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## Electrolytic co-deposition of silicate and mica particles with zinc

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**Abstract** Particles of silicate and mica were co-deposited with zinc from a weakly acid zinc electrolyte. The co-deposition became possible after 3 h of milling of the particles. A pH of 4.5, a rotation speed of 600 rpm and a particle concentration of 50 g/l were the optimal conditions. A change of the zeta potential to positive values was observed, caused by adsorption of zinc ions on the particle surface. Under these conditions the particle concentration in the zinc matrix was up to 20 mass per cent. The compound layers showed increased hardness and considerably improved corrosion resistance.

### Introduction

Composite coatings consist of a metal or metal alloy matrix containing a dispersed phase of non-metallic particles. Such coatings have been developed for improved material properties with regard to corrosion stability, wear resistance, friction protection, self-lubrication, high temperature stability, electrical contacts and improved catalytic activity.

The combination of positive properties of the different components, e.g. metals and ceramics, leads to materials with new and improved qualities. The metals providing the matrix are mainly nickel, cobalt, copper, silver, zinc or gold. The list of particles embedded into the metal matrix ranges from carbides (e.g. SiC, WC, TiC), oxides (e.g. Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>) to lubricants (e.g. MoS<sub>2</sub>, graphite, hexagonal BN) and polymer particles such as PTFE [1, 2, 3, 4, 5, 6].

Composite coatings based on zinc are finding increased interest in surface technology and corrosion

protection. Potential fields of application are improved corrosion and wear resistance of zinc composite layers with extended lifetime. Aluminium oxide-modified zinc deposits are the key for improved adhesion by use of adhesion promoters. The increased adhesion leads to improved corrosion protection of paints and coatings. But up to now no large-scale industrial application exists. The reason might be the lack of a stable plating process. The difficulties of incorporation of colloidal particles in a Zn matrix are connected with the crystal structure and the negative deposition potential of zinc as well as the amphoteric nature of the zinc hydroxide. Therefore, the electrodeposition and the properties of the composite coating of zinc with silicate particles (silica flakes and mica) were investigated. The results are presented in this paper.

Silicate particles of different size (Merck, Darmstadt, Germany) were investigated. The first group of particles had diameters of 1–15 µm (mica) and 10–50 µm (silica flakes) and gave conventional dispersion layers. Experiments were also made with a second group, so called “nanoparticles” of 10–100 nm, to achieve an increased hardness [5, 7]. It was found that nanoparticles were not incorporated into the zinc matrix, which corresponds to reports from the literature [8, 9, 10, 11]. Nanoparticles were found on steps and faces on the surface but not in the zinc matrix. Otherwise, for microparticles a complete incorporation into the metal matrix was achieved.

### Experimental

Functional zinc composite coatings on sheet steel have been electroplated from a low acidic zinc electrolyte of conventional composition (see section Zn plating electrolyte) mixed with suspensions of silica flakes or mica particles. The experimental parameters essential for an homogeneous particle incorporation into the zinc matrix were determined and optimised.

The following parameters were investigated: (i) chemical nature and size of the particles; (ii) cell

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construction with respect to electrode positions; (iii) type and composition of the electrolyte (particle concentration and pH value); (iv) hydrodynamic aspects of electrolyte convection and particle transport (stirring); (v) current density and plating time; (vi) temperature.

### Electrolytic cell

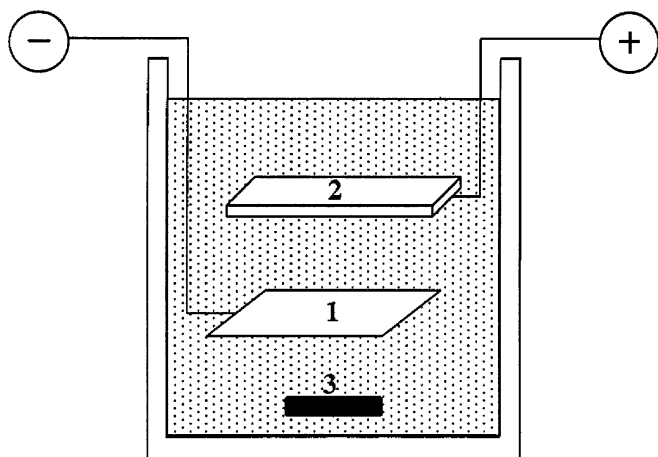
Different cell types were investigated to find out the most suitable electrode position and electrolyte convection. The electrode sheets were positioned in a vertical and in a horizontal manner. The electrolyte streamed parallel to the electrode sheet or hit the electrode perpendicular (the electrolyte was stirred by a magnetic stirrer). The optimised conditions were a horizontal electrode orientation and the undirected convection of the electrolyte as obtained by a magnetic stirrer (Fig. 1). A homogeneous composition layer was obtained on the underside of the electrode, because of the optimum electrical migration and mechanical transport conditions. Cross sections of the electrode were shown elsewhere [12].

### Zn plating electrolyte

A zinc sulfate electrolyte of the following composition was used:

ZnSO <sub>4</sub> ·7H <sub>2</sub> O	57 g/l
NaCl	40.6 g/l
Citric acid (buffer)	39 g/l
Benzalacetone (brightener)	0.08 g/l
Gelatine (wetting agent)	2 g/l

The electrolyte was prepared according to the following procedure. Gelatine powder was dispersed in 100 ml cold water and stirred for 60 min. The other chemicals were dissolved in 500 ml water. The two solutions were mixed, heated to 50 °C and after 15 min the micro- or nanoparticles were added under stirring.



