

Effect of Additives on Electrodeposition of Nanocrystalline Zinc from Acidic Sulfate Solutions

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The influence of polyethylene glycol (PEG), cetyltrimethylammonium bromide (CTAB), benzalacetone (BA), and thiourea (TU) on pulse electrodeposition of zinc from acidic sulfate baths was investigated by X-ray diffraction, scanning electron microscopy, and potentiodynamic polarization techniques. The results show that a mixture of PEG and CTAB can fully dissolve BA in the concentrated zinc sulfate solutions. This ternary additive can increase the overpotential of zinc electrodeposition markedly, and then gives rise to forming a bright nanocrystalline zinc coating on steel substrate, with an average grain size of 52 nm. The combination of these four compounds is more powerful for improving the cathodic polarization and inhibit hydrogen evolution during zinc electrodeposition in comparison with ternary additive systems. A bright and compact zinc coating with a grain size of 43 nm and the (110)(100)(201) preferred orientations are produced due to the coexistence of all four compounds. These compounds act in a synergetic way, especially between BA and TU, leading to the grain refinement of zinc deposits. © 2007 The Electrochemical Society. [DOI: 10.1149/1.2772093] All rights reserved.

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In recent years, nanosized metal electrodeposits have attracted great attention due to the merits of nanostructured materials. In the literature, many pure metals and alloys were electrodeposited with grain size less than 100 nm, such as Ni,¹ Cu,² Pd,³ Zn–Ni,⁴ Ni–Fe–Cr,⁵ and so on.

It is well known that electrocrystallization occurs by growth of existing crystals or formation of new nuclei.⁶ The latter is favored at high overpotential and low surface diffusion rates of adsorbed metallic ions on the growing surface and then benefits formation of nanocrystals.⁷⁻⁹ Practically, organic additives and pulse electrodeposition are utilized most frequently to produce homogeneous and ultrafine deposits. Organic additives, added commonly as leveler and brightener to electroplating baths, can increase the overpotential and nucleation rate and inhibit the surface diffusion of adions. These conditions also can be fulfilled by using pulse electroplating, because a higher peak current density is possible in comparison with direct current plating, i.e., much higher than the limiting current density attained during direct current plating in the same electrolyte.9-11 Thus, organic additives and pulse control are powerful means to achieve grain refinement down to the nanosized dimension of metallic deposits.

Zinc electrodeposition on steel surfaces is an important industrial process for protection of steels from corrosion. Nanocrystalline zinc coatings had been produced in different electrolytes in order to get better properties. In acetate-based bath without additives, several nanocrystalline zinc deposits were obtained by cyclic voltammetry and square wave pulsating potential methods, among which the smallest grain size was about 68 nm.¹² In chloride-based bath with a mixture of thiourea and polyacrylamide, a zinc deposit with an average grain size of 50 nm was produced by pulse current control.^{13,14} In sulfate-based bath in the presence of surfactants [cetyltrimethylammonium bromide (CTAB), sodium dodecyl sulfate (SDS), and Triton X-100] and N₂ bubbling, zinc coatings with different crystal shape and size (in the range 40–20 nm) were prepared on stainless steel substrates by pulse current electrolysis.¹⁵ Youssef et al. found that nanocrystalline zinc coatings had higher hardness and corrosion resistance in alkaline solutions in comparison with conventional polycrystalline ones.^{17,16}

In a previous work,¹⁷ a simple acidic sulfate-based bath without nonzinc supporting electrolyte was studied at high current densities on the basis of continuous zinc electroplating for steel plates. A synergetic effect between the two additives (benzalacetone and thiourea) induced the formation of particle-like nanocrystalline zinc with a grain size of 60 nm. However, benzalacetone with emulsifier OP (polyethyleneglycol *p*-isooctylphenyl ether) as solubilizer dissolved incompletely in the concentrated zinc sulfate solutions, giving rise to forming turbid baths. The aim of this work is to have an insight into the role of four commercial organic compounds in zinc electrodeposition and then produce zinc coatings with smaller grain size from the sulfate-based baths.

