

Electrodeposition of nanocrystalline zinc from acidic sulfate solutions containing thiourea and benzalacetone as additives

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Abstract Nanocrystalline zinc coatings were produced by pulse electrodeposition in acid sulfate bath containing thiourea and benzalacetone additives and characterized by X-ray diffraction and scanning electron microscopy techniques. The influence of benzalacetone concentration and pulse peak current density on the grain size and crystallographic orientation of zinc deposits was investigated. Zinc electrodeposited from additive-free solutions or with one of the two additives is not composed of nanosized crystals. The mixture additives of thiourea and benzalacetone give rise to the formation of particle-like nanocrystalline zinc with a (10 $\bar{1}$ 1) random orientation. A change in peak current density from 2 to 1 A/cm² only increases the grain size from 60 to 62 nm.

Keywords Zinc · Nanocrystalline · Electrodeposition · Benzalacetone

Introduction

Zinc is the most widely used material for protecting steels from corrosion, usually being used as a sacrificial coating on steels by hot dipping or electroplating. In recent years, nanocrystalline zinc coatings have received great research and business interests. The reason is that

nanostructured materials (i.e., materials with ultra-fine crystals less than 100 nm in size) show considerable changes in mechanical, physical, and chemical properties in comparison with conventional polycrystalline materials. For instance, nanocrystalline zinc coatings had higher corrosion resistance and hardness than the polycrystalline ones [1, 2].

Electrodeposition can be used to produce nanocrystalline zinc coatings. Nanolaminated zinc deposits were produced from an acid sulfate solution under direct current (DC) control [3]. Compared with DC plating, pulse electrodeposition usually yields zinc deposits with a finer grain size and more homogenous surface appearance because the current density is considerably higher. It is reported that high current density induces increased cathode overpotential and nucleation rate for the formation of finer grains [4–6]. By pulse current control, nanocrystalline zinc deposits were obtained both from an aqueous-chloride-based [6] and from a sulfate-based bath [7].

Organic additives are often present in zinc electroplating baths to improve the surface performances and refine the grain size of plated layers. The mixtures of polyacrylamide and thiourea (TU) were used as additives in zinc chloride electrolytes for electrodepositing nanocrystalline zinc coatings [1, 6]. The presence of additives in chloride-based baths, such as *o*-vanillin, polyethyleneglycol, benzylideneacetone, etc., also results in smoother surface and smaller grain size of the electrodeposited zinc layers [8–10]. The surfactants including cetyl trimethyl ammonium bromide, sodium dodecyl sulfate, and octylphenolpoly(ethyleneglycolether) were presented in zinc sulfate solutions for electrodepositing nanocrystalline zinc [7]. Thiourea, gelatin, glycine, benzalacetone (BA), etc., are traditional additives in sulfate baths, usually as grain refiners or brighteners for zinc electrodeposition [11–17].

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As far as continuous electroplating of steel plates is concerned, acid-sulfate-based baths are industrially used, but, to our knowledge, nanocrystalline zinc has not been obtained from this system. The main purpose of this study is to produce nanocrystalline zinc layers from acid sulfate solutions. The pulse electrodeposition method and mixed organic additives of thiourea and benzalacetone were attempted.

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. Cold-rolled, low-carbon steel specimens were used as the cathode with an exposed surface area of about 0.1 cm². Before 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 plating solutions were made of 350 g/l ZnSO₄·7H₂O 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 H₂SO₄. Thiourea (H₂NCSNH₂) and benzalacetone (C₆H₅CH=CHCOCH₃) with solubilizer (emulsifier OP, polyethyleneglycol *p*-isooctylphenyl ether) (about 0.2 ml OP per 100 mg BA) were used separately or in combination as additives.

Pulse electrodeposition procedure

Pulse electroplating was conducted by varying the peak current density (i_p) from 0.1 to 2 A/cm². The current-on time (T_{on}) and the current-off time (T_{off}) were optimized through pre-experiments and set at 4 and 8 ms, respectively, during all experiments. PAR system (Princeton Application Research, AMETEK), which comprised a M273A potentiostat/galvanostat and the PowerPulse software, was used to generate the current waveforms and supply the current. The plating time was 1 to 15 min according to the i_p value, i.e., the higher i_p , the shorter the plating time. All experiments were repeated using at least two specimens to confirm the reproducibility of the results.

