Electrochemical codeposition of inert particles in a metallic matrix

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A survey on electrochemical codeposition of inert particles in a metallic matrix is given. Particles held in suspension in an electroplating bath are codeposited with the metal during electrodeposition. The particles used are inert to the bath and can be of different types, that is, pure metals, ceramics or organic materials. Combining this variety of types of particles with the different electrodeposited metals, electrochemical codeposition enables the production of a large range of composite materials with unique properties. Many experimental factors were found to influence the codeposition process, which led to some understanding of the mechanism. Models to predict the codeposition rate were developed, but were only partly successful.

List of symbols

A	constant in Tafel equation for metal deposition (V^{-1})
B, B_1, B_2	constants in Tafel equation for particle deposition (V^{-1})
C^{∞}, C^0	concentration in bulk and at the cathode surface, respectively $(mol\,m^{-3})$
C^*	number of ions or particles per unit volume in the bulk bath (m^{-3})
Co	dimensionless constant
C_z^K	binomial constant
Dm	double layer dimensionless number
F	Faraday's constant $(C\,mol^{-1})$
g	acceleration due to gravity constant $(m\,s^{-2})$
Gq	particle embedment dimensionless number
H	hydrodynamic coefficient
i	current density $(A\,m^{-2})$
i_0	exchange current density $(A\,m^{-2})$
i_{tr}	transition current density $(A\,m^{-2})$
k	amount of adsorbed ions on particle that need to be reduced
k^*	Langmuir adsorption constant
k_1, k_2, k_3	rate constants for particle deposition $(m^4\,mol^{-1}\,s^{-1})$
K	amount of ions adsorbed on a particle
M	molecular weight $(kg\,mol^{-1})$
n	valence of electrodeposited metal
N	number of ions or particles crossing the diffusion layer per unit time and surface area $(s^{-1}\,m^{-2})$
p_i	probability for an ion to be reduced
P	probability for a particle to become incorporated
r_p	particle radius (m)
Re	Reynolds number
Sh'	modified Sherwood number
Sx	dimensionless number for bath particle concentration
t	time (s)
v_0	constant for particle deposition $(m\,s^{-1})$
V	deposition rate $(m\,s^{-1})$
W	weight (kg)

Greek letters

α	measure of the interaction between free and adsorbed ions due to current density
β	volume percent of embedded particles
δ	diffusion layer thickness (m)
ζ	ζ-potential (V)
ϑ	strong adsorption coverage
ν	solution viscosity $(kg\,m^{-1}\,s^{-1})$
η	overvoltage (V)
Γ	current efficiency
ρ	density $(kg\,m^{-3})$
σ	loose adsorption coverage

Subscripts

e	solution
m	metal
p	particle
H	hydrogen

1. Introduction

Several excellent review papers concerning electrolytic composite plating have been published in recent years by Celis *et al.* [1–4]. These papers mainly treat the uses and the mechanism and models of the codeposition process. The present paper will include the most recent developments in these fields, but will also give an overview of the experimental facts reported in the literature.

1.1. *History*

Although Fink and Prince investigated the possibility of using electrochemical codeposition to produce self lubricating Cu-graphite coatings for use in car

engines in 1928 [5], until about thirty years ago little research was done in this field. In the early sixties the first investigations started and soon after this new industrial applications of electrodeposited composites were found. Interest in the technique grew and a better understanding of the process was obtained.

There are other methods of producing composite materials with a metallic matrix. The most widely used are powder metallurgy, metal spraying and internal oxidation [6–8]. A major disadvantage of these methods is that they need to be performed at high temperatures. Furthermore, these methods often do not allow the production of thin foils. Because electroplating is a very suitable method to produce metal coatings, electrochemical codeposition is a good alternative in the field of composite coatings. It combines the advantages of metal electroplating with those of composite materials.

1.2. Uses

The main uses of electrodeposited composites are in wear resistance, corrosion resistance and lubrication [1, 3]. Metals are dispersion hardened by the incorporation of oxide particles like Al_2O_3 and TiO_2 or fibres and whiskers [1, 3, 8]. These composites have a considerably higher yield strength and hardness than the pure metal [8, 9]. By coating metals with a metallic matrix composite containing particles of hard materials, like diamond, WC and SiC [10–12], they can be protected from abrasion. These hard materials are too brittle and have too weak adhesion to metal surfaces to be used as coatings alone. Therefore, a metal matrix is used to hold the particles together and facilitate good adhesion to the metal surface being coated. These types of coatings, especially the use of Ni–SiC coatings in motor blocks of aluminium alloys, are the main cause of the growing interest in electrochemical codeposition [1, 3, 7, 8].

The incorporation of submicron powders, like Al_2O_3, $BaSO_4$, Si_3N_4, V_2O_5 and Cr_2O_3, in a metal decreases the corrosion rate of the metal considerably [1, 9, 13, 14]. A composite coating can also reduce the corrosion by enhancing the adhesion of a lacquer on a metal. The metal matrix adheres strongly to the metal base and the occluded particles adhere strongly to the lacquer [1, 3]. A different use of codeposition for corrosion protection of low alloy steel was reported by Watson [15]. A stainless steel coating was produced by heat treatment of a Fe–Ni deposit containing Cr-particles.

