affect composite deposition. Particle mass transfer and the particle-electrode interaction depend on the particle density, because of gravity acting on the particles. Since the particle density can not be varied without changing the particle material, experimental investigations on the effect of particle density have not been performed. However, it has been found that the orientation of the plated surface to the direction of gravity combined with the difference in particle and electrolyte density influences the composite composition. In practice it can be difficult to deposit composites of homogeneous composition on products where differently oriented surfaces have to be plated.

A horizontal cathode facing upward results in a high particle composite contents of particles denser than the electrolyte, because gravity causes the particles to settle on the cathode.⁵⁴ Using a mathematical model (Section IV.3.iii) Fransaei^{55,56} calculated a maximum particle density of 1240 kg m^{-3} for a rotating disc electrode facing downward, because gravity imparts heavier particles to come in contact with the electrode. In reality denser particle can be codeposited on a RDE, because particle-particle collisions allow heavier particles to reach the electrode and become incorporated.

Tacken *et al.*⁵⁷ showed that magnetically charged Ni particles retain their magnetization, when they are suspended in a zinc deposition electrolyte. This remanent magnetization attracts the particles to the steel cathode, where up to three times as much magnetically charged as uncharged particles are incorporated. Figure 3 clearly shows that the magnitude of the remanent magnetization determines the amount of incorporated Ni particles. The electrical conductivity of particles can not be controlled, but conductive particles behave different in composite plating from isolating ones. Conductive particles tend to agglomerate on the composite surface during deposition.⁵⁸ Rough and porous deposits are obtained,^{14,57} because as soon as the particles adsorb on the deposit surface metal deposition and hydrogen evolution occurs on them.

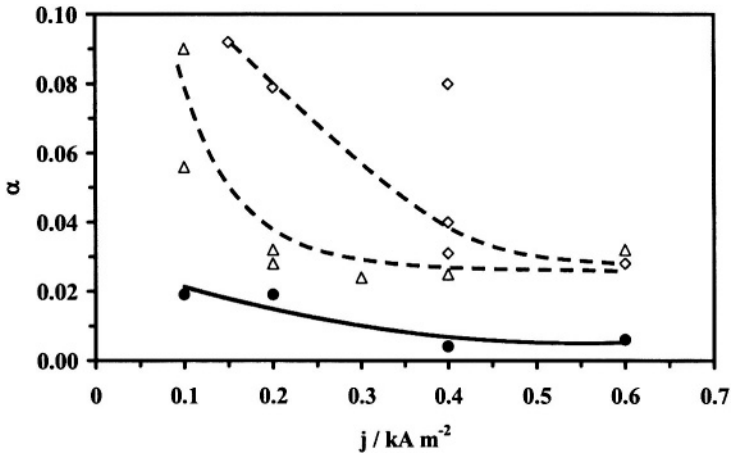


Figure 3. Mass fraction of Ni particles incorporated in Zn against the current density at $\phi_{\text{Ni}} = 0.0001$ and three remanent magnetizations of the particles: 0 (\bullet); 3300 A m^{-1} (Δ) and 8600 A m^{-1} (\diamond).⁵⁷

(ii) Particle Size

Regarding the effect of particle size on codeposition various results have been reported. For $\text{Ni-Al}_2\text{O}_3$,⁴⁵ Ni-SiC ⁴² and Ni-Cr ⁵⁸ an increase in the particle composite content was reported, if the particle size was increased. It was shown⁵⁹ that the amount of P codeposited with Cu increases linearly with the median volume size of the particles. Yet negligible influence of particle size for $\text{Ni-Al}_2\text{O}_3$ was observed¹¹ and for $\text{Ag-Al}_2\text{O}_3$ ⁶⁰ and $\text{Ni-V}_2\text{O}_5$ ³⁶ a lower deposition ratio for larger particles was reported. The latter behavior agrees with the obvious thought that smaller particles are more easily incorporated.

The inconsistency in these various investigations is possibly due to the choice of the units in which the particle content is expressed. Just as ion concentrations are expressed in moles, that is the number of ions per volume, the parameter to be considered is the number of particles suspended and incorporated.⁶¹ Volume or weight particle bath and composite content in fact yield an erroneous comparison of data obtained at different particle sizes. It was found⁶² that the weight percentage of SiC particles incorporated in Ni increases, whereas the number of SiC particle

incorporated decreases with increasing particle size. Even in this investigation the particle bath concentration is not expressed in numbers, however. It can be calculated from the presented data that if this done the difference between the SiC particle sizes considered is negligible. Further investigations, which take into account the particle number contents are required to unravel the exact effect of particle size on particle codeposition.

A negligible effect of the particle size would confirm the theoretical work of Bozzini *et al.*,⁶³ where it is predicted that instead of the absolute particle size the particle size distribution determines the particle composite content. This theoretical work is based on the discovery^{53,63,64} of preferential codeposition due to particle parking problems. Parking problems arise, because particles can not deposit onto particles already present on the cathode surface. Depending on the particle surface coverage there is a limiting particle size above which newly arriving particles can not find a site to deposit. Consequently a fraction of the particles does not contribute to particle incorporation. For Cr-Ni-Al₂O₃⁵³ the finer 50 % of the particles in the bath accounts for at least 80 % of the particle composite content. In current practice the particle size distribution is generally neglected, but a careful choice of the particle size distribution could be an prerequisite for operating a successful composite plating process.

(iii) Particle Shape

To the knowledge of the authors only one investigation on the influence of the particle shape on particle codeposition has been reported in the open literature.¹⁰⁸ It was found that codeposition of Al₂O₃ particles in electroless Ni(P) increases in the order fiber, irregular and spherical shaped particles. Again it should be noted that these results were obtained for similar particle mass bath load and not particle number bath load. The fiber shaped particles are the largest in size and therefore had the lowest number content, which could also explain their lower codeposition. The particle shape influence was not further investigated, but considering the particle incorporation mechanism several possible effects of particle shape can be imagined.⁶⁵

The particle shape determines the particles specific surface area and the observed order in increasing codeposition of the Al₂O₃ particle shapes corresponds to a decrease in the specific surface area.¹⁰⁸ The amount of

electrolyte ions adsorbed on the particles and thereby the strength of the cathode-particle adsorption will differ for the different particle shapes. Referring to the detailed discussion of the mechanism in section IV this might be related to a higher ratio of the hydration force to particle adhesion force for a larger particle specific surface area. Although it has not been reported until now anisotropy of particles could give rise to a preferred orientation of incorporated particles. For example, needle-like particles are expected to adsorb perpendicular and not normal to the growing metal surface.

2. Bath Composition

Although less constricted than the particle properties the electrolyte composition is also largely determined by the desired composite. The bath constituents and pH can be varied only within certain limits to ensure a metal matrix of sufficient quality. Additives present an effective way of regulating the particle composite content, but can have adverse effects on the deposit quality. Consequently, also the electrolyte composition poses restrictions on the attainable particle composite contents

(i) Bath Constituents

The influence of the main bath constituents on the incorporation of particles is evident. For different types of baths different incorporation rates are reported, when the same kind of particles are used. For example, Al_2O_3 particles codeposit in Cu- and Ni-baths, but not in a Cr-bath⁴⁵ and Cu- Al_2O_3 deposits could be produced in a copper cyanide bath, but not in a copper sulfate bath.⁴⁵ Quantitative investigations^{29,66} show that an increase in concentration of the main metal salt results in enhanced particle codeposition. Likewise, SiO_2 incorporation in Zn-Co, Zn-Ni or Zn-Fe alloy increases with increasing concentration of the Fe group metal salt.³⁹

Since the particle surface composition is determined by the adsorption of electrolyte ions, changes in surface composition of the particles are expected to play a role in the effect of the bath constituents. Kariapper and Foster⁶⁷ found that the amount of metal ions adsorbed on a particle increases with increasing metal ion concentration in the electrolyte. For SiC particles this was again related to the ζ -potential of the particles, because it was found⁶⁸ that the ζ -potential increases with

increasing electrolyte concentration. It should be mentioned that this was not a metal plating electrolyte. So a higher metal ion concentration is expected to increase the ζ -potential and consequently enhance the particle-cathode attraction and particle incorporation. As already discussed an electro-osmotic or electrophoretic attraction between the particles and the cathode, due to cation adsorption, is not essential for particle incorporation. In fact for α - Al_2O_3 in a copper sulfate bath it was found that about 7 times as much SO_4^{2-} is adsorbed on the particles as Cu^{2+} . It was concluded that indeed Cu^{2+} ions are adsorbed on the α - Al_2O_3 particles, but that their positive charge is more than compensated for by adsorbed SO_4^{2-} ions, resulting in a negative ζ -potential.

Figure 4 shows that in an electroless Ni(P) bath the H_2PO_2^- bath concentration reduces on addition of SiC or Al_2O_3 particles. The Ni^{2+} bath concentration and pH, not shown in Fig. 4, in contrast is not affected by particle addition. Very likely a negative charge is inferred on the particles

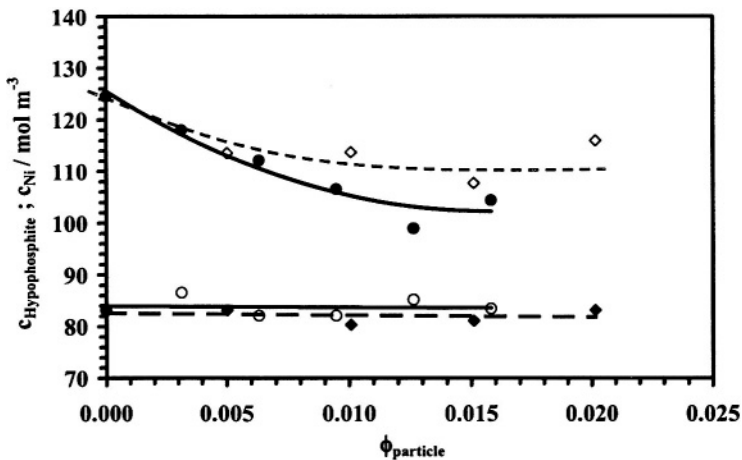


Figure 4. Nickel (\circ ; \bullet) and sodium hypophosphite (\diamond ; \blacklozenge) concentration in an electroless nickel plating solution at pH 5 as a function of the volume fraction suspended SiC (\circ ; \bullet) and Al_2O_3 (\diamond ; \blacklozenge) particles.¹⁰⁷

by strong adsorption of H_2PO_2^- anions instead of Ni^{2+} cations. The ζ -potential of the growing Ni(P) layer is unknown, but taking into account the fairly cathodic potential of -0.5 V vs. NHE measured for Ni(P) deposition it seems unlikely that the high particle incorporation, *i.e.*, 10–20 vol%, even at low particle bath contents, is caused by electro-osmotic interactions.