Characterization of zinc coatings

The surface morphology and grain size of zinc electrodeposits were observed using scanning electron microscopy (SEM) (FEI XL30). 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°/min for 2θ ranging from 30° to 90° or 0.5°/min from 41 to 46° for the line-broadened peak of zinc. Crystal size was also estimated by Scherrer's equation $D=K\lambda/B\cos\theta$, where D is crystal size, λ is the wavelength of the X-ray irradiation, K is usually taken as 0.89, B is the full-width half maxima of the diffraction peak after subtraction of the instrumental line broadening using silicon as a standard, and θ is the diffraction angle [18].

Results and discussion

Sulfate solutions without additives

It is a simple and ideal means to adopt electrolytes without organic additives for electrodepositing processes, especially for the producers. In addition, organic additives often result in high concentration of active elements (e.g., sulfur) in electrodeposited metallic coatings, which can easily segregate to grain boundaries and weaken coating properties (e.g., corrosion resistance) [1, 19]. Thus, the additive-free sulfate baths were examined through changing the pulse current parameters (i_p). Figure 1 shows the typical SEM micrograph of these zinc deposits, which were formed with a laminated texture. The grain size of the platelets is far larger than 100 nm, though their thickness is less than 100 nm. The zinc coating formed at $i_p=0.1$ A/cm² mainly had a basal texture (Fig. 1a). In the case of $i_p=2$ A/cm², XRD analysis observed a (10 $\bar{1}$ 3) preferred orientation without the line broadening as shown in Fig. 2. No peak appeared for the (10 $\bar{1}$ 0) plane, which may mean that the overpotential was not high enough to form this plane [6, 20]. By the way, the peaks of Fe from carbon steel substrate were relatively strong because zinc was deposited on the center surface of the steel substrate (about 0.2 cm²). These results indicate that the zinc electrodeposit has a nano-

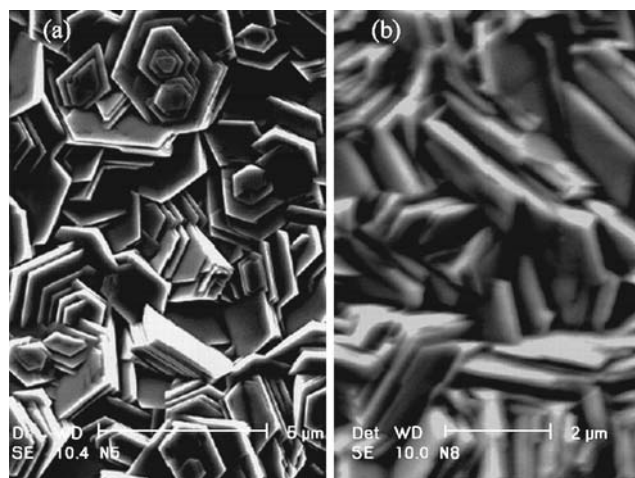


Fig. 1 SEM morphologies of zinc electrodeposited from an additive-free sulfate bath at different i_p values: **a** 0.1 A/cm²; **b** 2 A/cm²

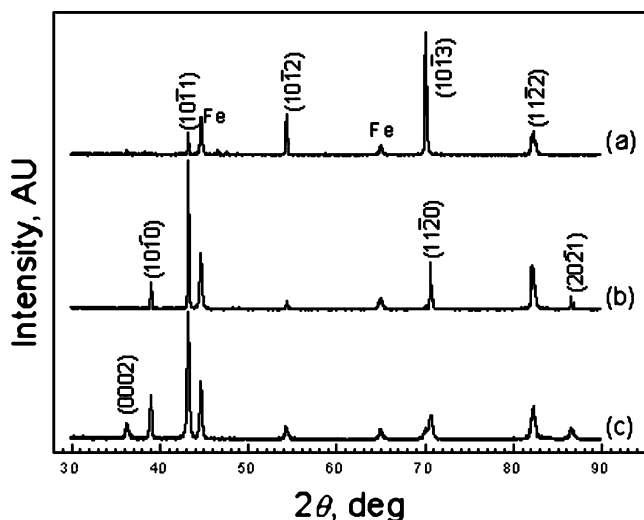


Fig. 2 XRD patterns of zinc deposited at $i_p=2$ A/cm² from different solutions: **a** without additives, **b** containing 1 g/l TU, and **c** containing 1 g/l TU and 0.5 g/l BA

laminated structure, similar to the DC-deposited zinc in the literature [3]. Even under 2 A/cm² conditions, it is obviously still difficult for pulse electrodeposition to prepare nanocrystalline zinc from additive-free sulfate baths.