Furthermore, electrodeposited composite coatings are used to increase the lifetime of metal surfaces that are in moving contact [1, 3]. Particles of low friction materials like graphite, MoS_2 and PTFE in these coatings reduce the friction between the metal surfaces [5, 16]. Again the metal matrix enables a better adhesion to the underlying metal surface. Apart from this dry lubrication a relatively new development in electrochemical codeposition also allows wet lubrication of metal surfaces. In this technique microcapsules containing a liquid lubricant are codeposited in a metal [1, 3]. During use of such a coating the metal matrix and the occluded microcapsules slowly erode away, thereby releasing the liquid lubricant. Electrochemical codeposition may be particularly useful in this context.

Finally, Keddam et al. [17] and Anani et al. [18] reported the use of codeposition in electrocatalysis. Electrodes are made by codeposition of particles of an electroactive material with a metallic matrix. The behaviour of these electrodes was seen to be controlled by the embedded material.

2. Experimental parameters

2.1. Particle concentration, type, shape and size

Sautter [19] found that the volume percentage of Al_2O_3 particles in a nickel matrix increases, with increasing particle concentration in the bath. This behaviour was confirmed by further investigators for a wide range of metal particle systems [8, 10, 12, 14, 16, 20–30]. On the other hand the absolute values of the particle content vary for different systems. For example, Greco and Baldauf [8] noticed that three times as much TiO_2 is built in a nickel matrix as Al_2O_3 for the same plating conditions. Moreover, Celis [22] showed that γ-Al_2O_3 codeposits with Cu in much smaller amounts than α-Al_2O_3.

No investigations on the influence of the particle shape on codeposition are reported. However, the particle shape affects the adsorption of the particles on the cathode, the adsorption of ions on the particle surface and the suspension stability, which are all factors influencing codeposition [31].

Regarding the effect of particle size on codeposition different results have been reported. For Ni–Al_2O_3 [32] and Ni–Cr [21] an increase in the percentage of incorporated particles was reported with increase in particle size. Furthermore, it was shown that the amount of P codeposited with Cu increases linearly with particle size [28]. In contrast, a negligible influence of particle size for Ni–Al_2O_3 [29] was observed and, for Ag–Al_2O_3, a lower deposition ratio for larger particles was reported [26].

2.2. Bath constituents, additives and ageing

For different types of baths different incorporation rates are reported, with the same kind of particles. For example, Brandes and Goldthorpe [32] observed that Al_2O_3 particles codeposit in Cu and Ni-baths, but not in a chromate-bath. Furthermore, they were not able to produce good Cu–Al_2O_3 deposits in a copper sulphate bath, while they obtained good deposits in a copper cyanide bath. In contrast to the extensive qualitative evidence for the effect of the bath constituents, there is little quantitative information regarding this effect. Williams and Martin [16] found that by increasing the CuCN concentration in a copper cyanide bath the density of codeposited

silica fibres increased. Experiments for Cr-graphite give similar results [24].

To standard plating baths brighteners or wetting agents are often added, which affect codeposition from such baths. Tomaszewski et al. [13] stated that different brighteners have a different effect, but generally they increase particle codeposition. Greco and Baldauf [8] confirmed this and named the use of wetting agents as one of the possibilities of increasing the number of occluded particles. On the other hand, some researchers [22, 32] observed a decrease in particle content on addition of wetting agents.

According to Tomaszewski et al. [33] the addition of small amounts of monovalent cations, like Tl^+, Ce^+, Rb^+ and NH_4^+, or amines, like TEPA (tetraethylene pentamine), alanine and EDTA (ethylene diamine tetraacetic acid) promote the codeposition of particles. The weight percentage of embedded $BaSO_4$ particles in copper increased from 0.5 to 4.5 with addition of $25\,g\,dm^{-3}$ EDTA. These promoting effects were confirmed by other authors [22, 34, 35].

Ageing of the codeposition bath seems to influence only certain metal particle systems. A decrease of Al_2O_3-content in copper on ageing, which might be caused by impurities in the bath, was observed [36]. Narayan and Chattopadhyay [25] reported no ageing effect up to 18 days for $Cr-Al_2O_3$. According to Buelens and Roos et al. [6, 37] codeposition of Al_2O_3 particles with Ni, Au and Cu did not show ageing effects, while they observed a pronounced ageing effect for Cu–SiC codeposition.

2.3. Temperature, pH and current density

The effect of temperature seems to vary for different codeposition systems. For $Ni-Al_2O_3$ no effect of temperature on the percentage of embedded particles was found [19, 29]. On the other hand the graphite content of a Cr-matrix increased with temperature up to $50°\,C$ [24], while for $Cr-Al_2O_3$ [25] exactly the reverse was reported, i.e. a decrease of particle content up to $50°\,C$. In both cases no effect above this temperature, was found. For $Ni-V_2O_5$ a maximum particle content at $50°\,C$ was reported [14]. A continuous decrease of the weight percent embedded particles in copper was observed by Tomaszewski et al. [33].

Investigations concerning the effect of pH give consistent results. Sautter [19] found no influence of pH above pH 2 and a sharp decrease in occluded particles below this value for $Ni-Al_2O_3$. This result was confirmed for different systems [12, 13, 22, 29, 32, 33]. Recently, Yeh and Wan [38] noticed that the current efficiency for nickel reduction decreased markedly below pH 2 if SiC particles were present. Moreover, this pH corresponds to the point of zero charge of SiC particles in a NaCl solution. It is not clear if these effects are accompanied by a decrease of particle content below pH 2, because the SiC content of the deposits was not measured.