An adverse effect of adsorption of H_2PO_2^- , which is the reducing agent in the bath, is a decrease in plating speed in the presence of suspended particles. Additionally, adsorption of stabilizers results in a reduced stability of electroless bath containing suspended particles. Typically, the life-time of a Ni(P) bath is reduced from 10–15 metal turn-overs in a particle-free bath to around 5 in a particle-containing bath. Hence, through adsorption bath constituents do not only affect particle incorporation, but suspended particles also influence the metal deposition.

In metal plating baths often brighteners or wetting agents are present to improve the appearance of the deposit. Some of these additives act as surfactants, which can strongly affect particle incorporation as will be discussed in Section III.2.iii. Tomaszewski *et al.*³⁴ stated that brighteners can have several effects, but generally enhance particle codeposition. Greco and Baldauf⁴ confirmed this and named the use of wetting agents as a tool to increase the particle composite content. On the other hand, a decrease in particle content on addition of wetting agents has also been observed.^{44,45} It was suggested⁴⁵ that this is due to an increase in micro-throwing power, which leads to metal deposition behind the particles adsorbed at the cathode surface.

The metal surface properties also change with the bath constituents and thereby affect the particle-electrode interaction. Metal deposition constitutes a multi-step reaction mechanism that depends on the bath composition. In quite a number of reaction mechanism adsorbed intermediates, *e.g.* the presence of chromium and catalyst polyoxides on the metal surface during chromium plating, are involved. Not the metal surface, but the adsorbed intermediates will determine the particle-electrode interaction and might even compete for adsorption sites on the electrode surface with the particle. Although the reverse, *i.e.*, the change in metal deposition mechanism due to the presence of particles has been investigated (see Section 3.ii), no studies on the effect of the deposition mechanisms on particle codeposition have been reported.

(ii) pH

Investigations^{11,12,16,17,34,36,44,45,47,50,53,62,69} concerning the effect of bath pH on the particle content of various composites give comparable results. Particle incorporation decreases sharply below pH 2 to 3 and is practically constant or decreases slightly above this value. An exception is the deposition of Ni-TiC composite,²³ where TiC codeposition reduces continuously with increasing pH. As evidenced by changes in bath pH on particle addition, adsorption of H^+ ions on the particles is considerable. Together with the other electrolyte ions adsorbed H^+ ions, determine the particle surface composition and thus particle adsorption to the electrode. Besides the objections raised elsewhere, particle charge effects are certainly not involved. It was shown^{68,70} that in the absence of metal ion adsorption the iso-electric point, where the ζ -potential equals zero, of SiC particles is reached at pH 2. Although the iso-electric point will be different in a plating bath due to the adsorption of other ions, the ζ -potential increases with decreasing pH, whereas particle incorporation decreases.

The amphoteric nature of oxide particles or oxide covered particles allows both H^+ adsorption and desorption. Due to the relatively high surface area of suspended particles H^+ adsorption or desorption can significantly alter the bath pH. Depending on the initial bath pH and the pretreatment of the particles, that is their initial surface composition, the bath pH either decreases or increases with time on addition of SiC⁷¹ or Al_2O_3 ^{47,52} particles. The magnitude of the change in bath pH on particle addition decreases with increasing metal ion concentration due to the competitive adsorption of metal ions and H^+ ions.^{47,71} Since adsorbed metal ions are by some (Section IV) considered essential for particle incorporation the decrease in particle composite content is attributed⁴⁷ to prevalence of H^+ adsorption at low bath pH. It has indeed been found⁷⁰ that metal ion adsorption increases with increasing bath pH.

Otherwise changes in metal deposition behavior with pH could be involved. Due to the competition between reduction of metal ions and hydrogen ions at the cathode the pH affects metal deposition. The current efficiency⁷⁰ of nickel deposition was seen to decrease markedly below pH 2 in the presence of SiC particles. Unfortunately, it was not determined if this effect is accompanied by a decrease in particle content below pH 2.

(iii) Additives

In order to enhance particle incorporation numerous additives for composite plating electrolytes were investigated. The addition of small amounts of monovalent cations, like Tl^+ , Ce^+ , Rb^+ and NH_4^+ , or amines, like tetra-ethylene pentamine (TEPA), alanine and ethylenediamine tetraacetic acid (EDTA) promotes particle codeposition.^{44,50,51,67} The $BaSO_4$ particle content in a copper matrix increases from 0.5 to 4.5 wt% on addition of 25 g l^{-1} EDTA.⁵⁰ Although the promoting effect is caused by the monovalent cations the anions of the added salts also play a role. For example, NH_4Cl yields a higher $BaSO_4$ composite content than NH_4F . An additional advantage of these additives is that they are not incorporated in the composite.^{44,50,72} The addition of Tl^+ , TEPA or EDTA raises the amount metal ions adsorbed on the particles,⁶⁷ but the additives themselves are not adsorbed on the particles.^{44,72}

It is assumed that these additives catalyze particle incorporation by enhancing metal ion adsorption. The relation between adsorbed metal ions and particle codeposition is still controversial (Section IV), so it can not be excluded that other processes play a role. The additives will also affect the metal deposition behavior through complexation of metal ions (EDTA, NH_4^+) or adsorption at the metal surface (Tl^+ , amines). These processes have to be investigated to obtain a definite explanation for the promoting effect of these additives.

Another class of additives, which were found^{10,30,31,42,65,68,73,74} to promote particle incorporation, are surface-active molecules or surfactants. Surfactants are usually employed to stabilize suspensions that are to prevent particle aggregation. In highly concentrated electrolytes the double layer of suspended particles is strongly compressed by the electrolyte ions. The repulsive electro-osmotic force between particles becomes negligible compared to the attractive London-van der Waals force and particles aggregate. Surfactants preferentially adsorb on particles and through mutual electro-osmotic or steric repulsion oppose particle aggregation. Despite the high electrolyte concentrations used in composite deposition baths particle aggregation was hardly found to be a problem. Only certain hydrophobic particles, like graphite,¹⁰ polystyrene^{54,75,76}, BN ¹⁰⁷ and $PTFE$ ^{31,73,74} require surfactant to prevent their agglomeration in a composite deposition bath.

For $PTFE$ incorporation in Ni non-ionic fluorosurfactants were used to obtain an agglomerate-free suspension. Combined with a cationic fluorosurfactant they allow the deposition of composites containing up to

70 vol% PTFE particles.^{31,73,74} Here, the use of surfactants is particularly successful, because PTFE particles are very hydrophobic and the affinity of fluorocarbon surfactants to the fluoropolymer PTFE is large. However, Helle^{31,73} showed that cationic fluorocarbon surfactant also produces a dramatic increase in particle composite content for SiC and diamond particles. It is assumed that the beneficial effect of a cationic surfactant is due to the positive charge they confer on the particles, which results in an electroosmotic and electrophoretic attraction to the negatively charged cathode. It was already discussed though that the significance of these interactions in composite plating is doubtful. Hu et al.⁷⁴ measured that the ζ -potential of PTFE becomes increasingly positive on addition of cationic fluorosurfactants, but contrary to their conclusions the obtained PTFE composite content does not vary correspondingly.

Other investigations also prove the assumption of an influence of surfactant charge wrong. The incorporation of polymeric microcapsules in Ni³² is enhanced by addition of sodium dodecyl sulfate, which is an anionic surfactant. Figure 5(a) and 5(b) show that for polystyrene incorporation in zinc^{54,75,76} in the presence of surfactant concentrations lower than 0.005 mol per kg of particles the volume fraction of incorporated polystyrene is equal to that without surfactant, namely 0.06 ± 0.02 , independent of surfactant type. In the presence of the cationic surfactant cetylpyrrolidinium chloride a strong increase in polystyrene incorporation is found at higher concentrations.

At higher concentration of other cationic surfactants, cetylammmonium chloride and bromide, the anionic surfactant sodium dodecylsulphate or the nonionic surfactant **nonylphenol(ethoxylate)₂₈(propoxylate)₁₃** polystyrene incorporation is reduced and becomes practically zero. It is clear that there is no correlation between the change in polystyrene incorporation and the surfactant charge. Increased wetting of the particles due to adsorbed surfactants does also not contribute to promotion or inhibition of particle codeposition by the surfactants. Aggregation of polystyrene particles is prevented at high surfactant concentrations,^{54,75,76} for all investigated surfactants but **nonylphenol(ethoxylate)₂₈(propoxylate)₁₃**.

The surfactants only slightly affect polystyrene incorporation up to the surfactant concentration where surfactant adsorption on the particles is maximal,^{54,76} that is **0.02 mol kg⁻¹**. At higher surfactant concentrations the amount of free surfactant that is not adsorbed on the particles

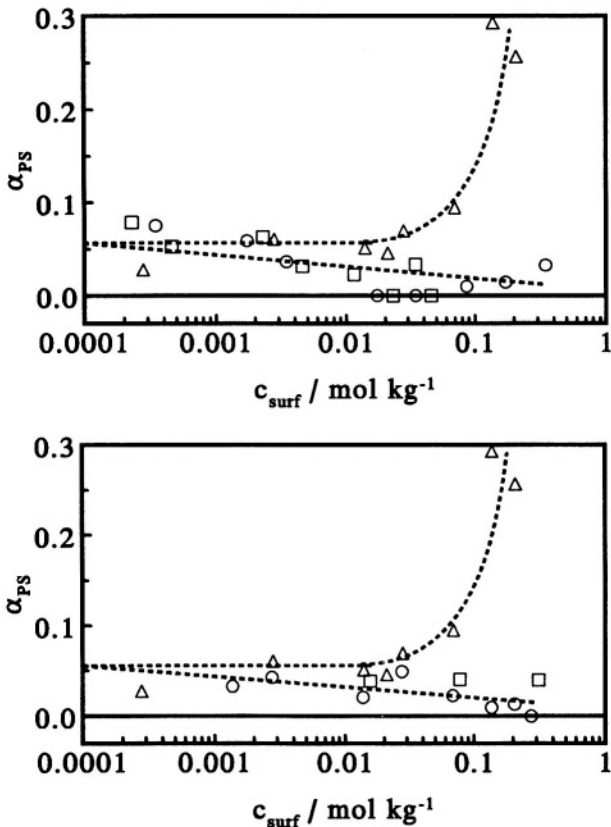


Figure 5. Volume fraction of polystyrene (PS) particles in zinc against the concentration of various surfactants at $j = 0.5 \text{ kA m}^{-2}$, $\phi_{\text{PS}} = 0.02$;^{54,76} (a): Cetylpyrridinium chloride (Δ); Sodium dodecylsulphate (\circ) and Nonylphenol(ethoxylate)₂₈(propoxylate)₁₃ (\square); (b): Cetylpyrridinium chloride (Δ); Cetyltrimethylammonium bromide (\circ) and Cetyltrimethylammonium chloride (\square).

becomes significant. It was found^{54,76} that at these high concentrations the free surfactant alters the morphology of the deposited zinc matrix. Therefore it was proposed^{54,76} that the effect of surfactants on the polystyrene incorporation in zinc is related to the changes in surface

roughness of the deposit. In Section IV.3.iv this will be discussed in more detail. Further investigations are necessary to see if such correlations are also found for other composites.