Effect of thiourea

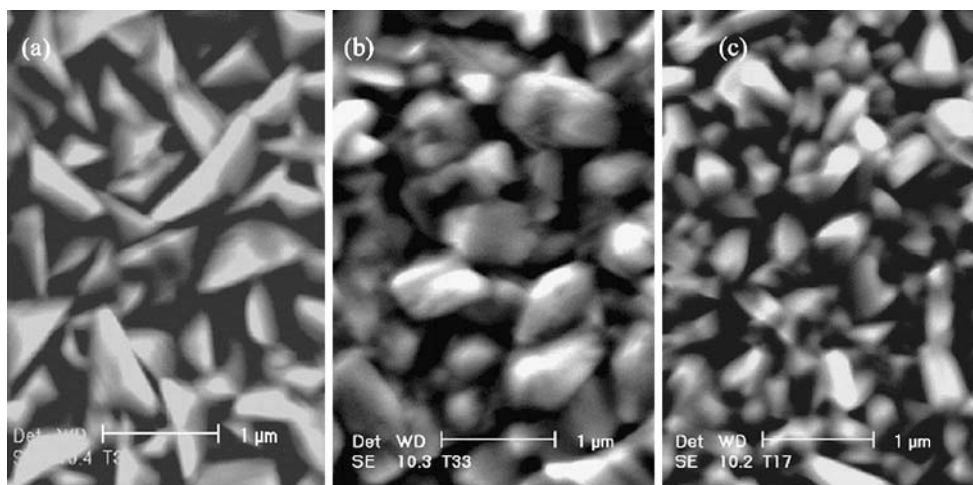
Organic additives are most widely used in plating electrolytes for controlling the various qualities of electroplated metallic coatings. It is possible to reduce the grain size of deposited metals into the nanometer range (<100 nm) by using additives. The reduction of grain size by organic additives is mainly related to a combined effect [6], i.e., (1) the increase of cathode overpotential and (2) the retardation of continuous grain growth and the increase of nucleation rate. Therefore, thiourea and benzalacetone with OP

solubilizer were added separately to sulfate-plating solutions to find the effective ones. The separate addition of these organic matters was unfortunately unable to obtain nanocrystalline zinc even at i_p values increasing up to 2 A/cm². Benzalacetone cannot sustain the $i_p=2$ A/cm² and resulted in black electrodeposits. Thiourea reduced the grain size to a value of about 0.3 to 1 μm in the case of $i_p=2$ A/cm², as shown in Fig. 3. The change in thiourea concentration from 0.2 to 1 g/l and the further increase of i_p up to 4 A/cm² had slight influence on the grain size of zinc. It can be seen from the change of strongest peaks in Fig. 2 that the addition of thiourea changed the (1013) preferred orientation to a (1011) random orientation.

Mixtures of thiourea and benzalacetone

As can be seen, the single addition of the above-mentioned additives was not effective enough to induce the formation of nanocrystalline zinc. The synergetic effect of these additives was studied. It was found that the mixtures of thiourea and benzalacetone reduced the grain size of zinc deposits markedly. Figure 4 gives the SEM morphology of zinc deposited at $i_p=2$ A/cm² from a sulfate solution containing 1 g/l thiourea and 0.5 g/l benzalacetone additives. The coating is composed of zinc particles with size of less than 100 nm. An XRD analysis (Fig. 2) indicated that the addition of benzalacetone to the thiourea-containing bath had insignificant influence on the (1011) random orientation, but the line broadening of the diffraction peaks clearly took place. According to the calculation by Scherrer's formula, the average grain size of zinc deposit was about 60 nm. In chloride-plating solution, a mixture of thiourea and polyacrylamide showed a similar synergetic effect, resulting in the high cathode overpotential and then the formation of nanocrystalline zinc [6].