Together with the particle concentration, the current density is probably the most extensively investigated parameter. Roughly two different current density dependencies can be distinguished. First, some authors found little or no influence of current density on the number of occluded particles [12, 24, 28]. Second, the current density versus particle content curve showed or suggested the presence of one or several maxima [10, 16, 18, 22, 23, 25, 27, 29, 39, 40–41].

For $Ni-TiO_2$ a shift of the maximum to a higher current density for a higher agitation rate was observed. Similarly, for $Cr-Al_2O_3$ a minimum was formed in the particle content against current density curve when the particle concentration in the bath was increased [25].

Apart from the fact that the current density influences the codeposition, the current density itself is affected by the presence of particles. Several authors determined cathodic polarization curves for the codeposition plating bath with and without particles. Most [15, 19, 22, 39, 42] found a higher current density for the same cathode potential when particles were present, indicating a depolarization of the cathode. Suzuki et al. [43] did extensive research on the polarization behaviour of the cathode for $Ag-Al_2O_3$. At low overvoltage the particles near the cathode suppress metal ion reduction. At high overvoltage the transport of the metal ions to the cathode becomes an important factor and it is known that the addition of inert particles enhances this transport [44, 45], which leads to depolarization of the cathode.

Buelens [37, 39] noticed that at the current density where a maximum in the particle occlusion is found a kink in the polarization curve for $Cu-Al_2O_3$ and $Au-Al_2O_3$ is present. Recently Webb and Robertson [46] reported that, apart from a large polarization of the cathode, the maximum is accompanied by a sharp decrease in current efficiency.

2.4. Agitation and surfactants

It is obvious that particles need to arrive at the cathode surface to be built in and therefore, have to be transported from the bulk to the cathode [31]. Greco and Baldauf [8] realized that agitation of the bath enhances the particle transport and stated that increasing the bath agitation results in a larger amount of embedded particles. However, four years earlier Williams and Martin [16] reported that too much agitation leads to a decrease of particle codeposition, because the particles are swept away from the cathode surface before they are built in. Both these observations were confirmed by Lee and Wan [34], who found that the curve of particle content versus electrolyte flow rate shows a maximum.

For the effect of bath agitation by a RDE, three different flow regimes can be distinguished: laminar, transition and turbulent [39]. In the laminar regime there is no influence of the rotation speed. For the transition regime a decrease, followed by a large increase, of the particle content is observed, while in

the turbulent regime a continuous decrease takes place. Furthermore, the particle content was determined to decrease going from the centre to the edges of a RDE [34, 47]. Correspondingly, Graydon and Kirk [48] were able to relate different zones of hydrodynamic flow to different zones of particle occlusion on the cathode for a channel electrode.

Apart from particle transportation, agitation also serves to keep particles in suspension. Therefore, all researchers have used some kind of bath agitation and sometimes [8, 19] even blended the electrolyte and particles before the experiments to obtain a stable suspension. Both the bath agitation and the blending break up agglomerates of particles, which is necessary to obtain homogenous deposits containing a fine dispersion of particles.

The effects of some of the parameters on codeposition discussed earlier could be connected to the way they affect the suspension stability [31]. The suspension stability increases with decreasing settling speed of the particles v, which, for spherical particles, is given by Stokes law, i.e.,

$$v = \frac{2gr_p^2(\rho_p - \rho_e)}{9\nu} \qquad (1)$$

The suspension stability directly depends on the particle size, r_p, and the particle density, ρ_p, i.e., the particle type. Furthermore, the density, ρ_e, and viscosity, ν, of the electrolyte are both determined by the bath constituents and temperature. The relative importance of the effect of these parameters on codeposition is difficult to assess.

Because their graphite particles agglomerated and precipitated Fink and Prince [5] needed another method, apart from bath agitation, to keep the particles suspended. They added the particles to the plating bath in a suspension stabilized by surfactants (i.e., tannin and gelatin). Surfactants improve the stability of a suspension by increasing the wettability of the suspended particles by adsorbing on their surfaces. The wettability of (inorganic) particles is not a major problem in codeposition, but additional advantages are obtained if cationic surfactants are used [31]. These cationic surfactants confer a net positive charge to the particles, which prevents them from agglomerating and attracts them electrostatically to the cathode.

Helle [49, 50] found that a combination of cationic and nonionic surfactants produced a stable suspension of PTFE particles in a Ni-bath, which allowed the plating of composites containing up to 70 vol % PTFE. In this system the use of surfactants was specially successful, because in comparison to inorganic particles the wettability of PTFE particles is more of a problem [31]. Furthermore, the affinity of the fluorocarbon surfactant to a fluoropolymer, like PTFE, is quite large. However, Helle also showed that these fluorocarbon surfactants produced a dramatic increase (up to 50%) in particle content for inorganic particles, like SiC and diamond. This increase in particle content was confirmed by

Meguno et al. [51], who found twice as much SiC particles embedded in a Ni-matrix if a nonionic surfactant was used. By using a surfactant, Chang and Lee [10] produced nickel deposits containing about five times as much Al_2O_3 particles, while using particle concentration about ten times as low as in experiments without surfactants [8, 19, 29].