A peculiar effect of composite electrodeposition in the presence of surfactant is the formation of a so-called “white layer”. The exact conditions, which lead to white layer formation have not yet been established, but it does require hydrophobic particles and surfactants. The white layer is a layer of particles that remains on the surface of the composite after removal from the composite plating bath. The layer adheres to the composite surface, but is not strongly bonded and can be rinsed off. Figure 6 shows that BN particles from a white layer can become incorporated in a Cu layer deposited on top of a Ni(P)-BN composite from a particle-free bath. The distribution of the particles through the Cu matrix suggests that the white layer is not overgrown by the Cu layer. The Cu deposits below the white layer, which remains on the surface steadily releasing particles into the growing Cu layer. The white layer formed on Ni-PTFE composites has been used to create PTFE film on the composites by sintering the particles in the white layer particles in a post heat-treatment.^{31,73}

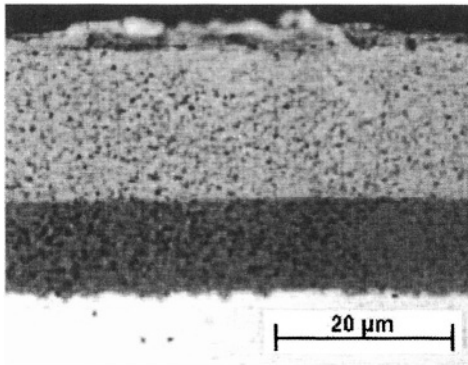


Figure 6. Cross-section of a copper layer deposited from a particle-free bath on an electroless nickel-phosphorous coating with incorporated BN particles.¹⁰⁷

(iv) Aging

In practice aging of the composite deposition electrolyte will be a major factor in deciding on the feasibility of industrially producing a certain composite. Aging was found to influence only particular composite deposition baths. Narayan and Chattopadhyay⁴⁶ reported no aging effect up to 18 days for Cr-Al₂O₃, except under certain conditions, where the particle composite content increases until it reaches a limiting value after 10 days. For Cu-SiC composites^{2,77,78} the SiC composite content fluctuates between 1 and 0.3 wt% during a period of 50 days. It was suggested that this is due to a time-dependent adsorption-desorption process of the electrolyte ions on the particles. However it was also noticed⁷⁸ that the changes in SiC composite content are accompanied by a change in surface morphology of the deposit.

The continuous decrease in Al₂O₃ incorporation in copper is also explained by a change in particle surface composition.⁴³ Chloride present as an impurity forms CuCl, which adsorbs on the particles and thereby inhibits the adsorption of copper ions on the particles. This is an effect characteristic for a copper sulfate bath and was not found in nickel or cobalt baths. A different type of aging was reported for the codeposition of aggregated polystyrene particles with zinc.^{54,76} Polystyrene incorporation increased continuously in successive experiments, where the rotation speed of a cylinder electrode was randomly varied. Thixotropic viscous behavior of the aggregated suspension causes changes in aggregate size and suspension viscosity with rotation speed of the same time-scale as the experiments.

3. Deposition Variables

The deposition variables are the process parameters most suited to regulate the particle composite content within the limits set by the particle properties and plating bath composition. Particle bath concentration is the most obvious process variable to control particle codeposition. Within the limits set by the metal plating process and the practical feasibility also current density, bath agitation and temperature can be used to obtain a particular composite. Consequently the deposition process variables are the most extensively investigated parameters in composite plating. The models and mechanisms discussed in Section IV almost exclusively try to explain and model the relation between these process parameters and the particle codeposition rate.

(i) Particle Bath Concentration

Sautter¹⁶ found that the volume percentage of Al_2O_3 particles in a Ni-matrix increases with particle bath concentration. In further investigations^{4,9,11,23,26-30,33,42,44,46,52,53,55,56,58-60,62,63,66,69,72,75,76,79-82} this behavior was confirmed for a wide range of metal particle systems (Fig. 7). With a few exceptions the particle composite content increases with decreasing rate until a limiting value is reached at high particle bath concentration. As will be discussed in the next section this behavior points to particle adsorption at the electrode surface according to a Langmuir adsorption isotherm (Section IV).

For incorporation of polystyrene particles in copper^{55,56} and zinc^{54,75,76} a deviation from the Langmuir adsorption behavior at high particle bath concentration was observed (Fig. 7). The obtained particle composite content is higher than expected from the extrapolated curve at

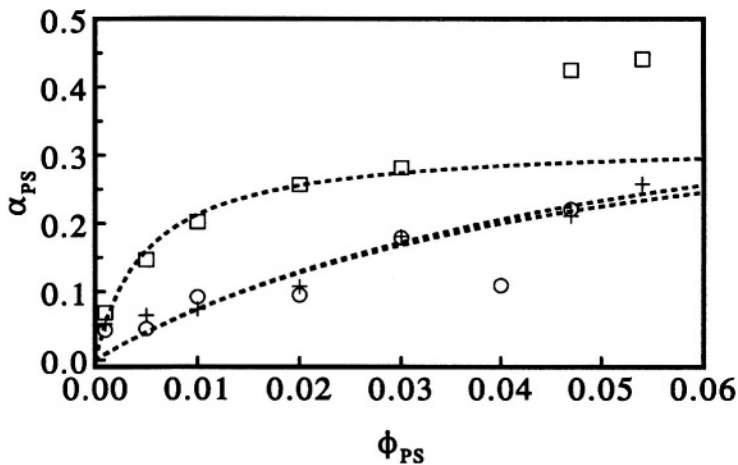


Figure 7. Volume fraction of incorporated polystyrene particles against the volume fraction of suspended particles at $j = 0.5 \text{ kA m}^{-2}$ and several concentrations of surfactant (cetylpyridinium chloride): 0 (\circ); 0.02 mol kg^{-1} ($+$) and 0.2 mol kg^{-1} (\square); Dotted lines are fits with a Langmuir isotherm.^{54,76}

lower particle bath concentration. Hydrodynamic effects,^{55,56} due to particle-particle interactions becoming significant at high particle bath concentrations, or additional particle adsorption^{54,75,76} at sites, which were not accessible at low particle concentrations, were named as cause for the augmented particle composite content. Occasionally, a decrease in particle composite content is reported^{17,23,36,69} at higher particle bath concentrations due to settling and agglomeration of the particles.

(ii) Current Density

Composites are deposited using both electroless⁶²⁻⁶⁴ and electrolytic plating processes. In the latter case composite deposition occurs in the presence of an applied electrical field, which is characterized by the cathodic potential or current density. The current density is the most extensively investigated process parameter. Roughly two types of current density dependencies can be distinguished. The particle composite content against current density curve either decreases or increases continuously^{4,11,16,24,27,30,42,59,66,67,79,82,83} or exhibits one or two peaks^{14,17,22,29,33,41,42,44,46,54,67,69,72,75,76,80,84-87} (Figs. 4 and 8). It can not be

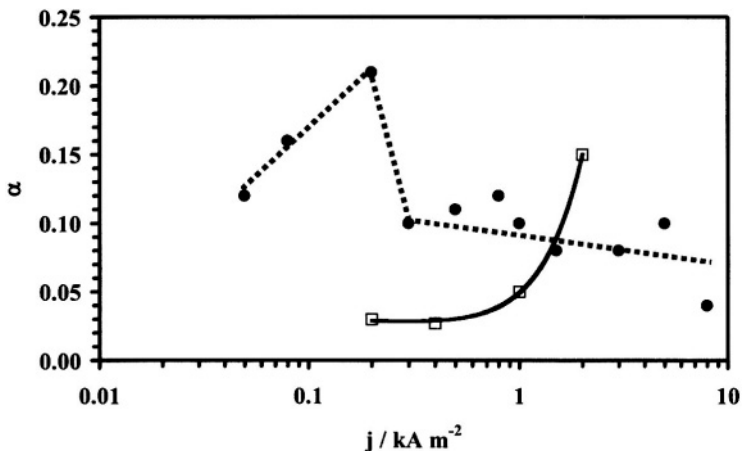


Figure 8. Current density variation of Si particle incorporation in Fe^{54,83} at $\phi_{\text{Si}} = 0.086$ (\square) and of polystyrene (PS) incorporation in Zn^{54,75,76} at $\phi_{\text{PS}} = 0.02$ (\bullet).

excluded that in the first cases peaks were not detected due to a too low accuracy of the data, a limited number of measurements or a too small current density range considered. The shape of the particle composite content against current density curves depends on other process parameters. The peak height and position change with agitation,^{42,81} particle bath concentration,^{14,46,69,80,81} and particle type.⁴² For Ni-SiC composites⁴² the curve of the SiC composite content against the current density shifts from a continuous decreasing curve to a curve with a maximum when the electrode rotation speed or particle size is decreased.