**Fig. 1** Schematic view of the electrolytic cell: 1, sheet steel cathode; 2, Zn anode; 3, magnetic stirrer

Then 100 ml cold water was poured into the mixture, the pH value was adjusted to 4.5 with NaOH and at regular intervals 200 ml water in small portions was added.

### Particle characterisation

The microparticles were:

- Mica (M-fraction) of 1–15 μm diameter and 0.1–0.5 μm thickness
  - Synthetic SiO<sub>2</sub> flakes (N-fraction) of 10–50 μm diameter and 0.1–0.5 μm thickness
- The size of the particles as well as their shape were determined with a scanning electron microscope (DSM 982, Zeiss, Oberkochen, Germany).

The two sorts of particles had the same surface density of OH groups and a negative zeta potential with approximately the same value over the entire pH range.

The zeta potential could be measured with a Zeta sizer 3 instrument (Malvern Instruments, Herrenberg, Germany).

The isoelectric point was determined between pH 1 and 2. The dry particles were milled in a ball mill for 3 h. The specific BET area (Sorptomatic 1900, Carlo Erba Instruments, Italy) increased from 7.6 to 11.8 m<sup>2</sup>/g (mica) and from 6.6 to 16.4 m<sup>2</sup>/g (SiO<sub>2</sub> flakes). Obviously, the milling was essential to achieve incorporation. Therefore it was assumed that the existence of fresh fractures was a prerequisite for incorporation.

### Electrolysis conditions

The co-deposition of silicate particles with zinc was carried out in the optimised electrolytic cell described in the section Electrolytic cell.

The steel sheets (cathodes) were degreased in (1) an alcoholic, (2) an alkaline and (3) an acidic degreasing solution. The final electrolytic degreasing was carried out with a direct current density of 10 A/dm<sup>2</sup> at 20 °C for 5 min.

The optimum current density for electrodeposition of zinc composites with mica or SiO<sub>2</sub> flakes is 2.5 A/dm<sup>2</sup> and 2.25 A/dm<sup>2</sup>, respectively.

The pH and the particle concentration were also optimised. The best co-deposition conditions for the two sorts of particles were pH = 4.5 and 50 g/l particle concentration.

## Results and discussion

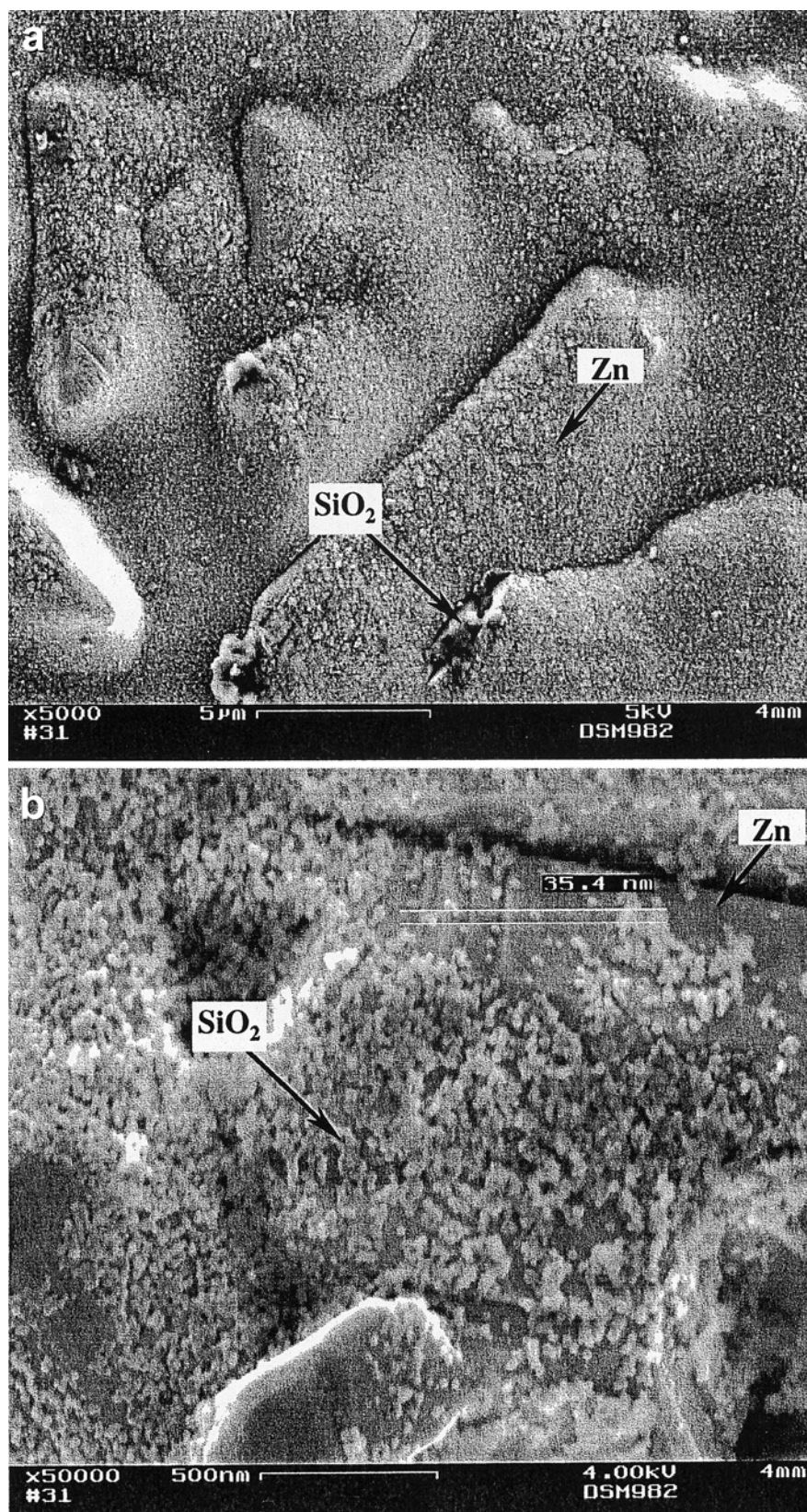
### Surface morphology and EDX analysis of the zinc composite coating