The disadvantage of using surfactants is that they are incorporated in the deposit [50]. Surfactant molecules adsorbed on a particle are embedded in the deposit together with the particle. Because of the relatively small amount of adsorbed surfactant, this hardly affects the deposit. However, free surfactant, that is, surfactant molecules which are not adsorbed on a particle, codeposits with the metal, which leads to stressed and brittle deposits.

Brighteners and wetting agents also act as surfactants, which explains their effect on codeposition [8, 13, 22, 32]. If they act as cationic surfactants, they promote codeposition. Correspondingly, some wetting agents or brighteners reduce codeposition by acting as anionic surfactants, conferring a negative charge on the particles [51].

2.5. Surface charge

Many parameters discussed above influence the surface charge of the particles. Fink and Prince in 1928 [5] already realized the importance of the surface charge and stated that a positive surface charge enhances codeposition, because the particles are electrostatically attracted to the cathode.

This was confirmed by Tomaszewski et al. [33], who found that the negatively charged silica particles transported less readily to the cathode than the positively charged Al_2O_3 particles. Furthermore, Narayan and Chattopadhay [25] were able to solve the problem of codepositing Al_2O_3 particles with chromium [32] by dry grinding them before an experiment, which changed their surface properties and conferred a positive surface charge.

In 1963 Tomaszewski et al. [13] had suggested that particles obtained a positive surface charge by adsorption of metal ions and H^+ ions. Kariapper and Foster [35] noticed that the amount of adsorbed metal ions increased with increasing metal ion concentration or the addition of Tl^+, TEPA or EDTA. Consequently, they assumed that the promoting effect on codeposition of these additives is derived from the fact that they enhance metal ion adsorption. Celis et al. [22, 23] confirmed these results and found that the additives themselves were not adsorbed on the particles. The reverse effect was described by Lakshminarayanan et al. [36], who noticed that Cl^- ions reduced codeposition of Al_2O_3 with copper. According to them CuCl is formed, which adsorbs onto the particle, thus inhibiting Cu^{2+} adsorption.

Meguno et al. [51] confirmed the suggestions of the earlier researchers by measuring ζ, which is a quantitative measure for the particle surface charge [31]. At high pH ζ of α-SiC and γ-SiC is negative, but it

increases with decreasing pH and becomes positive at low pH.

Lee and Wan [34] investigated the ζ of Al_2O_3 particles in a dilute copper sulphate bath. First, ζ of α-Al_2O_3 increases with copper sulphate concentration and becomes positive, while that of γ-Al_2O_3 becomes more negative. This explains why α-Al_2O_3 can be codeposited much more easily than γ-Al_2O_3. Second, codeposition promoters like Tl^+ and TEPA cause a large increase in ζ to positive values, confirming the enhanced metal ion adsorption as found by Kariapper and Foster [35]. Similarly, the addition of even a small amount of Cl^- ions decreases ζ of α-Al_2O_3 to a negative value, explaining their inhibitory effect.

Hayashi et al. [30] determined the ζ of α-Al_2O_3 particles in more concentrated copper sulphate baths, that is, comparable to standard plating baths. In contrast to all earlier investigations they observed that ζ is negative and becomes more negative with decreasing pH. The amount of SO_4^{2-} adsorbed on the particles was about seven times as high as the amount of adsorbed Cu^{2+}. So, they concluded that Cu^{2+} and H^+ ions are adsorbed on the α-Al_2O_3 particles, but that their positive charge is more than compensated for by the adsorption of SO_4^{2-} ions, resulting in a negative ζ.

Particles with a surface charge form more stable suspensions because, due to their mutual repulsion, they do not agglomerate. By addition of a cationic surfactant to initially negatively charged particles, Bartlett [31] showed that the dispersion stability reaches a minimum when ζ equals 0. Correspondingly, Helle [50] reported that codeposition is small when ζ is negative, inhibited when it is zero, and large when it is positive.

3. Mechanism and models

3.1. Early mechanisms and models

The first attempt to explain electrochemical codeposition was made by Whithers in 1962 [52]. He proposed that the particles with a positive surface charge are drawn to the cathode by electrophoresis. In 1964 Martin and Williams [16] suggested that the particles are also transported to the cathode by the agitation of the bath and are mechanically entrapped by the growing metal layer. In 1967 Brandes and Goldthorpe [32] rejected the idea of mechanical entrapment. They suggested that there is some attractive force holding the particles at the cathode long enough to be incorporated by the growing metal layer. This force could be an electrostatic one. At present it is still difficult to assess the relative importance of these three mechanisms.

In 1968 Saifullin and Khalilova [53] were the first to present a model to calculate the weight percent of incorporated particles. This model was based on mechanical entrapment only and has to be rejected. Three years later Bazzard and Boden [21] proposed

that particles collide with the cathode surface due to the bath agitation and that the particles have to stay at the cathode surface for a certain time to become occluded. They developed a simple equation to calculate the weight percent of embedded particles, but rightly stated that it lacked any physical significance.

3.2. Guglielmi's model

The model developed by Guglielmi in 1972 [20] presented an important contribution to the understanding of codeposition. He proposed a two-step mechanism taking into account electrophoresis and adsorption. In the first step, which is of a physical nature, particles approaching the cathode become loosely adsorbed on the cathode surface. These loosely adsorbed particles are still surrounded by a cloud of adsorbed ions. In the second step the particles loose this ionic cloud and become strongly adsorbed on the cathode. This step is thought to be of an electrochemical character, that is, it depends on the electrical field at the cathode. Finally, the strongly absorbed particle are occluded by the growing metal layer.

