Electrodeposition of zinc–silica composite coatings: challenges in incorporating functionalized silica particles into a zinc matrix

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Abstract
Zinc is a well-known sacrificial coating material for iron and co-deposition of suitable particles is of interest for further improving its corrosion protection performance. However, incorporation of particles that are well dispersible in aqueous electrolytes, such as silica particles, is extremely difficult. Here, we report a detailed study of Zn–SiO₂ nanocomposite coatings deposited from a zinc sulfate solution at pH 3. The effect of functionalization of the silica particles on the electro-codeposition was investigated. The best incorporation was achieved for particles modified with SiO₂–SH, dithiooxamide or cysteamine; these particles have functional groups that can strongly interact with zinc and therefore incorporate well into the metal matrix. Other modifications (SiO₂–NH₃³, SiO₂–Cl and N,N-dimethyldodecylamine) of the silica particles lead to adsorption and entrapment only.

Keywords: composite coating, corrosion protection, metallic coating, thin film, sacrificial coatings

1. Introduction
Composite coatings composed of nonmetallic particles or wires dispersed in a metal matrix can provide improved corrosion resistance, wear resistance, self-lubrication and high-temperature stability, as well as a better performance as electrical contacts and catalysts compared with the pure metal [1–5]. Nanocomposite coatings with unique magnetic, mechanical and optical properties have been produced in the last few decades [3]. Furthermore, interesting attempts were made in designing and fabricating ‘self healing’ materials that are mostly composite materials [6–11]. Among the various methods of producing metallic nanocomposite coatings, electrodeposition is regarded as one of the most convenient.

Since the early 1970s, electrogalvanization has been widely used to coat steel sheets with zinc, particularly for the automotive industries [12], where it plays an important role as a high-quality coating. Although zinc coatings provide excellent corrosion protection, there is a steady demand for improvement. An especially ambitious aim is to develop novel zinc coatings with the same or even better performance at reduced thickness, even under very demanding conditions, such as in the presence of defects in steel or at cut edges. One way to meet the demand may be to use novel zinc alloys, such as Zn–Mg [13]. An alternative could be zinc-based composite coatings where the natural self-healing and wear resistance properties of zinc are enhanced. The previously studied composite coatings include Zn–TiO₂ [14], Zn–Al₂O₃ [15] Zn–yttria-stabilized zirconia [16], Zn–Ni–SiC [17], Zn–SiO₂ [1], [18–22], Zn–mica [1], Zn–polystyrene [23] and Zn-hybrid nanoparticles [24]. Many of these coatings show better corrosion resistance than the pure zinc coating [1, 16, 22].
Inspired by these works, a concept was developed to load mesoporous silica particles with active agents, such as corrosion inhibitors, and encapsulate them with a silica-like coating [25]. Such inhibitor-loaded particles can be incorporated into zinc coatings. During corrosion of the zinc coating, the particles should be released to the exposed steel surface. There, the cathodic polarization of the steel by the zinc coating would create alkaline conditions. The silica will dissolve at high pH and release the stored inhibitor. By adjusting the thickness of the outer silica shell it should be possible to control the delay time for the inhibitor release, which is crucial for synergetic performance with the zinc coating. The outer silica shell may not dissolve at high pH and release the stored inhibitor. By adjusting the thickness of the outer silica shell it should be possible to control the delay time for the inhibitor release, which is crucial for synergetic performance with the zinc coating.

The industrial electrogalvanization of steel sheets is usually carried out at a low pH of approximately 2 and SiO$_2$ is stable under these conditions. However, the codeposition of silica is very low at this pH [1, 20]. Several reasons for this have been suggested. At low pH, the zeta (ζ) potential of silica is close to zero. This leads to the agglomeration of the particles owing to the compression of the diffuse double layer surrounding them because of the high ionic strength [27]. However, no correlation was observed between the ζ potential and colloidal stability in some studies [28]. Since the ζ-potential is an electrokinetic quantity, it does not always correlate with colloidal stability and incorporation tendencies, which are governed by the static charge distribution around the particles [29]. Moreover, some authors claim that electrostatic interaction with the surface is crucial for incorporation [2], i.e. a net positive charge is required for incorporation into the negatively polarized electrode, which is not the case for silica particles in the plating bath. However, the experimental results are not fully conclusive and a clear proof of the possible role of electrostatic interaction has not been provided yet.