Recently, it was found⁸⁸ that the use of pulse-reverse plating can significantly increase the incorporation of nano-sized γ - Al_2O_3 particles in a copper matrix. Instead of depositing at a constant cathodic current density the current density is periodically set at an anodic value, resulting in composite dissolution. The highest particle composite content is obtained when the thickness of metal deposited in one cycle equals the particle diameter. Four times as much Al_2O_3 particles are incorporated as compared to a constant current density. So pulse-reverse plating could present a very effective way of enhancing the particle composite content. Though it has to be established if the method is applicable for other composites, particularly when larger particles are used. An explanation for the codeposition enhancement has not yet been found. Particle parking problems related to preferential codeposition might play a role here.

The nature of the current density dependence of particle codeposition is the most disputed aspect in the mechanism of composite plating (Section IV). In the simplest case the particle deposition rate is not affected by the current density, either because of particle mass transfer limitations or a current density independent particle-electrode interaction. Since the metal deposition rate increases with current density, this results in a continuously decreasing particle composite content. In other cases the particle-electrode interaction has to be current density dependent. An unambiguous explanation for this dependence has not yet been found, but it is apparent that the metal deposition behavior is involved.

The peaks in particle incorporation often^{55,56,77,85,89} occur at the same current density as kinks in the polarization curve for metal deposition. For **Au- Al_2O_3** composite deposition⁷⁷ the peaks and kinks also correlate with the preferred orientation of the Au crystallites. Similarly, for zinc-polystyrene composites^{54,76} the peak in polystyrene codeposition corresponds to a change in morphology of the zinc deposit. Polarization

curves were not recorded, but the peak appears around the current density, where Wiart *et al.*^{90,91} found a 'S'-type kink in galvanostatic polarization curves for zinc deposition.

The presence of particles in the plating bath also changes the polarization behavior of the metal deposition. For silver deposition in the presence of Al_2O_3 particles⁹² the polarization curve shifts to lower current densities at low overpotentials and to higher current densities at high overpotentials. Generally, for the same cathodic potential a higher current density, that is a depolarization, is found^{44,58,77,83,85,89,93} in the presence of particles. In contrast for $\text{Ni-Al}_2\text{O}_3$ composite deposition a large polarization accompanied by a sharp decrease in the nickel deposition current efficiency was observed⁸⁹ at the current density, where a peak in Al_2O_3 incorporation occurs. It should be mentioned that contrary to other investigations the particles used were very fine, that is $0.01 \mu\text{m}$. Such small particles could disturb the electrical double layer at cathode and the reduction reactions occurring there.⁴² Moreover, the results could be obscured by the presence of surfactant in the plating bath, a fact which was not considered by the authors.

A depolarization up to 20 mV is shown in Fig. 9 for iron deposition in the presence of Si particle.⁸³ The depolarization is accompanied by an

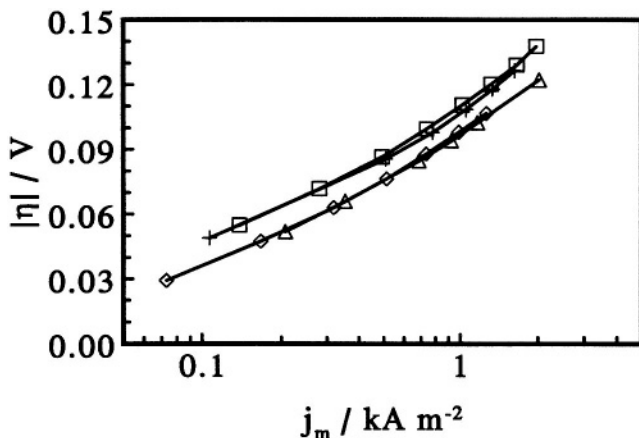


Figure 9. Modified Tafel plots for Fe deposition on a Pt-RDE from a 3 M FeCl_2 solution at 363 K containing various amounts of Si particles. $\omega = 100 \text{ s}^{-1}$. ϕ_{Si} : 0 (\square), 0.004 (+), 0.086 (\diamond), 0.172 (Δ).^{54,83}

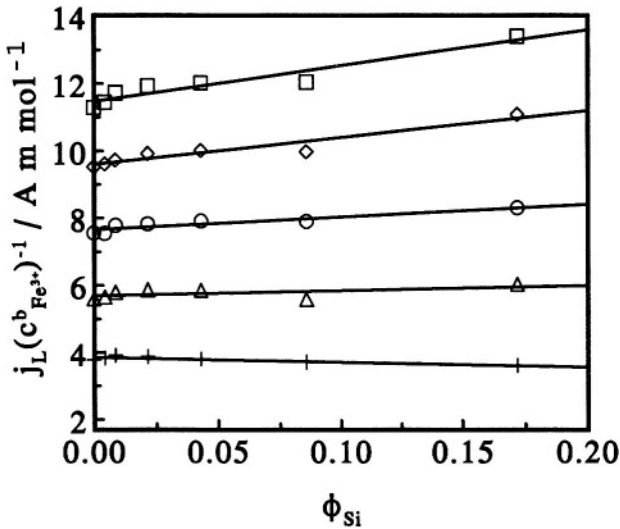


Figure 10. Concentration normalized limiting current density for Fe^{3+} reduction at a Pt-RDE in a 3 M FeCl_2 solution at 363 K as a function of ϕ_{Si} at different RDE rotation speeds, ω : 25 (+), 60 (Δ), 100 (o), 160 (\diamond) and 225 s^{-1} (\square).^{54,83}

increase in the current efficiency for iron deposition from 90 to 95%. The magnitude of the depolarization changes with the Si particle bath concentration, but not with the applied current density. The slope of the Tafel curve in Fig. 9 is independent of the particle bath concentration, whereas the exchange current density increases. Since, in Fig. 8 the particle composite content is seen to increase strongly with current density, it is concluded⁸³ that suspended Si particles and not the actually codeposited particles enhance the rate of iron deposition. The mechanism behind this catalytic effect was not elucidated.

For $\text{Ag-Al}_2\text{O}_3$ deposition the polarization found at low overvoltages is attributed⁹² to blockage of the cathode surface by the adsorbed particles and the depolarization observed at high overvoltages is explained⁹² by mass transfer enhancement of the Ag^+ ions by the particles. Yet investigations on other composite systems do not support these explanations. A simple calculation shows that in $\text{Ni-Al}_2\text{O}_3$ deposition the

observed polarization leads to unrealistically high particle cathode coverages close to 100%, when blockage is assumed. Mass transfer enhancement of ions by suspended particles is a well-known phenomenon,⁹⁴⁻⁹⁷ but in metal plating baths, due to the high metal ion concentrations, mass transfer limitation of the metal ions becomes significant only at very high current densities. Figure 10^{54,83} shows the variation in limiting current density for ferric ion reduction in a 3 M FeCl₂ iron plating bath as function of the amount of suspended Si particles. If the diffusion coefficient of a ferrous ion is taken equal to that of a ferric ion it can be calculated from Fig. 10 that the limiting current density for iron deposition is reached around 25 kA m⁻². A depolarization is already found at much lower concentrations (Fig. 9). Furthermore, Si particles only marginally enhance mass transfer of ferric ions. Only at high rotation rate of the RDE a slight increase in the limiting current density for Fe³⁺ reduction can be seen in Fig. 10.

From impedance measurement^{70,89,93} in nickel composite baths it was concluded that SiC and Cr particles cause a depolarization by catalyzing the formation of adsorbed nickel intermediates. Under certain conditions^{70,89} formation of adsorbed hydrogen intermediates is catalyzed even more, resulting in a decrease in current efficiency for nickel deposition. On the other hand the current efficiency for iron deposition increases with increasing Si particle bath concentration.^{54,83} Figure 9 shows that the Tafel curve^{54,83} for Fe deposition corrected for the current efficiency shifts to lower potentials in the presence of Si particles, but that the slope is not affected. Based on these facts it was suggested^{54,83} that the Si particles increase the iron deposition rate, but do not interfere in the deposition mechanism. The nature of this catalytic effect is however not clear.

(iii) *Electrolyte Agitation*

The primary purpose of electrolyte agitation is to keep the particles suspended and prevent them from settling or floating. Agitation is achieved by stirring, air bubbling, recirculation of the electrolyte and, on lab scale, by a rotating electrode. The rate of agitation affects particle codeposition in two opposite ways. Increased agitation results in a larger particle composite content,⁴ because particle transfer from the bulk of the electrolyte to the cathode surface is augmented. Too much agitation²⁹ decreases the particle composite content, because the particles are ejected

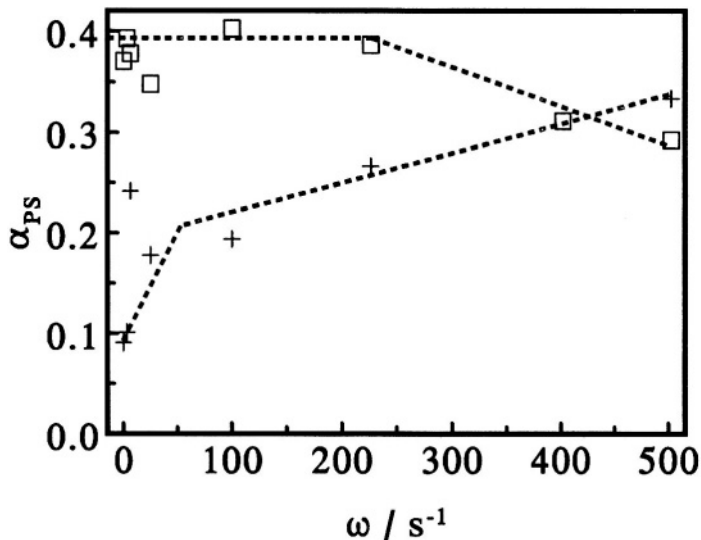


Figure 11. Volume fraction of polystyrene particles incorporated in Zn against the rotation speed of a cylinder electrode at $j = 0.5 \text{ kA m}^{-2}$, $\phi = 0.054$ and 0.02 mol kg^{-1} cetylpyrridinium chloride.^{54,76}

from the cathode surface before being incorporated. This is evidenced by the occurrence of a maximum in the particle composite against agitation rate curve.^{51,60}

The balance between particle mass transfer and particle removal depends on the agitation type and the particle properties as is shown for Fe-Si and Zn-polystyrene composites in Table 1. Under the turbulent flow conditions of the stirrer and the RCE particle removal is stronger than under the laminar flow conditions of the RDE and consequently Si codeposition is lower. For the polystyrene particles the agitation type has less effect, because particle removal is low at the agitation rates considered and particle mass transfer is not rate determining. Figure 11^{54,75,76} shows that at low rotation speeds of the RCE the effect of electrode rotation speed on the polystyrene incorporation is negligible and at high rotation speeds polystyrene codeposition is reduced due to particle ejection. The Al_2O_3 content of a Cu matrix composite deposited on a rotating disc electrode (RDE) varies in a similar way, that is no effect at low rotation rates and a decrease in Al_2O_3 content at high rotation

rates.^{77,92} Here the two cases correspond to different flow regimes, respectively laminar and turbulent flow. In the transition flow between these regimes the particle content successively decreases and increase with increasing rotation speed. The formation and incorporation of particle agglomerates explain this.

