

## Effects of Brightener CT-2 on Zinc Deposition from a Potassium Chloride Containing Bath

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**ABSTRACT** The brightener CT-2 was shown to be a strong inhibitor to the deposition of zinc, increasing cathodic polarization by about 100 mV, decreasing the cathodic peak current by about 20 times, and also to be a very strong promoter of nucleation, increasing the nucleus number density by 2 orders of magnitude, so that it would be reasonable to get quality electroplates with fine grains, bright and smooth surface and very few defects by using the brightener.

**KEY WORDS** zinc plating/brightener, inhibition, nucleation

Zinc has been used extensively as a protective coating of many metallic materials. The zinc electroplating from potassium chloride containing baths has a lot of advantages, such as quality plates with good brightness, fine grains, low hydrogen contents and high adhesion strength with the substrate; very high current efficiency; easy to electroplate on various materials (including casting parts), etc. The brightener CT-2 was used here for studying the effects of the brightener on the zinc deposition.

The kinetics of zinc deposition has been studied by quite a few researchers<sup>[1, 2]</sup>, and the nucleation has also been studied<sup>[3, 4]</sup>, but the results were quite different due to the differences in the electrolytes, additives, and electrode substrates used.

## 1 Experimental

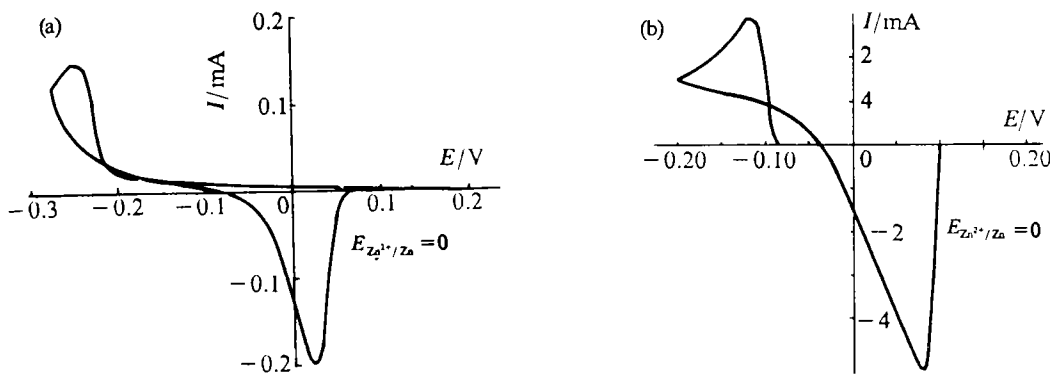
Cyclic voltammetry and potential step were used to study the cathodic reaction, especially nucleation/growth process of zinc deposition. A electrochemical system Model DHZ-1 was used to control the experiments and the transients were recorded by a X-Y recorder of Gould 60000 series. The temperatures were measured by alcohol thermometer. The bath contained ZnCl<sub>2</sub> 65 g/l, KCl 220 g/l, H<sub>3</sub>BO<sub>3</sub> 30 g/l, brightener

CT-2 16 ml/l or 0 ml/l. Analytical reagents and deionized water was used to prepare the bath. The pH was adjusted to 5.8 before the experiments were conducted. The working electrode was a micro-electrode of tungsten, its preparation was described elsewhere<sup>[5]</sup>. The reference electrode and counter electrode were zinc rod immersed in the bath. Both of them were made of granular zinc of analytical reagent by melting and sucking into a glass tube. The exchange current density of zinc electrode is large enough for it to behave reversibly as a reference electrode<sup>[6]</sup>. The potential of zinc was found to be -1.028 V in the bath with brightener against saturated calomel electrode and -1.048 V in the bath without brightener. In all experiments the Ohm drop of the electrolyte has been compensated by the built-in unit of the instrument used.

## 2 Results and Discussion

### 2.1 The inhibition of the cathodic reaction by the adsorption of brightener CT-2

The brightener CT-2 is some kind of non-ionic surfactants synthesized from several organic chemicals. The voltammograms obtained are shown in Figs.1(a) and (b) for zinc electrodeposition from baths with and without brightener, respectively.



**Fig. 1** The voltammograms for the deposition of zinc on tungsten from a chloride bath  
 (a) with brightener CT-2 16 ml/l; (b) without brightener

Electrode area  $S=0.0113 \text{ cm}^2$ , scanning rate  $\nu=45 \text{ mV/s}$ , temperature  $T=301 \text{ K}$ ,  $\text{ZnCl}_2 : 65 \text{ g/l}$

It can be seen that in the presence of the brightener(Fig.1 a) cathodic polarization increased by about 100 mV and cathodic peak current decreased by about 20 times compared with those obtained in the absence of the brightener (Fig.1 b). The concentration of the brightener in the bath was so small that the zinc species and their diffusion in the solution should not change considerably. Therefore, the increase in cathodic polarization and the sharp decrease in cathodic current should be caused by the blocking effect of the adsorption layer of the surfactants on the cathode sur-

face. Such a adsorption would be favourable to the renewal of growth sites<sup>[1]</sup> and would effectively avoid forming of dendritic crystals and magnifying of the roughness of the surface which might be caused to happen in a diffusion controlled reaction. An increase in cathodic polarization would lead to an increase in nucleus number density and a decrease in cathodic current to decrease in growth rate of the nuclei, both would be favourable to getting quality electroplates.