Codeposition of modified silica has already been reported [1, 18–22]. The reported electrochemical codeposition results in three types of zinc composite coating (see figure 1). Particles are merely adsorbed on type (a) coating, and thus no enhancement of its properties is expected. Type (b), which has entrapped particles, may show inferior mechanical properties compared to types (a) and (c), as this kind of composite coating is quite porous. Type (c) coating contains well-incorporated particles. The mechanical and chemical stabilities of this type of coating are expected to be the highest among the three types, and hence the potential use is expected to be greater. However, the deposition of such a coating is challenging.

Codeposition of SiO$_2$ flakes 10–50 µm in diameter has been reported [1]. Such flakes are unsuitable for the targeted delivery of the inhibitors as no diffusion of such large particles is expected. Furthermore, it is unclear from that work whether the large flakes are incorporated or just entrapped because of their special morphology. Convincing cross-sectional scanning electron microscopy (SEM) images have been shown of 2-µm-diameter particles entrapped in a zinc matrix when using a cationic surfactant N,N-dimethyldodecylamine (NND) [18]. The entrapment occurs into pores (case b) and the resulting surface has a large free surface prone to corrosive attacks. Codeposition experiments with 550-nm-diameter particles were reported to yield only adsorbed particles [20]. A precipitation codeposition of 10-nm-diameter particles via a locally increased pH at the cathode was reported in [22, 30], limiting the current efficiency. It is unclear whether these particles were entrapped or incorporated. The same is true for codeposition experiments reported in the presence of other metal salts [21].

In this paper, we report the deposition of Zn–SiO$_2$ composite coatings where particles are well dispersed in the zinc matrix, which corresponds to the desired case (c) and have a suitable morphology for applications. In these coatings, silica particles are incorporated inside a metal matrix which is compact and macroscopically smooth. To achieve this goal, we have modified silica particles with different functional groups and studied how they affect the incorporation of the particles into the zinc matrix during electrogalvanization.

2. Experimental details

2.1. Materials

SiO$_2$ and SiO$_2$–NH$_2$ particles (235-nm-diameter) were purchased from Micro Particles GmbH. All chemicals were used without further purification and the chemicals included NND and tetraethoxysilane (TEOS, Fluka), chloropropyltrimethoxysilane (CPTMS, Aldrich), 3-(mercaptopropyl)-trimethoxysilane (MPTMS, Alfa Aesar), ammonia solution (28–30%, Merck), zinc sulfate heptahydrate (Sigma...
Aldrich), dithiooxamide (also known as rubeanic acid, 98%, Sigma Aldrich), cysteamine (Fluka) and zinc (>99.95%, Goodfellow).

SiO$_2$ particles were prepared according to the Stöber process [31]: 60 ml of TEOS was directly added to a solution containing 14 ml of ammonia solution, 100 ml of H$_2$O and 720 ml of ethanol. The solution was stirred for 2 h and then the particles were separated by centrifugation; they were then cleaned with water and calcined at 550 °C for 8 h.

2.2. Modification of SiO$_2$ particles with rubeanic acid and cysteamine

The particles (100 mg) were dispersed in 100 ml of an ethanol–water mixture (95/5, w/w) and 120.2 mg of rubeanic acid or 77.2 mg of cysteamine was added to the solution. The solution was stirred for 2 days and then left unstirred for 6 days. The particles were separated by centrifugation at 5000 rpm and used for electrodeposition.

2.3. Modification of SiO$_2$ particles with –Cl and –SH terminated groups

Silica particles functionalized with n-propyl–Cl (SiO$_2$–Cl) were typically prepared by adding 1 mL of CPTMS to 100 ml of an ethanol–water mixture (95/5, w/w), which contained 100 mg of silica particles [32]. The solution was stirred for one day and the particles were separated from the solution by centrifugation at 5000 rpm. They were rinsed with water three times and then dried under vacuum. Mercaptopropyl–silica particles (SiO$_2$–SH) were synthesized according to the same procedure, but using 1 mL of MPTMS instead of CPTMS.