Experimental

Electrolytic cell and sulfate-plating bath.- Zinc electrodeposition was carried out in a two-electrode cell containing 200 mL sulfate-plating solution. A platinum foil served as the anode. Coldrolled low-carbon steel specimens were used as the cathode with an exposed surface area of about 0.1 cm² (i.e., electrodes with a dimension of 3.4×3 mm). Prior to each plating experiment, the specimen surface was ground with 800 grit waterproof abrasive paper and then pickled in 10 wt % H₂SO₄ at room temperature for 30 s. The anode and cathode were fixed with a space of about 5 cm and immersed vertically into the plating solution about 3 cm lower than the solution surface. The plating solutions were made of 350 g L⁻¹ ZnSO₄·7H₂O (i.e., about 1.22 mol L⁻¹) with or without organic additives, maintained at 23 ± 2 °C, and agitated slowly by a magnetic stirrer. The pH value was adjusted to about 1 by dilute H_2SO_4 . Polyethylene glycol (PEG, $C_{2n}H_{4n+2}O_{n+1}$) with a mean molecular weight of 600 g mol⁻¹, CTAB (C₁₉H₄₂BrN), benzalacetone (BA, C₁₀H₁₀O), and thiourea (TU, CH₄N₂S) were used separately or in combination as additives. The studied solutions were listed as follows:

- 1. S_0 : ZnSO₄·7H₂O, the base solution
- 2. $S_{\rm P}$: S_0 + PEG
- 3. $S_{\rm C}: S_0 + {\rm CTAB}$
- 4. S_{PC} : S_0 + PEG + CTAB
- 5. S_{CB} : S_0 + CTAB + BA
- 6. S_{PCB} : $S_0 + PEG + CTAB + BA$
- 7. S_{CT} : S_0 + CTAB + TU
- 8. S_{PT} : $S_0 + \text{PEG} + \text{TU}$
- 9. S_{PCBT} : S_0 + PEG + CTAB + BA + TU

In all cases, the concentrations of PEG, CTAB, BA, and TU were 2, 0.5, 0.5, and 1 g L^{-1} , respectively. All chemicals were analytical grade. Distilled water was used to make these solutions.

Electrodeposition procedure.— According to a previous study,¹⁷ zinc electrodeposits were prepared by applying a galvanostatic square wave for 10 min with a pulse peak current density of 2 A cm⁻². The current-on time and current-off time were set at 4

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and 8 ms, respectively. A PAR (Princeton Application Research, AMETEK, Inc.) system, which comprised an M273A potentiostat/galvanostat and the PowerSuite software, was used to generate the current waveform and supply the current.

Cathodic polarization curves were determined potentiodynamically with a potential scan rate of 2 mV s⁻¹ in the aforesaid electrolytic cell using a saturated calomel electrode (SCE) as the reference electrode. Each curve was corrected for ohmic potential drop deduced from the high-frequency electrode impedance. Potentiodynamic scans and impedance measurements were conducted using the above PAR system.

Characterization of zinc coatings.— The surface morphology and grain size of zinc electrodeposits were observed using scanning electron microscopy (SEM) (JSM 6700F). X-ray diffraction (XRD) analysis was conducted by using a Rigaku diffractometer (D/MAX 2550 V) with Cu K α irradiation ($\lambda = 0.15405$ nm). The scanning rate was 6° per min for 2 θ ranging from 30 to 90°, or 0.5° per min from 41 to 46° for the line-broadened peak of zinc. The crystal size was also estimated by the Scherrer's equation $D = K\lambda/B \cos \theta$, where *D* is average crystal size, λ is the wavelength of the X-ray irradiation, *K* is usually taken as 0.89, *B* is the full width half maximum (fwhm) of the diffraction peak corrected for the instrumental line broadening using silicon as a standard, and θ is the diffraction angle.¹⁸ Before XRD determination, zinc deposits with black surfaces were ground on filter paper to remove the black matter.