In the presence of brightener, zinc was deposited at more negative potential, no deposition wave of hydrogen was observed, showing that the hydrogen deposition was inhibited as well. The current efficiencies for zinc deposition at 1 A/dm<sup>2</sup> were 98.6% ~ 99.6% for baths without brightener and 99.25% ~ 99.75% for baths with brightener. This could also be considered as an evidence of the inhibition of the brightener on hydrogen deposition. This is an advantage over the use of a complexing agent which usually causes to a decrease in current efficiency.

## 2.2 The effects of brightener CT-2 on the nucleation/growth process

The potentiostatic transients for the electrodeposition of zinc on tungsten are shown in Fig.2. Assumed that nuclei distribute randomly on the cathode surface and grow under diffusion control, that the new nuclei can not form within the growing diffusion zones around the mature nuclei, and that the development and overlap of the diffusion zones are taken into account, the potentiostatic transients can be described by<sup>[7]</sup>

$$I = zFD^{1/2} C [1 - \exp(-N\pi kDt)] / (\pi t)^{1/2} \quad (1)$$

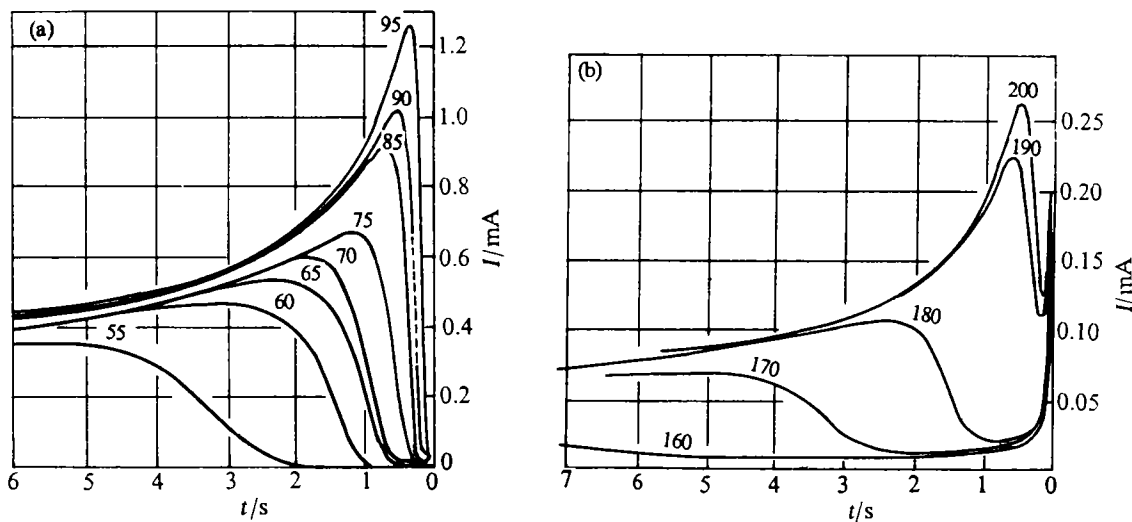


Fig. 2 The potentiostatic transients for the deposition of zinc on tungsten (a) with (b) without brightener ( $S=0.0114\text{cm}^2$ ,  $T=301\text{K}$ ,  $\text{ZnCl}_2$  content: 65g/l. Numbers shown on each curve are overpotentials in mV) for instantaneous nucleation with constant  $k=(8\pi CM/\rho)^{1/2}$  and

$$I = zFD^{1/2} C[1 - \exp(-AN_0 \pi k' Dt^2/2)]/(\pi t)^{1/2} \tag{2}$$

for progressive nucleation with constant  $k' = (4/3)(8\pi CM/\rho)^{1/2}$ .

where  $zF$  is the molar charge of the depositing species,  $D$  diffusion coefficient,  $C$  concentration of the depositing species,  $N$  nucleus number density,  $k$  and  $k'$  constants,  $A$  rate constant for nucleation,  $N_0$  active sites available,  $M$  and  $\rho$  molecular weight and mass density of the depositing species, respectively.

Equations (1) and (2) can describe all parts of the potentiostatic transients, including rising and falling parts as well as the current maxima. Setting the first derivative of equations (1) and (2) to zero, the corresponding functions of current,  $I_m$ , and of time,  $t_m$ , can be evaluated. The resulting expressions for these quantities for both instantaneous and progressive nucleation are given in Table 1.