2.4. Electrodeposition

Electrodeposition was carried out using Ag/AgCl 3 M KCl (SSE), zinc foil (99.95%) and stainless steel as the reference, counter and working electrodes, respectively. Before deposition, the stainless steel was ground with 1000 grade silicon carbide grinding paper followed by cleaning with ethanol and water in an ultrasonic bath. ZnSO$_4$ solution (1.2 M) was used as the electrolyte. For the codeposition, 150 mg of the modified silica particles were added into 10 ml of an electrolyte containing 100 mg of silica particles (SiO$_2$–SH) were synthesized according to the same procedure, but using 1 mL of MPTMS instead of CPTMS.

2.5. Chemical etching

The samples were immersed vertically in a 3 M HCl solution for a few seconds (5–10). Then they were rinsed with water and ethanol and dried under a nitrogen stream.

2.6. Characterization

SEM observations were carried out with a ZEISS LEO1550VP FE-SEM microscope operated at 11 keV. To estimate the amount of particles inside the zinc matrix, energy dispersive x-ray analysis (EDX) was performed on a cross-sectional cut at three different locations of 100 µm$^2$ area. The atomic percentages were deduced with Inca software and converted to volume fractions using the bulk densities of silica and zinc.

Transmission electron microscopy (TEM) specimens were prepared using a ZEISS 1540 XB focused ion beam system (FIB) with a Ga$^+$ ion accelerating voltage of 30 kV. The TEM sample of about 25 × 25 × 0.1 µm$^2$ was prepared so that the sample plane was remaining parallel to the polishing plane. The samples were cut from an area approximately in the middle of one edge at a depth of approximately 30 µm from the edge. Scanning TEM (STEM) and high-resolution TEM (HRTEM) imaging was performed using a JEOL JEM-2200 FS microscope operated at 200 kV.

The streaming potential was measured using the Stabisizer (Particle Metrix GmbH). Fifty microliters of the sample (SiO$_2$ or modified SiO$_2$) was dispersed into 10 ml of 1 mM NaOH solution. The mixture was titrated with 0.02 M HCl till pH 2.5.

Fourier-transform infrared (FTIR) spectra were recorded with a BioRad FTS-3000 spectrometer in transmission mode. The samples were prepared by pressing 200 mg of KBr and 2–3 mg of the studied material into a pellet. Some IR spectra were recorded in attenuated total internal reflection geometry (ATR–IR). Silicon wafers with two faces polished to an angle of 45° were used as substrates and background spectra were accumulated for 1500 scans with a nitrogen-cooled mercury–cadmium–telluride (MCT) detector. The sample (SiO$_2$ or modified SiO$_2$ dispersion) was cast on the silicon wafer and dried under vacuum prior to recording the spectra.

For ATR–IR of solutions, silicon wafers were polished to a trapezoidal shape with two faces at an angle of 30°. The crystals were mounted in a homemade cell with 60° angle of incidence on the silicon/sample interface. After measuring the background spectra with a nitrogen-cooled MCT detector, 10 µl of the MPTS sample solution was cast on the crystal and the spectra were recorded. Then, 15 ml of 1.2 M ZnSO$_4$ solution (pH 3) was added and the spectra were collected again.

Samples for x-ray photoelectron spectroscopy (XPS) were prepared by mechanically attaching particles on indium foil. The measurements were performed using a Physical Electronics Quantum 2000 Scanning ESCA Microprobe. Each analysis started with a survey scan from 0 to 1100 eV with a dwell time of 100 ms, pass energy of 58.7 eV at a step of 0.287 eV with 5 sweeps. CASA XPS software was used to analyze the data.

3. Results and discussion

3.1. SiO$_2$ particles and their modification with –SH and –Cl end groups

SEM images revealed that the particles had uniform size with an average diameter of 225 nm. The successful modification
by either –SH or –Cl end groups was proven by the detection of chlorine and sulfur in the XPS survey scans.