The texture of coating can be determined in terms of a preferred orientation factor, p(hkl), which is defined as¹⁹

$$p(hkl) = \frac{I(hkl)/I_o(hkl)}{\frac{1}{n}\sum \left[I(hkl)/I_o(hkl)\right]}$$

where I(hkl), $I_o(hkl)$, and n are the measured intensity of (hkl) reflections, the theoretical intensity of (hkl) reflections, and the number of reflections used in the analysis, respectively. In this treatment, p(hkl) is the relative fraction of crystals that have $\{hkl\}$ plane normals perpendicular to the surface of the electrodeposit. A value of p(hkl) larger than one indicates that the (hkl) reflection is more highly oriented than the (hkl) reflection of a random powder sample.

Results and Discussion

Using additives in plating baths is a fundamental factor to affect the growth and structure of the zinc electrodeposits. In order to make the best of the synergetic effect between BA and TU during zinc electrodeposition,¹⁷ PEG and CTAB were used to improve the dissolution of BA in concentrated zinc sulfate solutions. Obviously, all these compounds are common additives for zinc electroplating.²⁰⁻³⁰ The following results attempted gradually to show their effect and coeffect on the preparation of nanocrystalline zinc coatings on steel specimens. By the way, a small amount of ethanol or methanol was generally used to dissolve BA in aqueous solutions,^{27,28} but the pre-experiments found that these two compounds did not dissolve BA fully in the base solution S_0 , mainly due to the high concentration of zinc sulfate.

PEG and/or CTAB as additives.— PEG and CTAB used separately or together resulted in black zinc electrodeposits. Zinc deposits were characterized by XRD, as shown in Fig. 1. The coatings showed the line broadening of diffraction peaks and the (100)(110)(112) preferred orientations. In addition, the response of steel substrate and ZnO was detected. Table I gives the calculated grain size of zinc deposits. It can be seen that nanocrystalline zinc coatings were obtained from the three solutions S_P , S_C , and S_{PC} , and the combination of PEG and CTAB in solution, S_{PC} , led to a marked decrease of the grain size, about 20 nm, in comparison with the separate cases of S_P and S_C . As for Cu deposition, Kelly et al.^{31,32} found that Cl⁻ ions induced the adsorption of a nearly complete monolayer of PEG molecules in the form of collapsed spheres.



Figure 1. (Color online) XRD patterns for zinc deposits obtained from solutions S_C , S_P , and S_{PC} (\bigstar : ZnO; #: steel substrate).

Bonou et al.³³ also observed a similar blocking effect from them. In the same way, the adsorption of PEG might be enhanced by Br^- ions from CTAB, as these two compounds coexisted, which could be the main reason for the formation of a smaller grain size in solution S_{PC} . Nevertheless, the black appearance of the three layers indicated that the solutions were in need of other brighteners for producing nanocrystalline zinc with metallic luster.

BA in combination with CTAB and PEG as additives.— In recent years, BA has been increasingly used as an additive in plating baths to promote the formation of shiny zinc coatings.²⁵⁻²⁹ In the present case, a mixture of CTAB and PEG gave rise to the full dissolution of BA in the base solution, forming a transparent solution S_{PCB} . CTAB also could dissolve BA fully on its own, while PEG could not.

Zinc coatings electrodeposited from solution S_{PCB} were bright but were black from solution S_{CB} . The reason might be that PEG, as one type of nonionic surfactant, increased the solubility and brightening power of BA.²⁵ SEM observation (Fig. 2) found that the bright coating was composed of particle-like nanocrystalline zinc. Figure 3 gives the XRD patterns for them. For solution S_{CB} , the coating had a (110) preferred orientation, while there were (100)(110) orientations for solution S_{PCB} . ZnO content in the bright zinc coating was very low because the corresponding peaks were extremely weak.