As for an electrode in channel flow⁹⁸ and a RDE,^{42,51,55,56} the hydrodynamic conditions vary over the electrode surface, particles do not become homogeneously dispersed through the metal matrix. Different zones of hydrodynamic flow along a channel electrode⁹⁸ give rise to a distribution of particle contents over the cathode. On a RDE the centrifugal force, which is the removal force, exerted on a particle at the electrode surface increases radially. Accordingly at high rotation speeds and high particle bath concentration, where particle removal dominates, the SiC incorporation in Ni⁴² decreases going from the center to the edges of the electrode. The mean size of incorporated particles also decreases radially, because larger particles are removed more easily. In contrast under mass transfer control that is at low rotation speeds and low particle bath concentration SiC incorporation is constant over the electrode, due to the uniform mass transfer to a RDE. It can be concluded that the electrolyte agitation is one of the main process parameters governing particle incorporation.

(iv) *Temperature*

Electrochemical composite deposition is usually performed at temperatures typical for the utilized metal plating bath. It has been shown that the bath temperature can have a pronounced effect on the particle composite content, but the effect varies considerably per composite. For

Table 1
Effect of type of agitation on Si incorporation in Fe
($\phi_{\text{Si}} = 0.05$) and polystyrene (PS) incorporation in Zn
($\phi_{\text{PS}} = 0.05$) at $j = 500 \text{ A m}^{-2}$ and $\omega = 100 \text{ s}^{-1}$ for the
rotating electrodes.

Type of agitation	PS particles in Zn m%	Si particles in Fe m%
Magnetic stirrer	2.3 ± 0.5	0.05 ± 0.08
Rotating cylinder electrode	4.5 ± 0.5	0.10 ± 0.04
Rotating disc electrode	4.5 ± 0.5	2.8 ± 0.2

Ni-Al₂O₃, no effect of the temperature on the particle composite content was found.^{11,16} On the other hand a continuous decrease of the particle content of copper matrix composite deposition⁵⁷ and a continuous increase of TiC incorporation in nickel²³ with increasing temperature have been reported. A maximum particle composite content at 50 °C was observed for Ni-PTFE,⁶⁹ Ni-V₂O₅,³⁶ and Ni-BN.¹⁷ In a like manner a limiting particle incorporation in Cr above 50 °C preceded by either an increase⁶⁶ or a decrease⁴⁶ below this temperature was found.

This diversity in effects of bath temperature is a result of the various temperature dependent parameters affecting particle incorporation. The particle surface composition, electrolyte viscosity and density and metal deposition reaction all change with temperature. Ion adsorption on the particle and particularly lowered H⁺ adsorption was named⁴⁶ as a cause of the reduction in Al₂O₃ incorporation in Cr with temperature. However, the effect of changes in ion adsorption are small compared to the changes in particle mass transfer due to lowered electrolyte density and viscosity⁵⁶ and changes in metal surface composition and morphology. The augmentation in TiC incorporation in Ni²³ with temperature is for example accompanied by the occurrence of dull and gray deposits.

IV. MECHANISMS AND MODELS

In the previous section it was shown that a generalized mechanism underlying particle incorporation in a metal matrix allows some insight into the effect of process parameters on the particle composite content. However, it is evident that a more elaborate mechanism is required to fully comprehend the processes involved. A detailed mechanism is also a prerequisite for the development of a mathematical model describing the particle codeposition behavior. Ideally, such a model should be able to predict the particle composite content from a given set of process parameters. This would facilitate screening composite types and optimization of process conditions for industrial applications.

Several attempts have been made to elucidate the mechanism and to develop models based hereupon. Although an increased insight into composite deposition has been obtained, there still remains some ambiguity. This is partly caused by the tedious and time-consuming work necessary to acquire a set of experimental data sufficient to validate a proposed model and the numerous interrelated process parameters

involved. The evolution of the understanding of the mechanism through the years and the models proposed at certain stages are discussed in this section.

1. Early Mechanisms

Simultaneously with the growing interest in composite deposition the first explanations for particle codeposition with a metal were reported in the early sixties. Whithers⁹⁹ proposed that the particles having a positive surface charge are drawn to the cathode by electrophoresis. Williams and Martin²⁹ suggested that in addition the particles are transported to the cathode by bath agitation and are mechanically entrapped by the growing metal layer. Based on mechanical entrapment only Saifullin and Khalilova¹⁰⁰ presented the first model to calculate the amount of incorporated particles. The idea of mechanical entrapment was rejected by Brandes and Goldthorpe,⁴⁵ because it signifies that particle incorporation is independent of electrolyte composition and particle properties, in contrast to observations. They suggested the existence of an attractive force, for example an electro-osmotic one, holding the particles at the cathode surface long enough to be incorporated by the growing metal layer. Correspondingly Bazzard and Boden⁵⁸ proposed that particles collide with the cathode surface due to the bath agitation and should stay at the cathode surface a certain time to become incorporated. A simple equation to calculate the particle composite content was developed, but it was rightly stated that it lacks any physical significance. These first attempts can be summarized to the generalized two step mechanism involving particle mass transfer to the cathode followed by a particle cathode interaction.

2. Empirical Models

After the first initiatives, more extensive mechanisms and consequently more realistic models were developed. The break-through came with the model put forward by Guglielmi⁸² in 1972. It presented the basis for various models, which have in common that they are highly empirical. A mechanism is deduced from experimental data and mathematical equations describing these data are developed. Like this relatively simple models containing several fit parameters of sometimes limited physical significance were obtained.

(i) *Guglielmi*⁸²

From experimental data Guglielmi⁸² inferred two fundamental phenomena comprising the particle electrode interaction. The resemblance between the particle composite content versus particle bath concentration curve and a Langmuir adsorption isotherm (Section III.3.i) implies adsorption of particles on the cathode. Additionally, to account for the observed current density dependence of the particle composite content the electrical field at the cathode has to play a role. An electrophoretic interaction is rejected, because the high electrolyte concentration in metal plating baths completely shields the particle charge. Therefore, a field-assisted adsorption mechanism consisting of two steps is proposed. In the first step, which is of a physical nature, particles approaching the cathode become loosely adsorbed on the cathode surface. The loosely adsorbed particles are still surrounded by a cloud of adsorbed ions. In the second step the particles lose the ionic cloud and become strongly adsorbed on the cathode. This step is thought to be of an electrochemical character, *i.e.*, it depends on the electrical field at the cathode. Finally, the strongly adsorbed particle is incorporated in the growing metal layer.

The loose adsorption step is described by a Langmuir adsorption isotherm, taking into account the cathode area available for this loose adsorption:

$$\sigma = \frac{k\phi}{1 + k\phi}(1 - \theta) \quad (1)$$

where ϕ is the particle bath volume fraction, σ is the loose adsorption surface coverage, θ the strong adsorption surface coverage and k is a measure for the intensity of the particle cathode interaction. Obviously the second step depends on σ and Guglielmi considers this dependence linear. Together with a factor to describe its postulated dependence on the electrical field at the cathode, represented by the cathode overpotential (η), the following equation for the strong adsorption rate is obtained:

$$V_p = \sigma v_0 e^{B\eta} \quad (2)$$

where v_0 and B are constants.

The deposition rate of the metal is found using Faraday's law.

$$V_M = \frac{M_M j}{nF\rho_M} \quad (3)$$

Taking into account the area of the cathode available for metal deposition, that is $(1-\theta)$ for non-conducting particles the current density is related to the overpotential by the Tafel equation:

$$j = (1 - \theta) j_0 e^{A\eta} \quad (4)$$

where j_0 is the exchange current density and A is the Tafel slope. Assuming that the volume fraction of embedded particles $\alpha \approx \theta \ll 1$ these expressions give:

$$\frac{\phi}{\alpha} = \frac{M_M j_0^{B/A}}{nF\rho_M v_0} j^{(1-B/A)} \left(\frac{1}{k} + \phi \right) \quad (5)$$

The constants k , v_0 and B depend on the type of composite considered and have to be determined from experimental data using Eq. (5). A plot of ϕ/α against ϕ at constant j gives a straight line, from whose intercept at $\phi/\alpha = 0$ $1/k$ can be calculated. Plotting the logarithm of the slope of this line at different j against j will also yield a straight line, whose slope gives the ratio B/A and from whose intercept v_0 can be calculated. Other parameters can either be measured, that is A and j_0 , or are known constants, like ρ_M and M_M .

Guglielmi validated his model for Ni-TiO₂ and Ni-SiC composite deposition. From the obtained values for k it was found using Eq. (1) that $\theta \ll \sigma$ and it was concluded that the strong adsorption step is rate determining. The model was also successful in describing the variation of the particle composite content with the particle bath concentration and current density of several other composites.^{57,59,60,66,79,84} For example,

Table 2
Values of k and σ obtained
using Guglielmi's model for the
codeposition of Ni particles with
Zn at different remanent
magnetizations of the Ni
partilces.⁵⁷

$M_f / A\ m^{-1}$	k	σ at $\phi_{Ni} = 0.0002$
0	0.13	0.23
3300	0.24	0.34
8600-34000	0.90	0.64

Tacken *et al.*⁵⁷ adapted the model for conducting particles by leaving out the term $(1-\theta)$ in Eq. (4). From the modified Eq. (5) it was found that the increased incorporation of magnetically charged Ni particles in Zn is reflected in an increased k and σ (Table 2). Ramasubramanian *et al.*¹⁰¹ used Guglielmi's mechanism for particle deposition to model the deposition of Fe-Ni-SiO₂ composites. Equation (2) was introduced in a material balance for the electrochemical reaction kinetics in order to describe the competition for adsorption sites on the cathode surface between SiO₂ particles and intermediates in the alloy deposition reactions. Like this the reduction in SiO₂ incorporation with increasing deposition potential and the decrease in Ni and Fe partial current densities with increasing SiO₂ bath concentration were successfully modeled.