Silicate particles were preferentially built in at the underside of the cathode (horizontal orientation). Figure 2 shows scanning electron microscopy images. The optimized experimental conditions, as described in

the caption to Fig. 2, lead to homogeneous incorporation and an almost complete embedding of the particles in the zinc matrix (Fig. 2a). The visual interpretation

was corroborated by EDX point analysis. Particles not yet completely covered by Zn could be identified as silica. The same result was obtained for mica.

**Fig. 2** SEM micrographs of the surface of an electrodeposited zinc composite coating with: **a** included  $\text{SiO}_2$  flakes, **b**  $\text{SiO}_2$  nanoparticles, only found on the surface of the pure zinc crystallites (not included)



Special expectations were connected with experiments with nanoparticles of a silicate sol (Merck, Darmstadt, Germany). This sol is a stable alkaline dispersion (10% solid in water) with a particle size distribution from 10 to 100 nm and a maximum at 35 nm. The nanoparticles change their surface groups to SiO(OH) in the weakly acidic electrolyte. The zeta potential is changed too with the change of the surface groups. Characteristic properties of these particles are a low negative zeta potential as well as a large specific BET surface area. Under these conditions the silicate sol blocks the two organic additives of the plating electrolyte, necessary for co-deposition. Therefore the particles were not incorporated into the zinc matrix but only adsorbed on the surface of the pure zinc layer (Fig. 2b).

### Zinc ion adsorption

It was observed that particles were incorporated, if zinc cations of the electrolyte were adsorbed on the surface of the particles. For a better characterisation of adsorption processes on the particle surface two methods were employed:

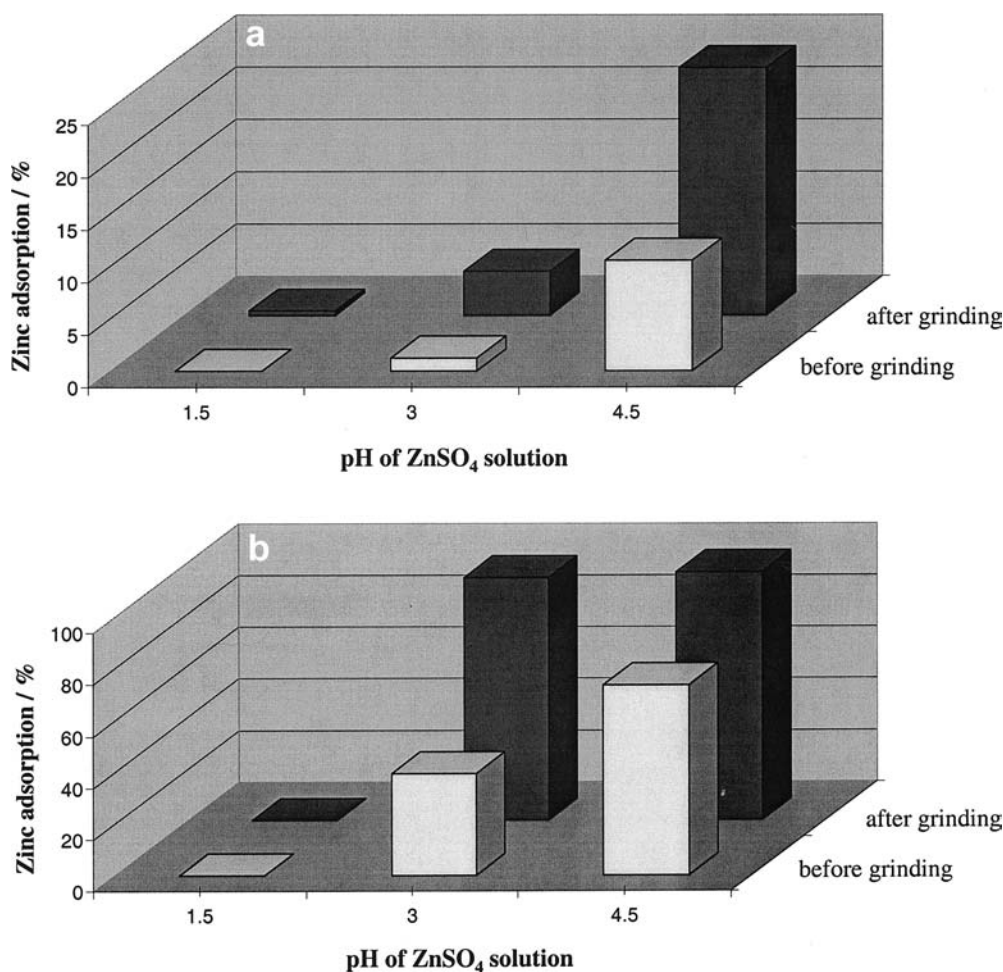
- (i) The direct determination of the amount of adsorbed Zn ions
- (ii) Measuring the zeta potential/pH diagrams with and without zinc sulfate ( $\text{ZnSO}_4$ )