Results in Table I for solutions S_{PC} and S_{PCB} displayed that adding BA to solution S_{PC} offered a bright appearance to the zinc coating but almost no decrease in grain size. It seems that the mixture of PEG and CTAB served as a grain refiner, while BA served mainly as a brightener in the electrodepositing process of zinc. Actually, the three additives should interact closely with each other, instead of independently. In the literature, ^{13,22,24,25} a synergetic effect was often noticed when several additives were added to the electroplating

Table I. The grain size and surface luster of zinc coatings deposited from different baths.								
Solution	$S_{\rm C}$	$S_{\rm P}$	$S_{\rm PC}$	$S_{\rm CB}$	$S_{\rm PCB}$	$S_{\rm CT}$	$S_{\rm PT}$	$S_{\rm PCBT}$
Grain size (nm)	77	72	53	69	52	78	90	43
Luster	Black	Black	Black	Black	Bright	Gray	Yellow	Bright



Figure 2. SEM morphology of zinc electrodeposited from solution S_{PCB} .

baths. The additives could form a strong adsorbed layer, even different kinds of associates, and then exerted a greater influence on zinc electrodeposition than the separate ones.

TU-combined mixtures as additives.— The influence of TUcombined mixtures was studied, and a bright zinc coating was electrodeposited from solution S_{PCBT} . The SEM image in Fig. 4 clearly shows that this coating consisted of nanocrystalline zinc. Zinc layers obtained from solutions S_{PT} and S_{CT} did not have bright surface qualities. Figure 5 presents the XRD patterns of these zinc coatings. In the case of solution S_{PCBT} , zinc deposits displayed the (110)(100)(201) preferred orientations, the line broadening of diffraction peaks, and the existence of ZnO. As for solutions S_{PT} and S_{CT} , ZnO almost was not found and the coatings had the (110)(100) orientations and the (100)(110)(112) preferred orientations, respectively.

A comparison of solutions S_P , S_C , S_{PT} , and S_{CT} from Table I indicated that the grain size was larger in the presence of TU than in



Figure 3. (Color online) XRD patterns for zinc deposits obtained from solutions S_{CB} and S_{PCB} (\bigstar : ZnO; #: steel substrate).



Figure 4. SEM morphology of zinc electrodeposited from solution S_{PCBT}.

the absence of it. This meant that TU did not interact with PEG or CTAB to reduce the grain size of zinc deposits, but the opposite was true. The result for solution S_{PCBT} indicated that adding TU to solution S_{PCB} decreased the grain size from 52 to 43 nm. It can be deduced that a synergetic effect existed between TU and BA and played an important role in the depositing process of nanocrystalline zinc coatings. The interaction mechanism of TU and BA in the deposition process of zinc had been scarcely investigated. According to Cu deposition,³⁴ TU might adsorb on the electrode and/or even form complexes with metallic ions during electrodepositing, leading to a promotion of the nucleation. The action of BA was principally on the electrode surface, blocking the discharge of metallic ions by creating a barrier in the vicinity of the electrode surface.²⁶ Mockute and Bernotiene²⁵ supposed that the formation of different associates by BA with other additives (e.g., benzoic acid, and even the reduced compounds of BA) was the reason for the emerged synergistic effect during zinc electrodeposition, because the associates occupied a larger area on the electrode surface than separate additives. There-



Figure 5. (Color online) XRD patterns for zinc deposits obtained from solutions S_{CT} , S_{PT} , and S_{PCBT} (\bigstar : ZnO; #: steel substrate).



Figure 6. (Color online) Polarization curves for steel electrodes in solutions S₀, S_{PCB}, and S_{PCBT}.

fore, the presence of a synergistic effect between TU and BA was possibly due to the simultaneous formation of complexes by zinc ions and TU and associates by TU and BA, and even involving PEG, CTAB, and the decomposed matters of these additives.

Polarization curves.- Bright nanocrystalline zinc coatings were obtained from solutions S_{PCB} and S_{PCBT} , while only nanolaminated zinc was produced from the base solution S_0 .¹⁷ Figure 6 gives the polarization curves for steel substrates in these three solutions to show the influence of the two mixed additives on zinc electrodeposition. In addition, the polarization curves for the other six solutions were not discussed here because the electrodeposited zinc layers had poor appearance, especially burnt deposits.