In the model the loose adsorption step is described by a Langmuir adsorption isotherm, taking in account the cathode area available for this loose adsorption:

$$\sigma = \frac{k^* C_p^\infty}{1 + k^* C_p^\infty} (1 - \vartheta) \qquad (2)$$

with σ is the loose adsorption surface coverage, ϑ the strong adsorption surface coverage and k^* depends on the intensity of the particle cathode interaction. Obviously the second step depends on σ and this dependence is considered linear by Guglielmi. Together with a factor to describe its postulated dependence on the electrical field at the cathode, represented by the cathode overpotential (η), the following formula for the strong adsorption rate was obtained:

$$V_p = \sigma v_0 e^{B\eta} \qquad (3)$$

where v_0 and B are constants. The deposition rate of the metal is found using Faraday's law:

$$V_m = \frac{M_m i}{nF\rho_m} \qquad (4)$$

Taking into account the area of the cathode available for codeposition the current density is related to the overpotential by the Tafel equation:

$$i = (1 - \vartheta)i_0 e^{A\eta} \qquad (5)$$

Assuming that the volume fraction of embedded particles $\beta \approx \vartheta \ll 1$ these expressions give

$$\frac{C_p^\infty}{\beta} = \frac{M_m i_0^{(B/A)}}{nF\rho_m v_0} i^{(1-B/A)} \left(\frac{1}{k^*} + C_p^\infty \right) \qquad (6)$$

The constants k^*, v_0 and B depend on the particle-metal system considered and have to be determined from codeposition experiments, while the other parameters can be measured (A and i_0) or are known

constants. Hence, the model is not able to predict the codeposition rate for a particular system.

Using some experimental information it was successful in describing the codeposition behaviour of Ni–SiC, Ni–TiO$_2$ [20], Cu–Al$_2$O$_3$ [23], Cr–C [24], Ag–Al$_2$O$_3$ [26], Cu–SiC [27] and Cu–P [28]. However, it was not able to describe Cr–Al$_2$O$_3$ codeposition [25]. The Langmuir isotherm and the Tafel equation seem to be incorrect descriptions to take into account the particle concentration and the current density, respectively. Moreover, other parameters, like bath agitation, bath constituents and particle size and type are disregarded. They are inherently accounted for by the constants k^*, v_0 and B but, of course, it is difficult to assess exactly how. Therefore, these constants have to be determined separately for every set of experimental conditions.

Regarding the role of the ionic cloud surrounding the particles some obscurity can be noted in Guglielmi's model [37]. Several authors already noted the importance of adsorption of ions on the particles in codeposition and in 1974 Kariapper and Foster [35] showed it quantitatively. They concluded that the adsorbed metal ions play a twofold role: they cause the particles to be electrostatically attracted to the cathode and they are reduced at the cathode thus creating a physical bond between the cathode and the particle by their reduction. They also found a strong dependence of the codeposition rate on the bath agitation. The particle content versus current density curves exhibit a maximum, whose position depends on the agitation rate.

They proposed a model based on these observations, taking into account the effect of most experimental parameters. However, the factors used to describe these effects cannot be easily measured or evaluated [37].

3.3. Model of Buelens and Celis et al.

Celis et al. [22, 23, 37, 39] noticed that Guglielmi's model cannot explain the maximum in the particle content against current density curve for Cu–Al$_2$O$_3$ codeposition. A comparison between this curve and the cathodic polarization curve, led to the suggestion that the particle deposition rate depends on the reduction rate of the Cu^{2+} ions adsorbed on particles.

It was concluded that two processes play a fundamental role in the codeposition mechanism: (i) the adsorption of ions onto the particle and (ii) the reduction of these adsorbed ions at the cathode surface.

Based on these postulates, and the pronounced effect of agitation on codeposition [39], Buelens [37, 40] proposed a five step mechanism for codeposition. In the first step particles in the bulk of the solution obtain an ionic cloud by adsorbing ions from the solution. Then, 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, similar to Guglielmi's model the particles are incorporated in two steps. They are adsorbed on the cathode surface still surrounded by their ionic cloud and then become embedded by the reduction of some of the adsorbed ions.

Using this mechanism a model for the calculation of the weight percent of embedded particles was developed. The basic hypothesis of the model is that a certain amount, k, of ions adsorbed on the particle, K, must be reduced at the cathode for the particle to become incorporated. This takes into account a certain residence time of a particle on the cathode surface necessary for it to be built-in, as stated by Bazzard and Boden [21]. Thus, not all particles present at the cathode surface will be embedded, which was also a basic assumption in Guglielmi's model.