Fig. 3 SEM morphologies of zinc electrodeposited at $i_p=2$ A/cm² from sulfate-bath containing different TU concentrations: **a** at 0.1 g/l, **b** at 1 g/l, and **c** at $i_p=4$ A/cm² from the same solution as in **b**



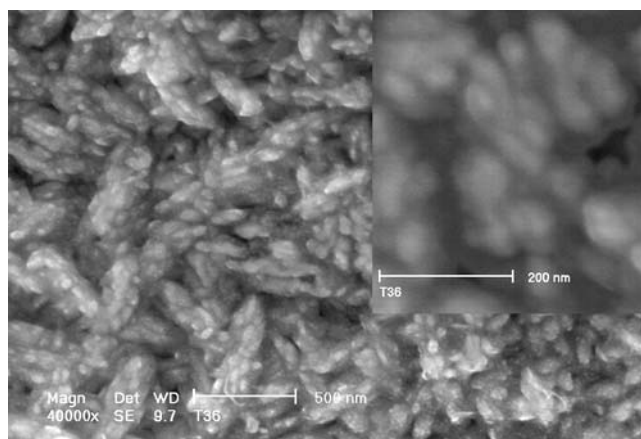


Fig. 4 SEM morphology of zinc deposited at $i_p=2$ A/cm² from a sulfate solution containing a mixture 1 g/l TU + 0.5 g/l BA. The inset shows an image at higher magnification

To examine the influence of benzalacetone concentration in the plating solution on the grain size of zinc deposits, the thiourea concentration and i_p were kept at 1 g/l and 2 A/cm², respectively. The benzalacetone concentration was 0.25, 0.5, and 1 g/l. The crystallographic orientation of zinc electrodeposits was characterized by XRD and is shown in Fig. 5. Three zinc deposits show a similar (10 $\bar{1}$ 1) random orientation and line broadening of the peaks. The calculated grain size of zinc deposits was in the nanometer range, i.e., 72, 60, and 77 nm, respectively, as the benzalacetone concentration varied from 0.25 to 1 g/l. It can be inferred that the concentration of benzalacetone at about 0.5 g/l produced the finest zinc deposit. This behavior, such that using an intermediate concentration of benzalacetone (0.5 g/l) resulted in smaller grain size than that using a higher concentration

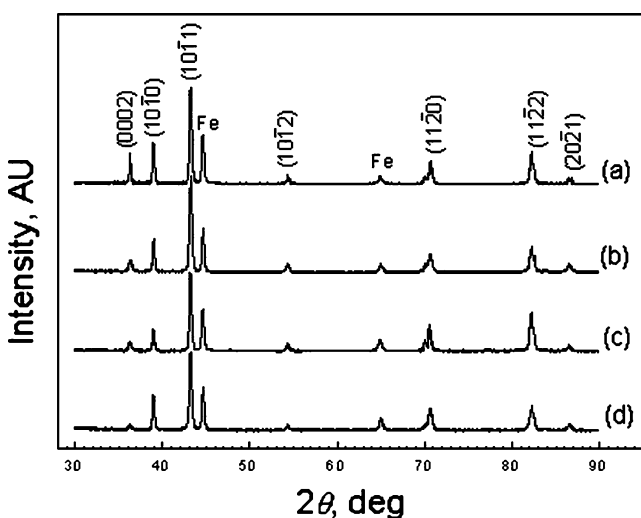


Fig. 5 XRD patterns of zinc electrodeposited at $i_p=2$ A/cm² from solutions containing TU (1 g/l) with different BA concentrations: **a** at 0.25 g/l, **b** at 0.5 g/l, **c** at 1 g/l, and **d** at $i_p=1$ A/cm² from the same solution as in **b**

(1 g/l), cannot be explained clearly yet on the basis of the present results.

Pulse peak current density i_p is a very important parameter for the continuous production of zinc-electroplated steel plates. When i_p decreased from 2 to 1 A/cm², zinc deposits obtained in a sulfate solution with 1 g/l thiourea and 0.5 g/l benzalacetone had similar XRD characteristics as observed from Fig. 5b,d. The calculated grain size was 60 and 62 nm for $i_p=2$ and 1 A/cm², respectively. This means that the slight change in current density in practical production of nanocrystalline zinc coatings has no significant influence on the grain size.

Conclusions

In organic additive-free electrolytes, only nanolaminated zinc can be prepared even at a peak current density of 2 A/cm². The single addition of thiourea reduces the grain size of zinc electrodeposits to about 0.3–1 μ m and changes the (10 $\bar{1}$ 3) preferred orientation to a (10 $\bar{1}$ 1) random orientation. Nanocrystalline zinc deposits are obtained from acid sulfate bath containing the mixtures of thiourea and benzalacetone by using pulse electrodeposition, with average grain sizes in the range of 60 to 77 nm and a (10 $\bar{1}$ 1) random orientation. The change in peak current density from 2 to 1 A/cm² only results in a slight increase of the grain size by about 2 nm.

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