3.2. Surface charge of the synthesized particles

The surface charge of the particles is an essential factor in colloidal systems. It is related to the streaming potential of the suspended particles inside a narrow capillary. Therefore, we performed measurements of streaming potential of the synthesized particles inside a Teflon capillary. Figure 2 shows the effect of pH on streaming potential in silica and modified silica particles. The streaming potential values of SiO$_2$, SiO$_2$–NH$_2$ and SiO$_2$–SH particles with respect to different pH and the isoelectric points (IEPs) are consistent with ζ potential measurements reported in the literature [33]. The streaming potentials were similar for almost all samples as they have their IEPs below pH 2.5 except for SiO$_2$–NH$_2$ and SiO$_2$–Cl. The NH$_2$-modified silica particles show a distinctly different behavior and have an IEP at around pH 7 due to protonation of the –NH$_2$ group to –NH$_3^+$3. Protonation implies a modification in the electrostatic interaction with the electrode surface. The stronger negative streaming potential of SiO$_2$–Cl is presumably due to its inability to undergo protonation and deprotonation. The OH- and SH-terminated surfaces possess groups that can take part in acid/base equilibria, and those equilibria are affected by acidic pH.

3.3. IR characterization

Figure 3(a) shows FTIR absorption spectra of SiO$_2$ particles (1) and SiO$_2$–SH particles (2). (b) ATR–IR spectra of SiO$_2$ (3) SiO$_2$–cysteamine (4) and SiO$_2$–rubeanic acid (5) samples on Si wafers. 1600 cm$^{-1}$ to be detected. However, using an ATR–IR setup, we observed peaks near 1535 cm$^{-1}$ from the –N–H bending mode in particles deposited on a silicon wafer, which indicates the presence of cysteamine and rubeanic acid on the silica particles (see figure 3(b)).

By combining the ATR–IR and SP results, we deduced that the NH$_2$ functional group (or better the –NH$_3^+$ group at pH 3) of cysteamine and rubeanic acid is facing towards the negatively charged silica particles, while the SH functional group of cysteamine and the sulfide functional group of rubeanic acid are facing away from the particles towards the electrolyte.

3.4. Particle deposition: adsorbed particles

A zinc coating without particle codeposition was prepared at pH 3 as a reference. The resulting surface morphology is shown in figure 4. An electrocodeposition experiment of Zn with unmodified SiO$_2$ particles was carried out at the same conditions. The surface morphology of such coating is shown in figure 5(a). In that case, the zinc structure remains unchanged, but particles are now adsorbed on the surface. The SEM image is similar to that reported in the literature for this case [1, 35]. No systematic attempts have been made to quantify the number of adsorbed particles because of their inhomogeneous distribution on the surface. SiO$_2$ has a negative surface charge at pH 3 and therefore zinc ions should surround the particles to give them an overall positive surface charge. As discussed above, according to some authors, this may lead to codeposition at the negatively charged cathode [1]. However, as shown in figure 5, no evidence for such codeposition was found in our experiments, even at pH 4. At room temperature, the Debye length in the divalent electrolyte used is 1.4 Å. Under these conditions, electrostatic interactions need to be considered locally, and the mean-field picture of a global surface charge of a particle is too simple [36].

To verify information obtained from the surface morphology, we tried to directly access particles possibly
entrapped in the bulk. Mechanical cross sectioning could be misleading because of smearing out of particles from the surface region onto the cross section. Hence, we etched the samples using HCl instead. During etching, it is expected that the dissolution of the zinc layer should expose the incorporated SiO$_2$ particles (if any). However, figure 5(b) shows no incorporation of particles. It should be mentioned that the etching is anisotropic and leaves complex surface morphologies including sub-micrometer-sized holes. Results described in the next section demonstrate that if particles were entrapped in such holes, they should still be visible after etching.

SiO$_2$ particles modified with the NH$_2$ group were merely adsorbed on the zinc coating (figure 6(a)). Here again, no particles were found inside the metal matrix after etching the samples with HCl (figure 6(b)), although the electrostatic forces were expected to favor incorporation, as the streaming potential measurements reveal a relatively high positive charge for these particles at pH 3.

We have carried out further zinc deposition in the absence of particles in the deposition bath, using a sample with adsorbed unmodified SiO$_2$ particles and a morphology similar to that shown in figure 5(a) as a substrate. After 10 min of deposition, the samples were removed from the deposition bath and subjected to SEM analysis. The resulting surfaces show voids in the new zinc layer, which contain a high concentration of particles, as shown in figure 7. The idea behind this experiment was to test whether the newly deposited zinc would grow over the particles adsorbed on the surface. However, we found that the growing Zn can push the particles aside instead of growing over them. This result clearly indicates that an attractive interaction between the particles and surface, which leads to particle adsorption, is not a sufficient condition for particle incorporation.