### Direct adsorption measurements

A solution of  $1 \times 10^{-5}$  mol/l  $\text{ZnSO}_4$  (0.65 mg/l Zn) was used to determine the surface concentration of Zn ions on the  $\text{SiO}_2$  particles. Measurements were made at three different pH values (pH = 1.3, 3.0, 4.5). The pH of the solution was adjusted with  $\text{H}_2\text{SO}_4$ .

10 g/l of  $\text{SiO}_2$  particles ( $\text{SiO}_2$  flakes or M-mica) were added to the solution. The solution was stirred for 17 h. Then the particles were separated from the solution using an ultracentrifuge and the amount of zinc ions in the solution determined by atomic absorption spectroscopy (AAS). The difference between the concentration before addition of the  $\text{SiO}_2$  particles and the concentration determined by AAS gave the amount of adsorbed zinc ions. The results are presented in Fig. 3 (per cent zinc ions adsorbed of the original amount of zinc ions). Zinc ions are more strongly adsorbed on mica

**Fig. 3** Zinc ion adsorption (in per cent) as a function of the pH value of the  $\text{ZnSO}_4$  solution before and after grinding of **a**  $\text{SiO}_2$  flakes and **b** M-mica



than on SiO<sub>2</sub> flakes. The amount of adsorbed ions increases after milling. The adsorption also increases with increasing pH of the solution.

### Zeta potentials

Another characteristic parameter of particle co-deposition in a plating process is the zeta potential of the particle–electrolyte interface. A strong dependence of the zeta potential on the zinc concentration was expected due to the absorption of the zinc ions. The zeta potential was measured for SiO<sub>2</sub> flakes and M-mica as a function of the pH in pure KCl solution and after addition of ZnSO<sub>4</sub>.

The results are shown in Fig. 4. In pure KCl solution the zeta potential was negative. The zeta potential shifted towards more positive values after the addition of the ZnSO<sub>4</sub>. At 0.05 mol/l ZnSO<sub>4</sub> the zeta potential became positive in acidic solutions. At higher concen-

tration of zinc ions (as under in situ conditions) the zeta potential should shift to even more positive values, but this could not be confirmed experimentally because of restrictions on electrophoretic measurements for high electrolyte concentrations.

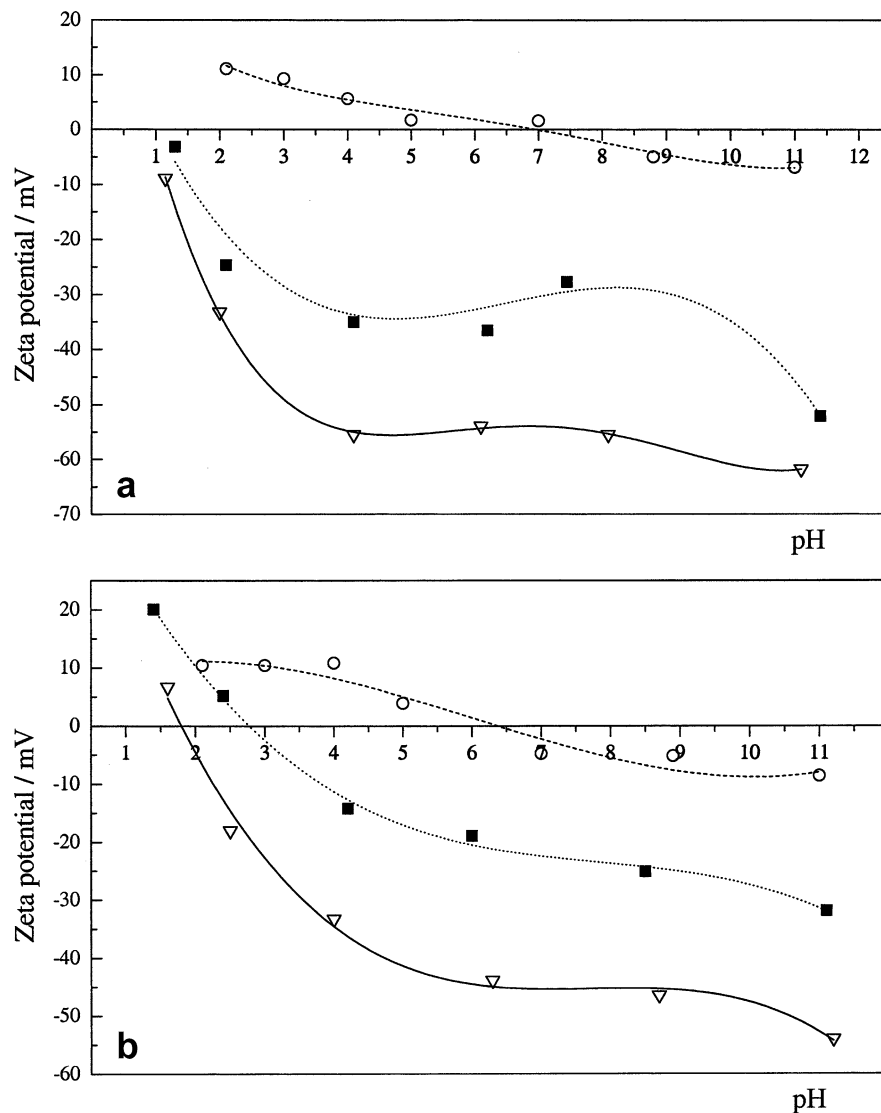
The incorporation of the SiO<sub>2</sub> particles on the negatively charged electrode surface is certainly enhanced by the positive shift of the zeta potential.