Despite these successes, important process parameters, like bath agitation, bath constituents and particle type are disregarded. The constants k , v_0 and B inherently account for these constants, but they have to be determined separately for every set of process parameters. Moreover, the postulated current density dependence of the particle deposition rate, that is Eq. (2), is not correct. A peak in the current density against the particle composite content curve, as often observed (Section III.3.ii), can not be described. The fact that the peak is often accompanied by a kink in the polarization curve indicates that also the metal deposition behavior can not be accounted for by the Tafel equation (Eq. 4). Likewise, the $(1 - \theta)$ term in this equation signifies a polarization of the metal deposition reaction, whereas frequently the opposite is observed (Section III.3.ii). It can be concluded that Guglielmi's mechanism

presented an important step in the understanding of composite deposition, but that his model has only limited validity.

(ii) *Kariapper and Foster*⁶⁷

Regarding the role of the ionic cloud surrounding the particles some obscurity can be noted in Guglielmi's model.⁸² It is stated that loosely adsorbed particles are surrounded by an ionic cloud indicating that the particles are adsorbed on the cathode through their ionic cloud. This is contradictory to the definition of k as the intensity of the particle cathode interaction. Kariapper and Foster⁶⁷ noted the importance of adsorption of ions on the particles and concluded that adsorbed metal ions play a twofold role. Firstly, the positively charged metal ions cause an electrostatic attraction of the particles to the negatively charged cathode. Secondly, the adsorbed metal ions are reduced at the cathode and create a physical bond between the particle and the cathode. It is striking that Guglielmi⁸² inherently took into account this second phenomenon by using a Tafel-type of equation to describe the particle deposition rate (Eq. 2).

Kariapper and Foster derived a simple model considering the effect of several process parameters. The particle deposition rate is again defined as a Langmuir adsorption isotherm, where the measure of the particle cathode interaction k depends on:

- The electrostatic interaction, which is determined by the charge q adsorbed on the particles and the potential field at the cathode E .
- The physical bond, which depends on the rate at which metal is deposited, that is the current density j . When L is the physical bond strength per unit area, the physical bond is a function of Lj^2 .
- Mechanical factors, like the particle properties a and the agitation rate b .

Taking N^* as the number of particle collisions with the cathode suitable for particle incorporation, which is affected by the agitation rate, the particle deposition rate is given by:

$$V_p = \frac{N^* k^* (qE + Lj^2 - ab)\phi}{1 + k^* (qE + Lj^2 - ab)\phi} \quad (6)$$

where k^* is a constant. The resulting equation was not verified with experimental data, but it was shown that theoretically it is able to predict a peak in the particle composite content versus current density curve. It is evident that the factors in this equation can hardly be measured or evaluated, and has to be fitted with experimental data. Due to the large number of fit parameters an extensive set of experimental data is necessary to obtain a reliable fit. Despite the academic value of the equation Kariapper and Foster introduced important mechanistic concepts.

(iii) *Buelens and Celis et al.*^{72,77}

Celis *et al.*^{44,72,77,84} also noticed the inability of Guglielmi's model to describe the variation in particle composite content with current density. Two current density ranges have to be distinguished to explain the peak in Al_2O_3 incorporation in copper, when using this model. In the low current density range the particle deposition rate increases faster with increasing overvoltage than the metal deposition rate, that is $B > A$ in Eq. (5), and the particle composite content, α , increases with j . In the high current density range on the other hand $B < A$ and α decreases with j .

At the transition between the two current density ranges, the polarization curve for Cu deposition starts diverging from the calculated Tafel curve. This divergence was attributed to the transition from charge transfer to concentration overvoltage control of the copper reduction. It was concluded from these results that the reduction at the cathode surface of metal ions adsorbed on the particles plays a fundamental role in the codeposition mechanism.

Based on this postulate and the pronounced effect of agitation on particle incorporation Buelens *et al.*^{72,77} proposed a five-step mechanism for composite deposition. In the first step particles in the bulk of the electrolyte obtain an ionic cloud by adsorbing ions from the electrolyte. In the second and third step the particles are transported by bath agitation to the hydrodynamic boundary layer and by diffusion through the diffusion layer to the cathode surface. Finally, the particles adsorb on the cathode surface still surrounded by their ionic cloud and are incorporated by the reduction of some of the adsorbed ions. A model for the calculation of the weight percent of incorporated particles was developed consistent with this mechanism. The basic hypothesis of the model is that a certain amount, x , out of X ions adsorbed on a particle must be reduced at the

cathode for the particle to become incorporated. Hence not all particles present at the cathode surface are incorporated, but a minimum residence time for a particle adsorbed on the cathode surface is assumed.

The mass fraction of embedded particles is defined as follows:

$$\beta = \frac{W_p N_p P}{\frac{M_M j}{nF} + W_p N_p P} \quad (7)$$

where W_p is the particle mass, N_p is the number of particles crossing the diffusion layer at the cathode per unit of time and surface area and P is the chance of a particle to become incorporated. Faraday's law gives the weight of deposited metal. From the basic hypothesis it follows that P depends on the probability $P_{(x/X,j)}$ that at least x out of X adsorbed ions are reduced. Hence, if p_j is the chance that one ion is reduced at current density j :

$$P_{(x/X,j)} = \sum_{z=x}^X C_z^X (1-p_j)^{X-z} p_j^z \quad (8)$$

To calculate p_j a new assumption is made, that is no distinction is made between the adsorbed ions and free ions and thus:

$$p_j = \frac{\frac{j}{nF}}{\frac{(c_M^b + c_M^s)\delta}{2} + \frac{j}{nF}} \quad (9)$$

Where δ is the diffusion layer thickness and c_M^b and c_M^s are respectively the bulk concentration and the concentration at the cathode surface of the metal ions. It is not clear why in Eq. (9) a time factor, which would make it dimensionless, is neglected. Buelens *et al.*^{72,77} just state that a negligible error is created. A factor H is introduced to take into account bath agitation:

$$P = H P_{(x/X,j)} \quad (10)$$

From experiments with varying bath agitation it was obtained that $H = 1$ under laminar flow conditions, $0 < H < 1$ under transition flow conditions and $H = 0$ under turbulent flow conditions.

Finally, N_p is related to the number of ions crossing the diffusion layer per unit time and surface area N_M and to the type of overvoltage control:

$$N_p = N_M \frac{C_p^*}{C_M^*} \left(\frac{j_{tr}}{j} \right)^\lambda \quad (11)$$

where j_{tr} is the transition current density from charge transfer to concentration overvoltage control and C_p^* and C_M^* are respectively the number of particles and the number of ions in the bulk. Under charge transfer overvoltage control $\lambda = 0$, because the ion-reduction is rate determining, while the diffusion rate is high enough for both particles and free ions. However, $\lambda \neq 0$ under concentration overvoltage control, because diffusion of ions is rate determining, which is obviously much slower for adsorbed ions than for the free ions.

The authors obtain a good agreement between the model and experiments for **Cu-Al₂O₃** and **Au-Al₂O₃** composite deposition, but some assumptions in the model can be questioned. The cathodic overvoltage at j_{tr} corresponds to the value where Degrez and Winand¹⁰² observe a change in the reduction mechanism of **Cu²⁺**. It was found that the cathodic charge transfer coefficient is 0.5 in the low overpotential region and 0.1 in the high overpotential region. This indicates that the change in codeposition behavior at j_{tr} is associated with a change in the metal deposition behavior and not with a transition from charge transfer to mass transfer overvoltage control of metal deposition. In general the peak in particle incorporation appears at current densities smaller than about **500 Am⁻²**, which in the concentrated plating electrolytes is much smaller than the limiting current density for metal ion reduction. For example, the peak in polystyrene incorporation in zinc^{54,75,76} is found at **0.2 kA m⁻²**, whereas composites can be deposited at least up to **8 kA m⁻²**. The reduction of x out of X adsorbed ions is also difficult to imagine^{55,56} considering that the particles are a few orders larger in size than ions. Only very few adsorbed ions will be close enough to the electrode surface, *i.e.*, in the inner Helmholtz plain, to be reduced. Hence the ratio x/X is either very small or the metal has to grow around the particle to reach a larger ratio. In the latter case it seems

improbable though that a partly incorporated particle will leave the electrode surface again if the required amount of reduced ions is not reached.

(iv) *Hwang and Hwang*⁸⁶

Hwang and Hwang⁸⁶ proposed an improvement on Guglielmi's model by adapting it to the mechanism put forward by Buelens *et al.*^{72,77} For three current density ranges the particle deposition rate is determined by the electrode reactions for ions adsorbed on the particles, whose rates are determined by kinetic and/or diffusion parameters. A diffusion layer and concentration profile equivalent to that at an electrode are thought to develop at the particle surface. Since, Co-SiC composite deposition was experimentally investigated, the starting point is the reduction of H^+ and Co^{2+} adsorbed on the particles. Three different current density ranges for the reduction of these ions are distinguished:

- Low current density where only H^+ ions are reduced
- Intermediate current density, where the H^+ reduction rate has reached its limiting value and also Co^{2+} is reduced.
- High current where for both ions the reduction rate is at its limiting value.

Similar to Guglielmi's model the metal deposition rate V_M is defined as:

$$V_M = \frac{M_M}{\rho_M n F} j \Gamma_M (1 - \theta) \quad (12)$$

where Γ_M is the current efficiency. The factor v_0 in Eq. (2) is similar to the exchange current density j_0 in electrochemical reactions. Since, j_0 depends on the concentration of reacting species, v_0 depends on the concentration of reacting species in particle deposition that are the adsorbed ions. In the low current density range the particle deposition rate V_p is determined by the reduction of the adsorbed H^+ ions:

$$V_p = k_1 c_{\text{H}^+}^s \sigma e^{B_1 \eta} \quad (13)$$

where $c_{H^+}^s$ is the concentration of H^+ ions adsorbed on the particle surface, which decreases with increasing H^+ reduction:

$$c_{H^+}^s = \left(1 - \frac{V_p}{V_{p,H^+}} \right) c_{H^+}^b \quad (14)$$

where V_{p,H^+} is the maximum particle deposition rate due to H^+ reduction and $c_{H^+}^b$ is the H^+ ion concentration in the bulk solution.