3.5. Entrapment and partial incorporation of particles

Entrapment of particles was observed when electrodeposition was carried out with the addition of cationic surfactants such as N,N-dimethyldecylamine [18]. Figure 8 shows an example for deposition at pH 3. The surface morphology of the zinc coating is different from the ones shown above because of the use of surfactants. After etching the surface, numerous entrapped and coagulated particles can be seen inside the metal matrix (figure 8(b)). Obviously, this entrapment occurs in pores inside the zinc coating. Pore formation is not desirable, as it weakens mechanical stability. Therefore, the amount of surfactant was optimized, and the least porous surfaces were obtained when using 3 µL of NND and 150 mg of particles in 10 ml of ZnSO$_4$ electrolyte. Still, compact coatings could not be obtained.
Complete incorporation (figure 1(c)) has been reported in nickel for hydrophobic particles of 50-µm-diameter in a sedimentation deposition [18, 37]. Making particles strongly hydrophobic is, however, detrimental for the bath stability [38]. Instead, we used particles that were modified by molecules that can chemically interact with zinc. Thiols can form metal–sulfur bonds with many metals including zinc [39–41]. Consequently, we succeeded in incorporating \(\text{SiO}_2–\text{SH}\) particles in zinc, as shown in figure 9(a).

Evidently, particles are embedded in the metal matrix but adsorbed coagulated particles can be seen on the surface of the zinc coating as well. Embedded particles in the early stages of incorporation show light gray colors in the SEM images. Adsorbed particles appear white because many secondary electrons can leave them. The deeper the particles are incorporated into zinc, the fewer electrons can escape; this leads to an increasingly darker color in the SEM images. After etching, the adsorbed particles are removed from the surface and the incorporated ones can be clearly seen (figure 9(b)). However, the morphology of the deposited surface is not as good as expected and shows some pits and holes. The average volume fraction of the \(\text{SiO}_2–\text{SH}\) particles in the zinc matrix was estimated as 1 vol%.

Codeposition was observed for silica particles modified with rubeanic acid (deposited at pH 3), and approximately 1.5 vol% of particles were incorporated in the metal matrix at the same codeposition conditions as those for \(\text{SiO}_2–\text{SH}\). We have also electro-codeposited particles modified with cysteamine with zinc at pH 3 and the particle incorporation into the metal matrix was more efficient (about 2 vol%).

3.6. Incorporation of particles

Figure 6. SEM images of zinc–\(\text{SiO}_2–\text{NH}_2\) coatings: (a) as-prepared and (b) etched with HCl.

Figure 7. SEM image of a surface produced by depositing zinc, in the absence of silica particles in the bath, on a surface with adsorbed particles. The inset shows a magnified region in the void containing silica particles.

Figure 8. SEM image of zinc–silica coating produced with the \(N,N\)-dimethyldodecyl amine surfactant: (a) as-deposited and (b) etched with HCl. The arrows indicate the particle position.
Figure 9. SEM image of (a) zinc–SiO$_2$–SH coatings and (b) etched with HCl.

Figure 10. SEM images of zinc–SiO$_2$–cysteamine coatings: (a) as-deposited and (b) etched with HCl.

3.7. Driving force for the particle incorporation

The particle incorporation might be caused by a change in the particle’s surface energy upon surface modification [37, 38]. This hypothesis can be checked by comparing particles with different surface termination which has the same surface energies. As particle incorporation was observed for SH-terminated particles, a control experiment with Cl-terminated particles was conducted. The critical surface tensions for SiO$_2$–SH and SiO$_2$–Cl have similar values of 40.5 and 41 mN m$^{-1}$, respectively [42, 43].

For particles modified with CPTMS, however, only adsorption was observed and very few particles could be detected inside the zinc matrix after etching with HCl. In this case, the decrease in the surface energy was not sufficient for enabling incorporation. Instead, a specific chemical interaction between metallic Zn or Zn$^{2+}$ ions and the modified particles, as is the case for SH termination, is expected to play a key role.