The weight percent of embedded particles is defined as follows:

$$w(\%) = \frac{W_p N_p P}{\dfrac{M_m i}{nF} + W_p N_p P} \times 100 \qquad (7)$$

where W_p is the weight of one particle, N_p is the number of particles crossing the diffusion layer at the cathode per unit 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 $P_{(k/K,i)}$ that at least k out of K adsorbed ions are reduced, hence if p_i is the chance that one ion is reduced at current density, i:

$$P_{(k/K,i)} = \sum_{z=k}^{K} C_z^K [1 - p_i]^{K-z} p_i^z \qquad (8)$$

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

$$p_i = \frac{i/nF}{(C_m^\infty + C_m^0)\delta/2 + (i/nF)} \qquad (9)$$

where C_m^∞ and C_m^0 are, respectively, the bulk concentration and the concentration at the cathode surface of the metal ions. Now a factor H is introduced to take into account bath agitation:

$$P = HP_{(k/K,i)} \qquad (10)$$

Following from the bath agitation experiments, $H = 1$ 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:

$$N_p = N_m \frac{C_p^*}{C_m^*} \left(\frac{i_{tr}}{i}\right)^\alpha \qquad (11)$$

where i_{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 $\alpha = 0$, because the ion-reduction is rate determining, while the diffusion rate is high enough for both particles and free ions. However, $\alpha \neq 0$ under concentration overvoltage control, because diffusion of ions is rate determining, which is obviously much slower for adsorbed ions than for the free ions.

Similar to earlier models this model cannot predict the particle content directly from the experimental conditions. The factors k, K and α need to be determined by fitting the model with experimental results. The authors obtained a good agreement between the model and experimental results for Cu–Al$_2$O$_3$ and Au–Al$_2$O$_3$ codeposition [37, 40]. However, the assumption that at i_{tr} a transition from charge transfer to mass transport overvoltage control occurs can be questioned. For copper deposition the cathodic overvoltage of this transition corresponds to the value where Degrez and Winand [54] observe a change in the reduction mechanism of Cu^{2+}. This indicates that the change in codeposition behaviour at i_{tr} is associated with a change in the metal deposition mechanism and not with diffusion limitation of the particle deposition as proposed in this model. Furthermore, it is not clear why in Equation 7, for p_i, a time factor, which would make it dimensionless, is neglected. Celis et al. [40] do not give any explanation for this, while Buelens [37] just states that a negligible error is created.

3.4. Recent models

Hwang and Hwang [41] proposed a more general model than that of Celis and Buelens, in which some of the factors, like H and i_{tr}, are interrelated. Based on the model of Guglielmi, for various current density ranges, the particle codeposition rate is determined by the electrode reactions for adsorbed species on the particles, whose rates are determined by kinetic and/or diffusion parameters. They investigated Co–SiC codeposition, hence their starting point is the reduction of H$^+$ and Co^{2+} adsorbed on the particles. Three different current density ranges for this reduction of adsorbed ions are distinguished: (i) low current density, where only H$^+$ ions are reduced; (ii) intermediate current density, where the H$^+$ reduction rate has reached its limiting value and also Co^{2+} is reduced; and (iii) 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

$$V_m = \frac{M_m}{\rho_m nF} i\Gamma(1 - \vartheta) \tag{12}$$

where Γ is the current efficiency.

In the low current density range the particle deposition rate, V_p, is determined by the reduction of the adsorbed H$^+$ ions and it has been deduced that

$$V_p = k_1 C_H^0 \sigma e^{B_1 \eta} \tag{13}$$

where C_H^0 is the concentration of adsorbed H$^+$ ions on

the particle surface, which decreases with increasing H$^+$ reduction:

$$C_H^0 = \left(1 - \frac{V_P}{V_{p,H^+}}\right) C_H^\infty \tag{14}$$

where V_{p,H^+} is the maximum particle deposition rate due to H$^+$ reduction and C_H^∞ 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^+}, while 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

$$V_p = V_{p,H^+} + k_2\left(1 - \frac{V_p}{V_{p,m}}\right) C_m^\infty \sigma e^{B_2 \eta} \tag{15}$$

where $V_{p,m}$ is the limiting particle deposition rate due to the metal reduction and C_m^∞ 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 ion concentration. Hence, Equation 13 is simplified to

$$V_p = k_3 \sigma \tag{16}$$

The volume percent of embedded particles can now be calculated using Equation 12 and, depending on the current density range, using Equation 13, 15 or 16. This model is an improvement on that of Guglielmi. However, inherently the assumption is made that the reduction of adsorbed ions differs 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, while for adsorbed ions different regimes are distinguished. The authors do not discuss the validity of this assumption.

The present mechanism can be generalized to a two step process, that is, transport of the particle to the cathode surface and a particle-cathode interaction [2]. As can be seen from the foregoing discussion, the mass transport step was not treated or was only just globally incorporated in the models. From related fields of research, like filtration, detailed descriptions of mass transport of solid particles and particle surface interactions are known [55]. Recently, several authors [27, 47, 56] tried to develop a model for codeposition using such descriptions. In comparison to the earlier models the present models are much more elaborate. They are built up of many, often interrelated, equations containing an extensive set of parameters. This renders it difficult to get an easy insight into the effect of an experimental parameter and necessitates the use of extensive computer calculations.

Guo et al. [27] proposed a model based on a description of the mass transport by so-called similitude numbers, which are dimensionless numbers determined by the factors influencing the

mass transport. A standard description of the Sherwood number for mass transport of solid particles in a dilute suspension to a fixed plate was modified for codeposition. A factor Sx was introduced for the effect of the particle concentration in the bath and a factor Gq for the incorporation process of the particles in the metal matrix. Among others Gq contains a time factor describing the earlier-mentioned residence time of a particle at the cathode surface. If certain parameters, like temperature and bath constituent are considered to be constant, the particle deposition rate can be calculated from the similitude number Sh':

$$Sh' = Co\,Re^c Dm^d Sx^e Gq^f \qquad (17)$$

where Re is the Reynolds number and Dm is the electrical double layer number, while Co, c, d, e and f are constants, which have to be determined by fitting the model with experimental data. Satisfactory agreement with experimental data were obtained for Cu–SiC codeposition in channel flow. However, because of the limited range of experimental data it is not clear if the model is able to predict important features like the peak in the particle inclusion versus current density curve.