The principal influence of the particle and electrode charging on co-deposition is discussed in detail in [13].

### Mechanism of particle co-deposition

The mechanism of the composite deposition depends on several parameters, e.g. the type of metal, the nature of the particle and the electrolyte composition. For different systems special mechanisms are discussed in the literature [6, 14, 15, 16, 17]. For the deposition of composites of zinc with metal oxides a first model was

**Fig. 4** Zeta potential versus pH of: **a** SiO<sub>2</sub> flakes; **b** M-mica; both after grinding. open triangles, 10<sup>-3</sup> M KCl, filled squares, 10<sup>-3</sup> M KCl + 10<sup>-3</sup> M ZnSO<sub>4</sub> (1:1), open circles, 10<sup>-3</sup> M KCl + 0.05 M ZnSO<sub>4</sub> (1:1)



presented in [14]. This model can now be specified. The following steps are discussed:

- Decomposition of agglomerates into single particles in the bulk electrolyte
- Positive charging of the suspended particles by adsorption of zinc ions at a pH of the electrolyte near to the isoelectric point of the particle material
- Transport of the positively charged particles as macro-ions to the electrode surface by electrical migration supported by mechanical stirring
- Adsorption of the macro-ions to the metal surface; this process will be stimulated by the positive particle charge and the milling increased surface energy
- Discharging of the macro-ions covered with adsorbed zinc ions (together with reduction of zinc ions in the electrolyte) and embedding of the particles into the growing metal matrix

A schematic representation of this mechanism is shown in Fig. 5. Suppression of one or the other of the different steps blocks the particle incorporation. Optimisation of the experimental conditions provides conditions with a balanced rate of the steps. Further details will be presented in the following paragraphs.

#### Optimisation of the co-deposition plating process

##### *Variation of the pH of the electrolyte*

To find the best conditions for electrochemical co-deposition of SiO<sub>2</sub> particles and zinc the pH of the electrolyte was varied. Electrodeposition experiments were made at three pH values (pH = 1.5, 3.0, 4.5). The

particle concentration (50 g/l) and the rotation speed of the magnetic stirrer (600 rpm) were kept constant.

The change of the particle mass fraction with the pH is shown in Fig. 6. The comparison of the results in Fig. 6 with those in Fig. 3a and b obviously demonstrates that the particle mass fraction in the zinc matrix (gravimetrically determined after dissolution of the zinc metal in 1 M HCl) is correlated to the adsorption of zinc ions on the particle surface.

At higher pH values (measurements were done at pH 6.0) the particle concentration in the zinc matrix went down to zero. Therefore, pH values around 4.5 provided the optimal conditions for co-deposition which is near to the isoelectric point of the silicate particles.

##### *Variation of agitation speed and of particle concentration*

In a second optimisation experiment the pH value was adjusted to pH = 4.5 and the rotation speed of the magnetic stirrer was varied between 200 and 800 rpm. This experiment was made for three different particle mass concentrations (10, 30, 50 g/l).

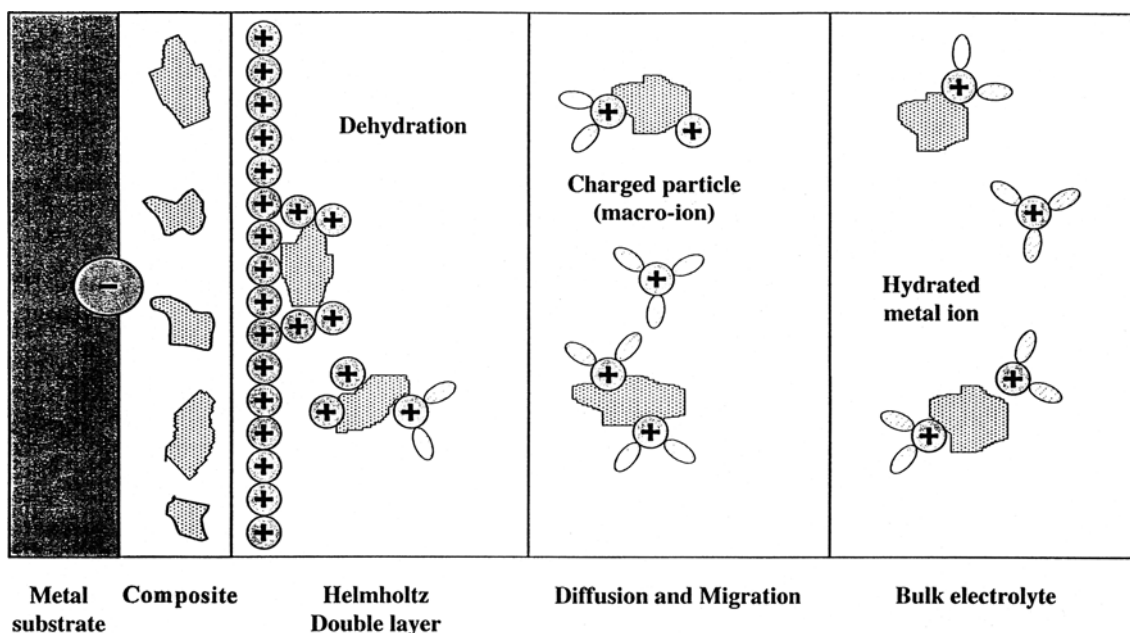
The influence on the particle concentration is shown in Fig. 7. With increasing rotation speed the particle concentration increases with a maximum at 600 rpm (except for M-mica at 10 g/l where a maximum at 400 rpm is observed). The particle concentration for mica is higher than that for SiO<sub>2</sub> flakes as already observed in Fig. 6.