The interaction between thiols and metallic Zn is known [41]. There is less interaction between thiols and Zn$^{2+}$ ions in the presence of other ions such as Hg$^{2+}$ [42]. In order to obtain information on the interaction between thiol and Zn$^{2+}$ ions, ATR–IR experiments were performed.

The spectra displayed in figure 14 show that the frequency of the –SH stretching mode shifts by approximately 1 cm$^{-1}$ (2565–2564 cm$^{-1}$) upon addition of zinc solution at pH 3. The shift is small and presumably caused by the
involvement of the -SH groups in the hydrogen bonds with water. This result shows no evidence for a strong interaction between the thiols and zinc cations.

As already discussed above, electrostatic forces are possibly not the main parameter governing the incorporation. Another hypothesis in the literature suggests that hydrophilic particles are pushed away by the growing metal, while hydrophobic particles are incorporated from the start of the metal deposition [37, 38]. However, this mechanism cannot fully explain our observations. It is true that modification of silica particles with thiols makes them somewhat more hydrophobic compared with unmodified silica particles [32, 45]. The contact angles of self-assembled MPTMS on silicon oxide are 71° and 84° for the well-ordered and partially ordered structures, respectively [45, 46], but the contact angle for CPTMS has a similar value of about 80° [46]. Moreover, the surface tensions for SiO$_2$–SH and SiO$_2$–Cl are 40.5 and 41 mN m$^{-1}$, respectively [42, 43], i.e. nearly the same. Hence, the hydrophobicity of SiO$_2$–Cl particles is similar to that of SiO$_2$–SH particles. However, only very few SiO$_2$–Cl particles incorporate inside the zinc matrix, whereas the incorporation is efficient for SiO$_2$–SH particles.

The mechanism of interaction between the different functional groups and the surface of the growing metal must be fundamentally different from previously proposed mechanism. Covalent bonds between SiO$_2$–SH particles and the surface can be formed as observed for alkanethiols on zinc [39–41]. SiO$_2$–Cl, SiO$_2$–NH$^+$ and other particles do not have this option under aqueous conditions. However,
the sulfur-containing molecules such as rubeanic acid and cysteamine can also form covalent bonds with the metal. These results lead to the conclusion that functional groups, such as thiols, which show strong interaction with zinc, are crucially important for successful incorporation. The strong interaction of zinc with these groups results in low interfacial energies between the particles and the zinc matrix, leading to incorporation. The same mechanism applies to particles modified with rubeanic acid and cysteamine. In both cases an attractive interaction with the substrate leads to incorporation, while the hydrophobicity of the particles is not sufficiently high enough to promote incorporation into zinc.

4. Conclusions and outlook

We have characterized zinc–silica composite coatings where silica particles are embedded in the metal matrix. Surface modification of the particles is necessary for such incorporation. Instead of making the particles more hydrophobic, i.e. increasing the interface energy between the particles and the aqueous electrolyte, we have modified the particles with functional groups that have strong affinity to the zinc matrix. This has decreased the interface energy between the particles and zinc matrix, providing a driving force for the incorporation of the particles in the metal matrix. This approach should allow a much easier bath management than with the use of hydrophobic particles. Although the particles were not agglomerated, their distribution was inhomogeneous throughout the zinc coating. This is attributed to the conditions of the electrolyte flow near the surface. The final goal of this study is the realization of a zinc coating that contains particles loaded with a corrosion inhibitor and the evaluation of its corrosion protection capabilities.