In 1987 Valdes [56] developed a model for codeposition at a RDE taking into account the various ways in which a particle is transported. As starting point an equation of continuity for the particle number concentration based on a differential mass balance was chosen. In this equation the particle flux is composed of expressions for the different mass transport processes (i.e., 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.

Valdes noticed the difficulties in obtaining a good description of the particle–electrode interaction. For nonelectrochemical 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 most simple model. However, Valdes showed that this model cannot be used, because it predicts maximum codeposition at the limiting current density, which contradicts experimental observations. Therefore, he proposed another model based on the generally accepted assumption that the reduction of adsorbed ions is the determining factor for particle deposition. This electrode–ion–particle electron transfer (EIPET) model leads to a Butler–Volmer like expression for the particle deposition rate. With this model the experimentally observed peak in the particle inclusion versus current density curve is predicted.

Due to the fact that no experimental work has been done on this model it is impossible to assess its validity

for real codeposition systems. However, it presented a good basis for the more precise theoretical model of codeposition at a RDE reported by Fransaer et al. [47]. These workers developed a trajectory description for a particle based on all the forces and torques acting. This included the forces due to fluid convection and particle motion and the forces acting directly on the particle (e.g., gravity, the electrophoretic force and the double layer force). Expressions for all these forces were developed and led to a set of equations describing the particle trajectory. Now the particle volume flux can be 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. Hence, the authors introduced a reaction term characterizing the particle–electrode interaction. A force balance on the particle led to an equation for the probability that a particle at the electrode surface will be incorporated. This force balance includes an adhesion force, which was determined from Cu–polystyrene codeposition experiments. Using this adhesion force the trajectory model gives a good description of the variation of the particle content in the deposit as function of the particle concentration in the bath.

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 double layer 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. A strong repulsive force between the particle and the electrode is present at short distances. Therefore, the structural or hydration force was introduced, which is a short range repulsive force due to the ordering of solvent molecules at interfaces in concentrated electrolytes.

This hydration force is minimal if the electric field at the electrode is minimal (i.e., at the potential of zero charge). So the maximum in the particle inclusion versus current density curve could be caused by 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 also be given using the hydration force.

Although, experiments will have to show if a hydration force is actually present, the trajectory model offers a good mathematical description for gaining a better theoretical insight into the codeposition process. Experimental investigations into the actual nature of the particle electrode interaction are necessary to get a better understanding and, consequently, a better modelling of the codeposition process.

However, the trajectory model, just as all earlier models, does not consider the growth behaviour of the metal deposit. As previously noted the maximum in the particle occlusion against current density curve for Cu-matrix codeposition occurs at the same overpotential as a kink in the $E/\ln i$ curve measured by Degrez and Winand [54]. From this curve they concluded that the cathodic charge transfer coefficient is 0.5 in the low overpotential region and 0.1 in the high overpotential region. This change in charge transfer coefficient is accompanied by a morphological change in the copper deposit. Such a dramatic change in the charge transfer coefficient suggests a strong change in the nature of the electrode surface, possibly, in the case of copper deposition, the presence of a copper hydride compound at high overpotential.

4. Concluding remarks

Electrochemical codeposition of inert particles in a metal matrix is a suitable technique to produce composite materials. Especially in the field of coatings it offers a good alternative to other techniques and enables the production of composites with unique properties.

Many interrelated experimental parameters influence the codeposition process. A clear picture of the exact effect of each parameter is difficult to obtain, because often different, or even contradicting, results are reported by different authors. Particle concentration in the bath, current density and bath agitation seem to be the most important parameters. Several investigations suggest that the metal growth mechanism also plays a role, but this has to be investigated further.

The mechanism for codeposition, which is generally accepted, involves particle transport to the cathode surface by bath agitation and embedment in the metal by reduction of adsorbed ions.

Attempts to develop models, which are able to predict the amount of incorporated particles from the experimental conditions have so far failed. Some encouraging results were obtained with fitted parameter models. Presently, models involving detailed descriptions of particle transport and particle-cathode interactions offer a promising perspective.