##### Layer properties

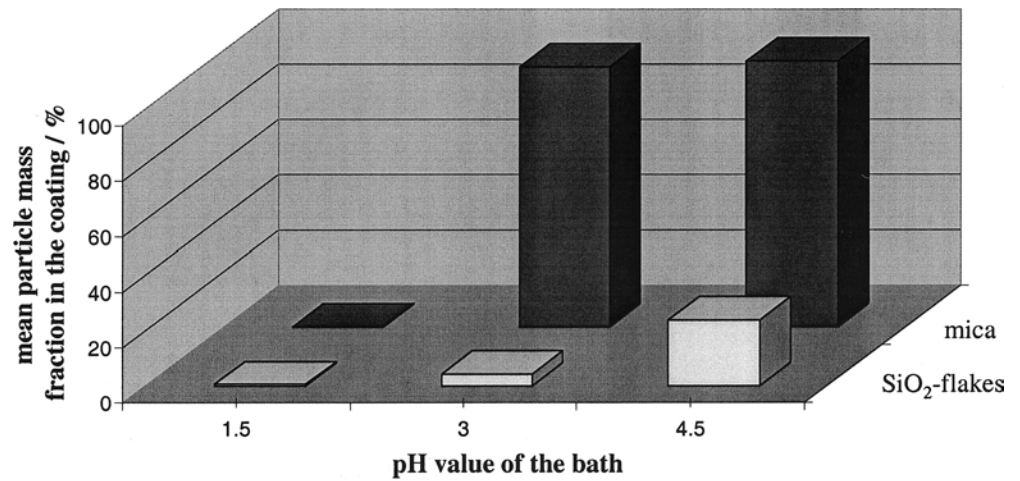
##### *Hardness*

Characteristic properties of co-deposits are increased hardness and improved wear resistance. Only the hardness was measured. The results are shown in

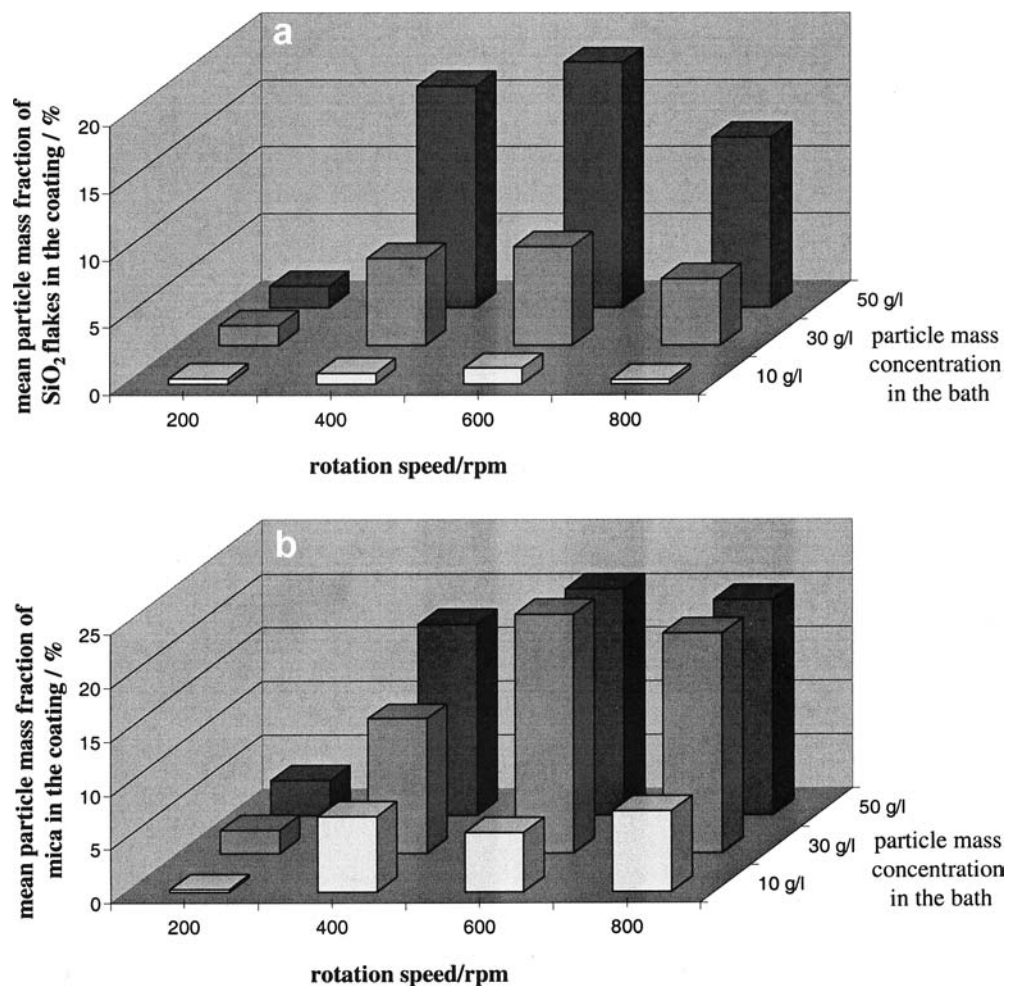
**Fig. 5** Mechanism of electrochemical co-deposition of dispersed particles with electrochemical deposition of a metal