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References

[1] Azizi M, Schneider W and Plieth W 2005 J. Solid State Electrochem. 9 429
[2] Bund A and Thiemig D 2007 J. Appl. Electrochem. 37 345
[3] Podlaha E J 2001 Nano Lett. 1 413
[4] Musianti M 2000 Electrochim. Acta 45 3397
[5] de Tacconi N R, Boyles C A and Rajeshwar K 2000 Langmuir 16 5665
[6] Skorb E V, Fix D, Andreeva D V, Mohwald H and Shchukin D 2009 Adv. Funct. Mater. 19 2373
[7] Zheleukhevich M L, Shchukin D G, Yasakau K A, Mohwald H and Ferreira M G S 2007 Chem. Mater. 19 402
[8] Shchukin D G and Mohwald H 2007 Small 3 926
[9] Paliwoda-Porebska G, Stratmann M, Rohwerder M, Potje-Kamloth K, Lu Y, Fich A Z and Adler H 2005 Corros. Sci. 47 3216
[10] Rohwerder M, Isik-Uppenkamp S and Amarnath C 2011 J. Electrochem. Soc. 158 209
[11] Amendola V and Meneghetti M 2009 Nanoscale 1 74
[12] Landolt D 2002 J. Electrochem. Soc. 149 S9
[13] Hosking N C, Strom M A, Shipway P H and Rudd C D 2007 Corros. Sci. 49 3669
[14] Gomes A, Pereira M I D, Mendonca M H and Costa F M 2005 J. Solid State Electrochem. 9 190
[15] John V 1995 Galvatech’95 Conf. Proc. (Warrendale: Iron and Steel Society)
[16] Xia X, Zhitomirsky I and McDermid J R 2009 J. Mater. Process. Technol. 209 2632
[17] Muller C, Sarret M and Benballa M 2002 Surf. Coat. Technol. 162 49
[18] Tuwareti T J and Wilcox G D 2006 Surf. Coat. Technol. 200 5921
[19] Caboi B and Foissy A 1998 J. Mater. Sci. 33 3945
[20] Aslanidis D, Fransaer J and Celis J P 1997 J. Electrochem. Soc. 144 2352
[21] Takahashi A, Miyoshi Y and Hada T 1994 J. Electrochem. Soc. 141 954
[22] Hashimoto S and Abe M 1994 Corros. Sci. 36 2125
[23] Hovestad A, Heesen R J C H L and Janssen L J J 1999 J. Appl. Electrochem. 29 331
[24] Kammona O, Kotti K, Kiparissides C, Celis J P and Fransaer J 2009 Electrochim. Acta 54 2450
[25] Stempniewicz M, Rohwerder M and Marlow F 2007 ChemPhysChem. 8 188
[26] Simoes A M, Torres J, Picciocchi R and Fernandes J C S 2009 Electrochim. Acta 54 3857
[27] Fransaer J, Leunis E, Hirato T and Celis J P 2002 J. Appl. Electrochem. 32 123
[28] Zhitomirsky I 2002 Adv. Colloid Interface Sci. 97 277
[29] Lyklem J 2001 Fundamentals of Interface and Colloid Science Vol II (London: Academic)
[30] Shiohara Y, Okado A, Abe M and Sagiyma M 1991 Tetsu to Hagane 77 878
[31] Stober W, Fink A and Bohr E 1968 J. Colloid Interface Sci. 26 62
[32] Witucki G L 1993 J. Coat. Technol. 65 57
[33] Samuel J, Raccourt O, Poncelet O, Auger A, Ling W L, Cherns G, Prunwald D and Tillement O 2010 J. Nanopart. Res. 12 2255
[34] Caregnato P, Forbes M D E, Soria D B, Martire D O and Gonzalez M C 2010 J. Phys. Chem. C 114 5080
[35] Kondo K, Ohgishi A and Tanaka Z 2000 J. Electrochem. Soc. 147 2611
[36] Bazant M Z, Kilic M S, Storey B D and Ajdari A 2009 Adv. Colloid Interface Sci. 152 48
[37] Stappers L and Fransaer J 2006 J. Electrochem. Soc. 153 C472
[38] Secchi D, Martens J, Claessens S and Fransaer J 2011 J. Electrochem. Soc. 158 D515
[39] Matsuzaki A, Nagoshi M and Hara N 2011 ISIJ Int. 51 108
[40] Nogues C and Lang P 2007 Langmuir 23 8385
[41] Hedberg J, Leygraf C, Cimatu K and Baldeghi S 2007 J. Phys. Chem. C 111 17587
[42] Zeilina S L, Rammer D R and Stone D S 2009 Silanes and Other Coupling Agents vol 5 ed K L Mittal (Leiden: Koninklijke Brill NV)
[43] Lee L H 1968 J. Colloid Interface Sci. 27 751
[44] Feng X, Fryxell G E, Wang L Q, Kim A Y, Liu J and Kenmer K M 1997 Science 276 923
[45] Hu M, Noda S, Okubo T, Yamaguchi Y and Komiyama H 2001 Appl. Surf. Sci. 181 307
[46] Scola D A and Brooks C 1970 J. Adhes. 2 213