In the case of base solution S_0 , a cathodic peak appeared in the potential range $-0.7\ \text{to}\ -1.1\ V_{SCE},$ which was related to the hydrogen evolution and formation of adsorbates (e.g., ZnH_{ad} , ZnO_{ad} and $ZnOH_{ad}$).^{35,36} Zinc started to deposit at about –1.1 V_{SCE}. The rapid deposition at more negative potentials led to formation of a quasivertical curve, similar to the results in Ref. 15, 37, and 38. The data with current density larger than 50 mA cm⁻² were deleted in view of the marked ohmic drop. In solution S_{PCB} , the analogous hydrogen evolution peak was markedly suppressed, which could be ascribed to the inhibitive action of organic additives, especially PEG. It was reported that PEG could form a strongly adsorbed layer with a wellordered structure on the cathode surface and prevented protons from accessing the electrode, leading to the suppression of hydrogen evolution.^{22,24} However, in comparing solution S_{PCBT} with S_{PCB} , the evolution peak was enhanced in the presence of TU. This was possibly due to the conflicting effect of PEG and TU in this potential region. As mentioned above, the addition of TU to solution $S_{\rm P}$ (i.e., solution S_{PT}) resulted in the increase of grain size from 72 to 90 nm, which suggested these two additives competed with each other during the adsorption process and then gave rise to a reduction in the overall adsorption, as observed between PEG and benzoic acid in chloride solutions. $^{\rm 22}$

In solutions S_{PCB} and S_{PCBT} , the presence of organic mixtures promoted a shift of the zinc deposition potential to much more negative values, i.e., about -1.56 and -1.6 V_{SCE}, respectively. A synergetic effect between TU and BA created an extra overpotential of about 40 mV. It can be inferred that the formation of bright nanocrystalline deposits was mainly due to the high overpotentials induced by the mixture additives, and the higher the overpotential the smaller the grain size (Table I). In spite of the very high overpotential, ZnO was clearly identified, being inconsistent with the reaction

model for zinc deposition in acidic electrolytes.^{35,37} This might be caused by the blocking effect of additives adsorbed on the electrode surface, which led to the increase of local pH values with hydrogen evolution. Gomes and daSalva Pereira obtained similar results.

The quasi plateaus appeared in the polarization curves before the rapid deposition of zinc, especially in solution S_{PCBT} . In these potential domains, the current response could be attributed to the predominant hydrogen evolution on the adsorbed species.³⁷ Furthermore, compared with solution S_{PCB} , the current density was much lower in solution S_{PCBT} , which implied that the hydrogen evolution became slower during zinc electrodeposition in the presence of TU, as observed by Song et al.²¹ This change in the lower potential regions was mainly due to the dominant effect between TU and BA in solution S_{PCBT} and the partial desorption of PEG in solution S_{PCB} ²² It was reported that a vigorous hydrogen evolution was able to achieve porous copper and tin electrodeposits.^{39,40} Thus, as a result of the different hydrogen evolution rate, zinc deposits prepared from solutions S_{PCBT} (Fig. 4) were evidently more compact and homogeneous than from solution S_{PCB} (Fig. 2).

Conclusion

Organic compounds PEG, CTAB, BA, and TU, used separately or in combination as additives, have great effect on the morphology and structure of zinc electrodeposits obtained in concentrated acidic sulfate baths by a high pulse current control.

A mixture of PEG and CTAB, compared with the separate ones, leads to the formation of a nanocrystalline zinc coating with much smaller grain size and burnt deposits. This mixture is able to enhance the solubility of BA in the concentrated zinc sulfate baths, forming transparent baths. A mixed additive of these three compounds shows a strong inhibiting effect, which promotes a shift of zinc deposition potentials to much more negative values in comparison with additive-free case. As a result, bright nanocrystalline zinc with an average grain size of 52 nm and the (100)(110) preferred orientations is produced in the presence of this ternary additive.

Compared with the above ternary additive, all four compounds used together in the plating bath can shift zinc deposition potentials to more negative values and more powerfully inhibit the hydrogen evolution during zinc electrodeposition. The synergetic effect of these compounds, especially for BA and TU, is of great influence on the zinc deposition process to achieve the grain refinement. As for this four-additive bath, the electrodeposited zinc is bright and compact, with a particle-shaped morphology, an average grain size of 43 nm, and the (110)(100)(201) preferred orientations. In addition, a small amount of ZnO is identified in the deposits.

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