**Fig. 6** Mean particle mass fraction in the zinc coating vs. pH value of the electrolytic bath



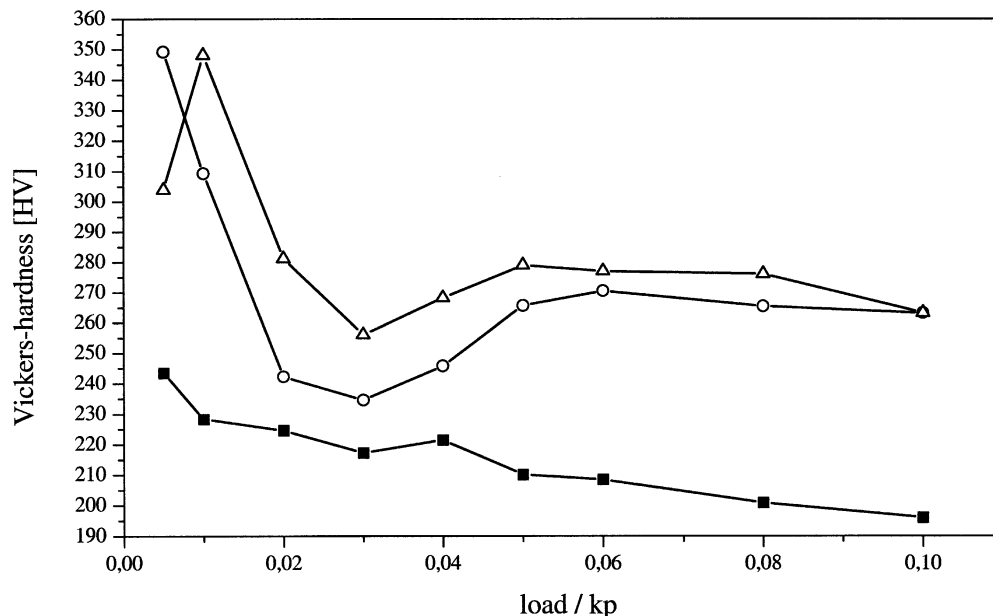
**Fig. 7** Mean particle mass fraction in the coating of: **a** SiO<sub>2</sub> flakes; **b** M-mica versus rotation speed and versus particle mass concentration of the electrolyte



**Fig. 8.** The Vickers microhardness (HV) was measured on the surface of the layers with a thickness greater than 50  $\mu\text{m}$ , and therefore with no influence of the steel support. The hardness of the composite layers

first decreased up to about 0.03 kp and around 24 HV, caused by the modified zinc matrix, and then increasing to a constant value of around 27 HV, caused by the growing influence of the particles

**Fig. 8** Vickers hardness HV ( $\text{N}/\text{mm}^2$ ) versus load for pure Zn (filled squares), Zn with  $\text{SiO}_2$  flakes (open triangles) and Zn with mica (open circles)



with increasing depth of penetration of the Vickers pyramid.

#### *Corrosion resistance of the zinc composite coating*

The properties of the composite layers are different from those of a pure zinc layer. A very important property of a zinc layer is its corrosion protection. Therefore, the corrosion resistance of the composite layers was tested. Pure zinc and three different particle concentrations were compared. The test was made by keeping the samples in a 1-mol/l NaCl solution at 25 °C and by measuring the free corrosion potential as a function of time (in days). The zinc compound layers were prepared by deposition under optimised conditions (pH = 4.5, rotation speed 600 rpm, 25 °C, particle concentrations 10, 30, 50 g/l) for 20 min. The results are shown in Fig. 9.

For comparison, the free corrosion potentials of pure zinc and pickled steel were measured after 30 and 15 min, respectively. These potentials (versus a saturated calomel electrode (SCE)) are given in Fig. 9 (straight lines parallel to the  $x$ -axis).

At the beginning the measured potentials are similar to the free corrosion potential of the pure zinc electrode. After 15 min white corrosion products (“white rust”) are observed for all samples. After several days, when the corrosion process leads to a perforation of the zinc layer and the cathodic protection mechanism of the zinc for the steel substrate started, a shift of the free corrosion potentials towards the free corrosion potential of the steel was observed. The shift began after 6 days but was considerably slower for the compound layers. The layers with the highest particle concentration showed the slowest shift and a shift of the final breakthrough from 6 to 13 days. This surprising result is reminiscent of similar effects of mica and flakes in polymer coatings. Here the explanation

of the effect is that the disk shaped particles act as diffusion barrier for  $\text{H}_2\text{O}$  and  $\text{O}_2$ . Obviously a similar barrier protection mechanism acts in the zinc composite coatings in connection with the cathodic protection mechanism by the zinc matrix.