In the intermediate current density range the particle deposition rate due to H^+ reduction is at its limiting value V_{p,H^+} , whereas the contribution of the metal reduction is similar to that of H^+ in the low current density range. Consequently, the equation for V_p in this range is given by:

$$V_p = V_{p,H^+} + k_2 \left(1 - \frac{V_p}{V_{p,M}} \right) c_M^b \sigma e^{B_2 \eta} \quad (15)$$

where $V_{p,M}$ is the limiting particle deposition rate due to the metal reduction and c_M^b is the metal ion concentration in the bulk. Finally, in the high current density range the particle deposition rate is solely determined by diffusion and is independent of the current density and the adsorbed ions concentration. Equation (13) is simplified to:

$$V_p = k_3 \sigma \quad (16)$$

The volume fraction of embedded particles can now be calculated using Eq. (12) and, depending on the current density range, Eq. (13), (15) or (16). The deposition of Co-SiC composites, including the peak in SiC incorporation, can indeed be described by the model.

The model presents an improvement of Guglielmi's model, but it also suffers from the same limitations. Process parameters, like bath agitation and particle properties, are not taken into account and even more fit parameters have been introduced. The reduction of adsorbed ions again leads to some debatable assumptions. Inherently the reduction of adsorbed

ions is supposed to differ completely from that of free ions. The efficiency of the metal deposition, that is the competition between the reduction of free H^+ and Co^{2+} , is considered to be independent of current density, whereas for adsorbed ions different regimes are distinguished. The authors do not discuss the validity of this assumption. Besides it is difficult to imagine how reduction of adsorbed H^+ ions can create a bond between the metal matrix and a particle.

3. Advanced Models

Considering the mechanisms treated so far in view of the generalized two step mechanism it is noticed that the nature of the particle-electrode interaction is based on disputable hypotheses, particularly the necessary reduction of adsorbed ions for which only indirect evidence exists. The particle mass transfer step has just been globally treated. This is related to the empirical character of these mechanisms and models. From other fields of research detailed descriptions of mass transfer of solid particles and particle-surface interactions are known.^{61,103} Recently, researchers' tried^{55,56,79,104} to develop a model for composite deposition using such descriptions. In comparison to the earlier models these models are much more elaborated. They are building up of various often interrelated equations containing numerous parameters, which necessitate the use of extensive computer calculations. Although this renders it difficult to get an easy insight into the effect of a particular process parameter, the number of questionable assumptions and fit parameters without physical meaning is greatly reduced.

(i) *Valdes*¹⁰⁴

In 1987 Valdes¹⁰⁴ developed a model for composite deposition at a RDE taking into account the various ways in which a particle is transported to the cathode surface. As starting point an equation of continuity for the particle number concentration, C_p^* , based on a differential mass balance was chosen, that is:

$$\frac{\partial C_p^*}{\partial t} + \frac{\partial}{\partial r} N_p = 0 \quad (17)$$

where the particle flux, N_p , is composed of expressions for the different mass transfer processes, which is Brownian diffusion and convection. The convection term takes into account all the forces and torques acting on a particle due to hydrodynamic migration, electromigration and diffusiomigration. Together with expressions for the local electrical field and the local electrolyte concentration for a binary electrolyte a highly coupled set of transport equations is obtained.

Next the difficulties in obtaining a good description of the particle electrode interaction are noticed. For non-electrochemical systems several particle surface interaction models exist of which the 'perfect sink', that is all particles arriving within a critical distance of the electrode are captured, is the simplest one. However, the 'perfect sink' condition can not be used, because it predicts a continuous increase in particle codeposition with increasing current density, which contradicts experimental observations. Therefore, an interaction model based on the assumption that the reduction of adsorbed ions is the determining factor for particle deposition is proposed. This electrode-ion-particle electron transfer (EIPET) model leads to a Butler-Volmer like expression for the particle deposition rate:

$$V_p = k_0 c_{ion}^s \left[\exp\left(\frac{-\alpha_T nF}{RT} \eta\right) - \exp\left(\frac{(1-\alpha_T)nF}{RT} \eta\right) \right] \quad (18)$$

where k_0 is an electrochemical rate constant, c_{ion}^s , is the concentration of ions adsorbed on the particles, η is the overpotential and α_T is the cathodic transfer coefficient. Using this model a peak in the particle inclusion versus current density curve is predicted, but it is found close to the limiting current density instead of at low current densities. It can be concluded that Valdes model uses a far better description of particle mass transfer than previous models, but the particle-electrode interaction again relies on the controversial necessity of the reduction of adsorbed ions

(ii) Guo *et al.*⁷⁹

Guo *et al.*⁷⁹ proposed a model based on a description of the mass transport by so-called similitude numbers. Similitude numbers are dimensionless numbers determined by factors influencing mass transfer. A standard description of the Sherwood number for mass transfer of solid

particles in a dilute suspension to a fixed plate was modified for composite deposition. If certain parameters, like temperature and bath constituents are considered to be constant, the particle deposition rate can be calculated from the similitude number Sh' :

$$Sh' = CoRe^c Dm^d Sx^e Gq^f \quad (19)$$

where Re is the Reynolds number describing mass transfer and Co , c , d , e and f are constants, which have to be determined by fitting the model with experimental data. Co contains among others the Van der Waals attraction that is the physical adsorption of particles on the cathode. Electro-osmotic interactions between particles and the cathode are accounted for by the electrical double layer number Dm . The factor Sx is introduced for the effect of the particle bath concentration and comprises a Langmuir adsorption isotherm. The factor Gq describes the incorporation process of the particles in the metal matrix. It is determined by the ratio of the particle diameter and the thickness of metal deposited during the residence time of a particle at the cathode surface. This residence time is obtained from the electrolyte flow velocity at the center of a particle on the electrode surface. Hence, Gq accounts for the removal of particles from the electrode surface by electrolyte agitation (Section III.3.iii).

Satisfactory agreement with experimental data was obtained for Cu-SiC composite deposition in a channel flow. Because of the limited range of experimental data it is not clear if the model is also able to describe important features, like the peak in the particle composite content versus current density curve. In comparison to Valdes model, the particle mass transfer is poorly taken into account by using the Reynolds number. The particle-electrode interaction on the other hand is treated much more adequately by the balance between particle adsorption (Co , Sx and Dm) and particle ejection due to hydrodynamics (Gq). For example, a small value for d is obtained, indicating that, in accordance with experimental data (Section III), electro-osmotic interactions between particles and the cathode (Dm) are negligible.

(iii) Fransaer et al.^{55,56}

Fransaer *et al.*^{55,56} adapted both existing particle mass transfer and particle-electrode interaction descriptions to composite deposition at a RDE. A trajectory description for a particle was developed based on all the forces and torques acting on it. This comprises the forces due to fluid convection and particle motion and the forces acting directly on the particle. Expressions for all these forces were developed and lead to a set of equations describing the particle trajectory. The particle volume flux to the cathode is determined by calculating the limiting particle trajectory that is the particle trajectory separating the trajectories of particles reaching the electrode from those passing by.

Close to the electrode surface the trajectory description fails, because it leads to the 'perfect sink' condition, which was seen to be wrong. A reaction term characterizing the particle electrode interaction is introduced. A force balance on the particle gives an equation for the probability that a particle at the electrode surface is incorporated (Fig. 12). A

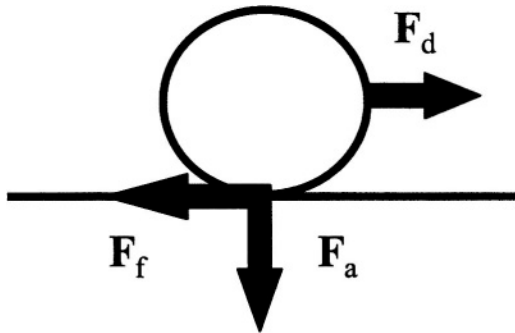


Figure 12. Particle adsorbed on the electrode; \mathbf{F}_f is the friction force, \mathbf{F}_a is the adhesion force and \mathbf{F}_r is the removal force.^{55,56}

friction force, \mathbf{F}_f which results from forces responsible for particle adhesion, \mathbf{F}_a , counteracts forces tending to remove particles from the electrode, \mathbf{F}_r . The adhesion forces consists of particle-electrode interaction forces, like the London-van der Waals force, the electro-osmotic force and the electrophoretic force. Depending on the electrode geometry, forces acting only on the particles, like gravity, buoyancy and hydrodynamic forces, contribute to \mathbf{F}_a . The removal forces, \mathbf{F}_r , are of hydrodynamical origin, for example due to electrode rotation. Using the adhesion force determined from Cu-polystyrene codeposition data, the trajectory model gives a good description of the variation of the polystyrene composite content with the polystyrene bath concentration.

The trajectory model does not predict the maximum in the particle inclusion versus current density curve. Experiments indicate that this maximum is related to the potential of zero charge of the copper electrode, which suggests that the electro-osmotic force is responsible for the maximum. Calculations of the adhesion force dependence on the current density from experimental data do not support this last suggestion. It is concluded that the electro-osmotic and electrophoretic force do not affect particle incorporation in agreement with several experimental data discussed in Section III. The electrical double layers of the particles and the electrode are strongly compressed due to the high electrolyte concentration. Another strong repulsive force between the particle and the electrode has to be present at short distances. Therefore, the structural or hydration force is introduced, which is a short range repulsive force arising from the work required to remove the ordered hydration layers at the solid/liquid interfaces of solids coming into close contact in concentrated electrolytes.^{105,106} This hydration force will be minimal if the electric field at the electrode is minimal, that is at the potential of zero charge (p.z.c.). The occurrence of a maximum in the particle inclusion versus current density curve is attributed to changes in the ordering of the water dipoles due to changes in electrode charge. Plausible explanations for the effect of particle type, monovalent cations and surfactants on the codeposition rate can be given using the hydration force.