References

[1] J. R. Roos, J. P. Celis, J. Fransaer and C. Buelens, *J. Metals* **42** (1990) 60.
[2] J. P. Celis, J. R. Roos, C. Buelens and J. Fransaer, *Trans. Inst. Met. Finish.* **69** (1991) 133.
[3] C. Buelens, J. Fransaer, J. P. Celis and J. R. Roos, *Bull. Electrochem.* **8** (1992) 371.
[4] J. Fransaer, J. P. Celis, J. R. Roos, *Met. Finish.* **91** (1993) 97.
[5] C. G. Fink and J. D. Prince, *Trans. Am. Electrochem. Soc.* **54** (1928) 315.
[6] J. R. Roos and J. P. Celis, Proceedings AESF'84, New York (1984) p. 1.
[7] J. R. Roos, Proceedings INCEF'86, Bangalore (1988) p. 382.
[8] V. P. Greco and W. Baldauf, *Plating* **55** (1968) 250.
[9] N. Periene, A. Cesuniene and L. Taicas, *Plat. Surf. Finish.* **80** (1993) 73.
[10] Y. S. Chang and J. Y. Lee, *Mater. Chem. Phys.* **20** (1988) 309.
[11] A. E. Grazen, *Iron Age* **183** (1959) 94.
[12] F. Mathis, B. Pierragi, B. Lavelle and B. Criqui, Proceedings 24th ISATA, Florence (1991) p. 171.
[13] T. W. Tomaszewski, R. J. Clauss and H. Brown, *Proc. Am. Electroplaters Soc.* **50** (1963) 169.
[14] G. N. K. Ramesh Bapu and M. Mohammed Yusuf, *Mat. Chem. Phys.* **36** (1993) 134.
[15] S. W. Watson, *J. Electrochem. Soc.* **140** (1993) 2235.
[16] R. V. Williams and P. W. Martin, *Trans. Inst. Met. Finish.* **42** (1964) 182.
[17] M. Keddam, S. Senyarich, H. Takenouti and P. Bernard, *J. Appl. Electrochem.* **24** (1994) 1037.
[18] A. Anani, Z. Mao, S. Srinivasan and A. J. Appleby, *ibid.* **21** (1991) 683.
[19] F. K. Sautter, *J. Electrochem. Soc.* **110** (1963) 557.
[20] N. Guglielmi, *ibid.* **119** (1972) 1009.
[21] R. Bazard and P. J. Boden, *Trans. Inst. Met. Finish.* **50** (1972) 63.
[22] J. P. Celis, PhD thesis, Catholic University, Leuven (1976).
[23] J. P. Celis and J. R. Roos, *J. Electrochem. Soc.* **124** (1977) 1508.
[24] R. Narayana and B. H. Narayana, *ibid.* **128** (1981) 1704.
[25] R. Narayan and S. Chattopadhyay, *Surf. Technol.* **16** (1982) 227.
[26] Y. Suzuki and O. Asai, *J. Electrochem. Soc.* **134** (1987) 1905.
[27] H. Guo, Q. Qin and A. Wang, *Proc.-Electrochem. Soc.* **88-18** (1988) 46.
[28] J. W. Graydon and D. W. Kirk, *J. Electrochem. Soc.* **137** (1990) 2061.
[29] M. Verelst, J. P. Bonino and A. Rousset, *Mat. Sci. Eng.* **A135** (1991) 51.
[30] H. Hayashi, S. Izumi and I. Tari, *J. Electrochem. Soc.* **140** (1993) 362.
[31] P. K. N. Bartlett, Industrial training report AKZO, Arnhem, (1980) pp. 10–39.
[32] E. A. Brandes and D. Goldthorpe, *Metallurgia* **76** (1967) 195.
[33] T. W. Tomaszewski, L. C. Tomaszewski and H. Brown, *Plating* **56** (1969) 1234.
[34] C. C. Lee and C. C. Wan, *J. Electrochem. Soc.* **135** (1988) 1930.
[35] A. M. J. Kariapper and J. Foster, *Trans. Inst. Met. Finish.* **52** (1974) 87.
[36] G. R. Lakshminarayanan, E. S. Chen and F. K. Sautter, *Plat. Surf. Finish.* **63** (1976) 38.
[37] C. Buelens, PhD thesis, Catholic University, Leuven (1984).
[38] S. H. Yeh and C. C. Wan, *J. Appl. Electrochem.* **24** (1994) 993.
[39] C. Buelens, J. P. Celis and J. R. Roos, *ibid.* **13** (1983) 541.
[40] J. P. Celis, J. R. Roos, C. Buelens, *J. Electrochem. Soc.* **134** (1987) 1402.
[41] B. J. Hwang and C. S. Hwang, *J. Electrochem. Soc.* **140** (1993) 979.
[42] S. W. Watson and R. P. Walters, *ibid.* **138** (1991) 3633.
[43] Y. Suzuki, M. Wajima and O. Asai, *ibid.* **133** (1986) 259.
[44] P. J. Sonneveld, W. Visscher and E. Barendrecht, *J. Appl. Electrochem.* **20** (1990) 563.
[45] D. W. Gibbons, R. H. Muller and C. W. Tobias, *J. Electrochem. Soc.* **138** (1991) 3255.
[46] P. R. Webb and N. L. Robertson, *ibid.* **141** (1994) 669.
[47] J. Fransaer, J. P. Celis and J. R. Roos, *ibid.* **139** (1992) 413.
[48] J. W. Graydon and D. W. Kirk, *Can. J. Chem. Eng.* **69** (1991) 564.
[49] K. Helle, Proceedings, 4th International Conference in Organic Coating Science and Technology, Athens (1978) 264.
[50] K. Helle, Report AKZO Research, Arnhem (1993).
[51] K. Meguno, T. Ushida, T. Hiraoka and K. Esumi, *Bull. Chem. Soc. Jpn.* **60** (1987) 89.
[52] J. C. Whithers, *Prod. Fin.* **26** (1962) 62.
[53] R. S. Saifullin and R. G. Khalilova, *J. Appl. Chem. USSR.* **43** (1970) 1274.
[54] M. Degrez and R. Winand, *Electrochim. Acta* **29** (1984) 365.
[55] Z. Adamczyk, *Colloids and Surfaces* **35** (1989) 283.
[56] J. L. Valdes, *J. Electrochem. Soc.* **134** (1987) 223C.