#### **Conclusions**

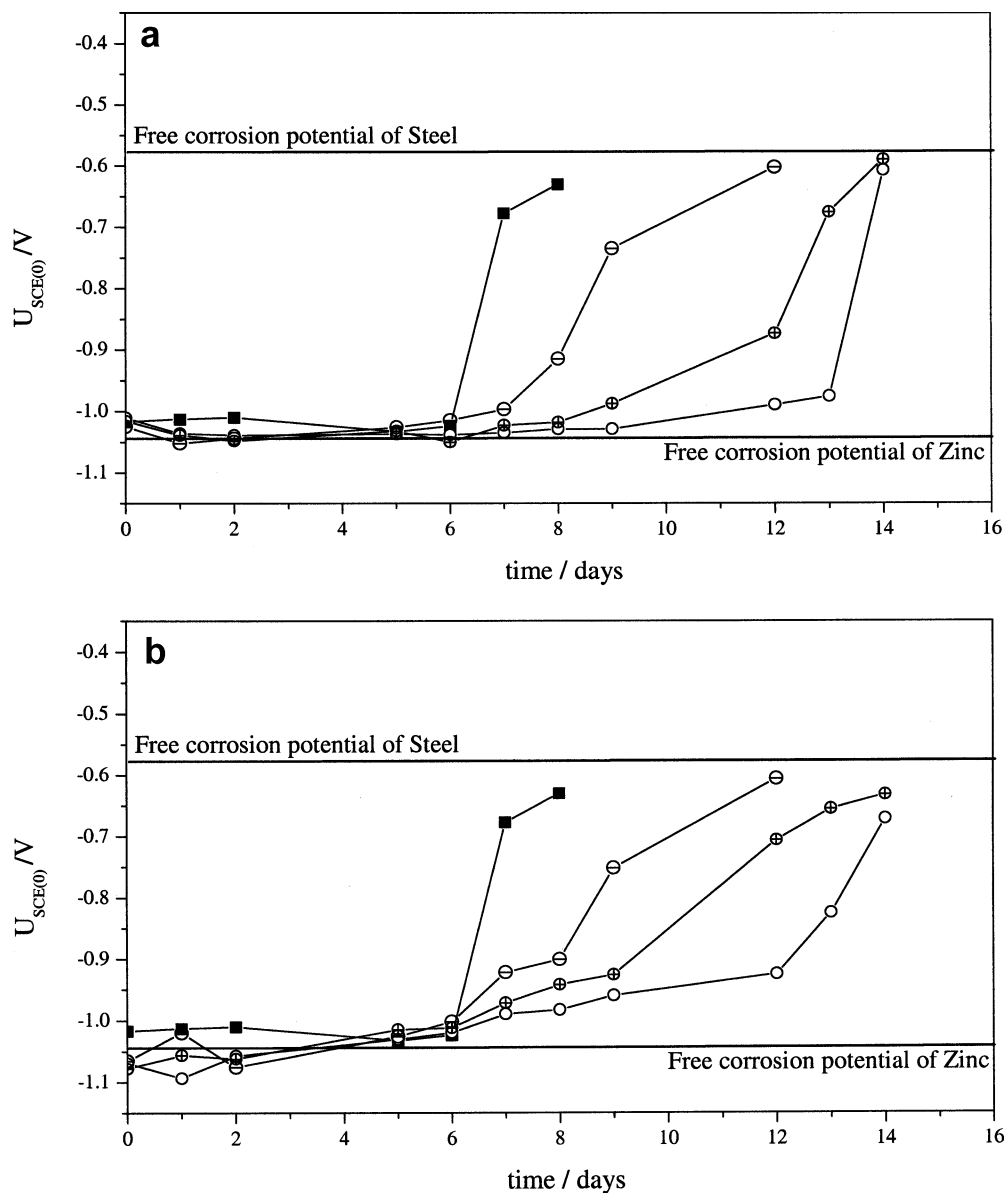
It was shown in this paper that oxide particles could be co-deposited with zinc in a plating process from a weakly acidic zinc electrolyte. The optimal conditions for the co-deposition were experimentally determined. The following points are important:

- A compound layer was observed on the lower side of the cathode in the electrode arrangement shown in Fig. 1.
- A positive effect on co-deposition was obtained by 3 h milling of the particles. Obviously, surface energy generated by the milling supported the inclusion.
- A pH of 4.5, rotation speed of 600 rpm and a particle concentration of 50 g/l were the conditions to obtain deposits with the highest particle mass fraction in the zinc matrix (up to 20 mass per cent).
- Most important for the incorporation was the adsorption of zinc ions on the particle surface, providing the necessary surface conditions for a compact embedding of the particles in the metal matrix.
- Also of positive influence on the deposition is the change of the zeta potential to positive values due to the adsorption of the zinc ions.

The experimental results of this work provide considerable details for an understanding of co-deposition of particles with metals in the plating process, as described in the schematic diagram given in Fig. 5.



**Fig. 9** Potential versus time diagram of zinc and different zinc composite coatings in 1 mol/l NaCl (25 °C): **a** SiO<sub>2</sub> flakes; **b** M-mica. Particle concentration in the electrolyte: 0 g/l (pure Zn), 10 g/l, 30 g/l, 50 g/l



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