In contrast to earlier models the trajectory model is based on widely accepted descriptions of particle mass transfer and particle-substrate interactions and does not heavily rely on assumptions, like the reduction of adsorbed ions, for which only indirect evidence exists. The extensive mathematical calculations and the complexity of an adaptation to other electrode geometries than a RDE have prevented further quantitative

investigations. In spite of that from a mechanistic point of view the trajectory model offers a very good description for gaining a better insight into composite deposition. Particularly, the force balance depicted in Fig. 12 is a very powerful, but relatively simple, tool for the understanding of particle codeposition phenomena. It was, for example, successful in qualitatively explaining experimental data for Ni-SiC⁴² and Zn-polystyrene^{54,76} composite depositions. Nevertheless the particle-electrode interaction forces and their relative importance remain a point of discussion.

(iv) *Hovestad et al.*^{54,76}

A description of the effect of surfactants on zinc polystyrene composite deposition^{54,76} using the hydration force is not entirely satisfactory. Fransaer proposed that the changes in hydrophobicity of the particles, and thus the hydration force, due to surfactant adsorption determine the effect of surfactants on particle codeposition. As discussed in Section III.2.iii up to the concentration of maximum surfactant adsorption (0.02 mol kg^{-1})^{54,76} surfactants hardly affect polystyrene codeposition, although the particles become increasingly hydrophilic. Figure 13 indicates that the variation in polystyrene incorporation in zinc due to the surfactant addition correlates with changes in the zinc appearance and surface morphology.^{54,76}

Figure 14 shows a generalized picture of the main types of growth morphologies which can be encountered for zinc deposition from acid solutions.^{109,110} Zinc deposits as hexagonal platelets, which are oriented at different angles to the substrate depending on the plating conditions. At intermediate current densities the platelets are stacked at random angles to the substrate as observed for deposition from a particle-free electrolyte. At high current densities a vertical type of deposit is formed where the platelets make an angle of 90° with the electrode surface. A basal type of deposit characterized by the platelets lying parallel to the electrode surface is formed at low current densities.

A basal type of deposit is also obtained in the presence of impurities like Co, Ni and Sb, which deposit in between the stacks of platelets resulting a nodular structure.^{109,110} Such morphology is found in the presence of high concentrations cetylpyrrolidinium chloride. Cetylpyrrolidinium chloride produces basal type deposits (Fig. 13), because

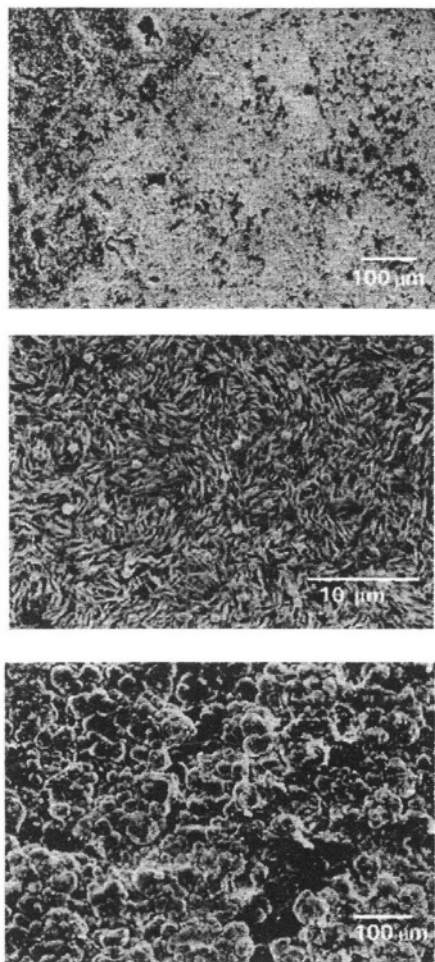


Figure 13. Electron microscope picture of the surface morphology of zinc polystyrene composites deposited from, from top to bottom, surfactant-free, $\phi_{PS} = 0.05$; 0.3 mol kg^{-1} CTAC, $\phi_{PS} = 0.02$ and 0.2 mol kg^{-1} CPC.

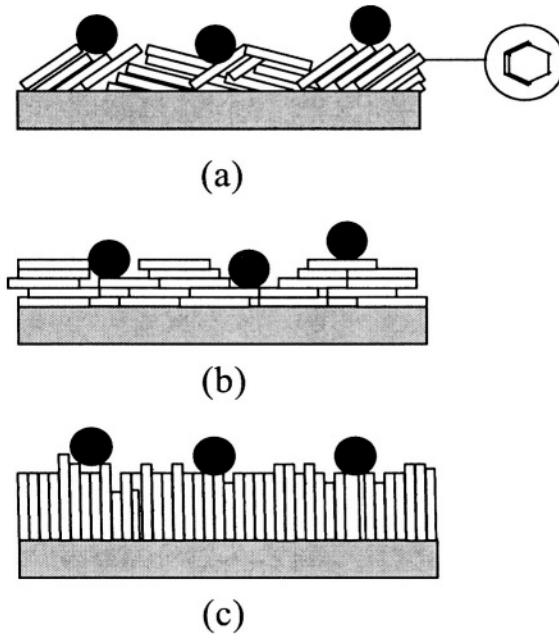


Figure 14. Growth morphologies of zinc deposits; (a) intermediate type, (b) basal type, (c) vertical type; Black spots represent particles.

it can be reduced at the cathode to a dimer, which deposits in between the nodules. Addition of organics, like glue, changes the morphology to the vertical type. Cetylammmonium chloride has a similar effect on the composite deposits (Fig. 13), although the platelets are changed into needle-like crystallites. In the presence of polystyrene particles and low surfactant concentrations the intermediate type of growth is observed (Fig. 13).

It is obvious that there is a difference in surface roughness between the different morphology types. Therefore, it was proposed^{54,76} that a change in surface roughness is responsible for the differences in polystyrene codeposition. For example glue is used, because the vertical

type morphology yields smooth deposits. The friction force, which prevents a particle from being removed from the surface before being incorporated depends on the local surface roughness around the particle.

Particles are depicted in Fig. 14 to show how they can be adsorbed onto the deposit. A particle adsorbed in a recessed area has a much larger probability of becoming included than one adsorbed on a flat surface. Particularly if particles are able to move along the surface due to shearing forces or Brownian rotation to recessed areas, a rough surface leads to higher amounts of embedded particles. Comparing the roughness associated with the growth morphologies of zinc, particle incorporation will decrease in the order: basal, intermediate and vertical type. Correspondingly polystyrene codeposition is the largest at high concentrations of cetylpyrridinium chloride, the lowest with high concentrations of cetylammmonium chloride or the other surfactants and in between for suspensions containing up to 0.02 mol kg⁻¹ surfactant.

A similar reasoning could explain the peaks at low current density in the polystyrene codeposition versus current density curves (Fig. 8). A deposit consisting of mossy nodules was found at the peak in the presence of 0.02 mol kg⁻¹ cetylpyrridinium chloride. Similar to composites prepared at high cetylpyrridinium chloride concentrations this is a basal type of morphology, where particles deposit in between nodules. Consequently increased codeposition compared to the intermediate type of morphology obtained at higher current densities is expected. For Au-Al₂O₃⁷⁷ codeposition an equivalent correlation between the orientation of Au crystallites and peaks in codeposition with current density were reported. Also the maximum in the particle incorporation versus current density curve for Cu-matrix composites is accompanied by a morphological change of the Cu deposit.¹⁰² As discussed in Section III.3.ii these peaks occur at the same current density as kinks in the polarization curves. Similarly, Wiart *et. al.*^{90,91} found a kink in polarization curves at low current density for Zn deposition from acidic ZnSO₄ electrolyte, where the morphology changes from the mossy basal type to the compact intermediate type.

LIST OF SYMBOLS

a	particle properties parameter (-)
A	constant in Tafel equation for metal deposition (V^{-1})

b	agitation rate parameters (-)
B, B_1, B_2	constant in Tafel equation for particle deposition (V^{-1})
c_i	concentration of species i (mol m^{-3})
c_{surf}	amount of surfactant per unit weight of particles (mol kg^{-1})
C^*	ion or particle number concentration (m^{-3})
Co	dimensionless constant (-)
C_z^X	binomial constant (-)
Dm	double layer dimensionless number
E	electrode potential (V)
F	Faraday constant ($C \text{ mol}^{-1}$)
F	force (N)
Gq	particle incorporation dimensionless number (-)
H	hydrodynamic coefficient (-)
j	current density ($A \text{ m}^{-2}$)
J_L	limiting current density ($A \text{ m}^{-2}$)
j_o	exchange current density ($A \text{ m}^{-2}$)
j_{tr}	transition current density ($A \text{ m}^{-2}$)
k	Langmuir adsorption constant (-)
k_0	constant (-)
k^*	electrochemical rate constant ($\text{m}^4 \text{ mol}^{-1} \text{ s}^{-1}$)
k_1, k_2, k_3	rate constants for particle deposition ($\text{m}^4 \text{ mol}^{-1} \text{ s}^{-1}$)
L	physical bond strength (m^{-2})
M	molecular weight (kg mol^{-1})
n	number of electrons transferred for the oxidation or reduction of an ion (-)
N	flux of ions or particles ($\text{m}^{-2} \text{ s}^{-1}$)
N^*	number of particle collisions (m s^{-1})
P	particle incorporation probability (-)
p_j	probability for an ion to be reduced at current density j (-)
q	charge (C)
Re	Reynolds number (-)
R	gas constant ($J K^{-1} \text{ mol}^{-1}$)
r	radial distance (m)
Sh'	modified Sherwood number (-)
Sx	dimensionless number for particle bath concentration (-)
t	time (s)

V	deposition rate (m s^{-1})
v_0	constant for particle deposition (m s^{-1})
W	weight (kg)
X	amount of ions adsorbed on a particle (-)
x	amount of ions adsorbed on a particle that need to be reduced (-)

Greek letters

α	volume fraction of incorporated material (-)
α_r	charge transfer coefficient (-)
β	mass fraction of incorporated material (-)
δ	diffusion layer thickness (m)
ϕ	volume fraction of suspended particles (-)
Γ	current efficiency (-)
η	overpotential (V)
λ	measure of interaction between free and adsorbed ions due to current density (-)
θ	strong adsorption coverage (-)
ρ	density (kg m^{-3})
σ	loose adsorption coverage (-)
ω	angular velocity of rotating electrode (s^{-1})

Subscripts

a	adsorbed
f	friction
M	metal
p	particle
r	removal

Superscripts

b	bulk
s	surface

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