Table 1 Expressions obtained from the derivation of equations (1) and (2)

Quantities	Instantaneous nucleation	Progressive nucleation
$t_m =$	$1.2654/N\pi kD$ (3)	$(4.6733/AN_0\pi k'D)^{1/2}$ (7)
$I_m =$	$0.6382zFD C(kN)^{1/2}$ (4)	$0.4615zFD^{3/4}C(k'AN_0)^{1/4}$ (8)
$I_m^2/t_m =$	$0.1629(zFC)^2D$ (5)	$0.2598(zFC)^2D$ (9)
$I^2/I_m^2 =$	$1.9542\{1 - \exp[-1.2564(t/t_m)]\}^2$ (6)	$1.2254\{1 - \exp[-2.3367(t/t_m)^2]\}$ (10)

In the case of progressive nucleation, new nuclei cannot form when the electrode surface is completely covered by the diffusion zones, then the saturated nucleus number density is given by

$$N_s = (AN_0/2k'D)^{1/2}$$

The solid lines in Fig.3 are the theoretical non-dimensional plots of  $I^2/I_m^2$  vs  $t/t_m$  calculated by equations (6) and (10) and the points are experimental data taken from Fig. 2.

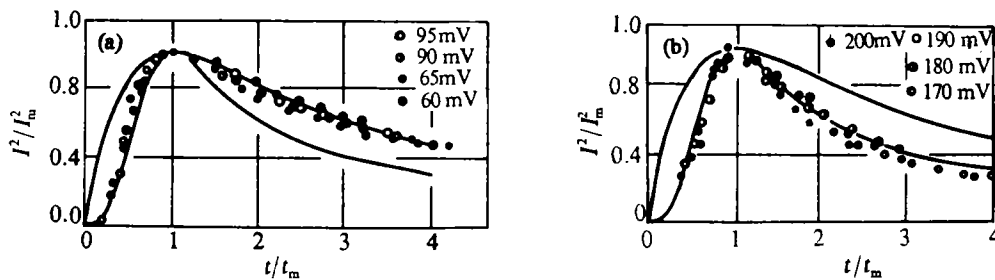


Fig. 3 Theoretical non-dimensional plots of  $I^2/I_m^2$  vs  $t/t_m$  and experimental data

Solid lines: theoretical plots for instantaneous (above) and progressive (below) nucleation

Points: Experimental data for experiments with brightener (a) and without brightener (b)

Fig.3 (a) shows that in the presence of the brightener the nucleation for the

deposition of zinc on tungsten is a progressive one, which is in agreement with the results of cyclic voltammetry, i.e. the further growth of the mature nuclei is inhibited by the adsorption of the brightener, so that some new nuclei must form somewhere else before the electrode surface is completely covered by both the diffusion zones and the adsorption zones of the brightener around the nuclei. The lasting duration that this process would mainly depend on the values of the overpotential applied, which would determine the rate of nucleation and the equilibrium of the adsorption of the brightener. The higher the overpotential, the smaller the critical radius for nucleation, the larger the nucleation rate, the smaller the space occupied by each diffusion zone of each nucleus on average, and thus the shorter the time for the electrode surface to be completely covered. After that time, no new nuclei can form, so that the nucleus number density would reach its saturated value.

The diffusion coefficient of zinc species in the bath with brightener was calculated by equation (9) to give  $D = (6.98 \pm 1.1) \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ . This  $D$  value is lower than that for experiments without brightener by 3 orders of magnitude. As stated above, the addition of brightener would not lead to considerable changes in both zinc species and their diffusion in the bath, such a huge change in  $D$  value would be caused by the blocking effect of the adsorption layer of the brightener. During the derivation of equations (1) and (2), adsorption were not considered. But the rates of adsorption happen to be controlled by diffusion<sup>[8]</sup>, i.e., the expansion of diffusion and adsorption zones around the nuclei follows the same kinetics, equations (1) and (2) could be applicable to the case of adsorption of surfactants in first approximation. In fact, all potentiostatic transients took the form of 3-D nucleation with diffusion controlled growth in cases both with and without the brightener. But in the presence of the brightener, the values of  $D$  in equations (1) ~ (11) can no longer be regarded as a diffusion coefficient, but combined the coefficient of diffusion and adsorption. The separately quantitative expression of adsorption of surfactants and diffusion on potentiostatic transients needs to be further studied. Using this  $D$  value, the nucleation rates,  $AN_0$ , and saturated nucleus number densities,  $N_s$ , have been calculated and shown in table 2 (left). The diameters of the exclusion zones for nucleation,  $D_{ez}$ , and the time required for reaching saturated nucleus number densities,  $T_s$ , are also shown here.

It can be seen from Fig.3 (b) that the experimental data are close to the theoretical plot for progressive nucleation before current maxima are reached, so that these data are processed by equations for progressive nucleation. The diffusion coefficient obtained,  $D = (1.64 \pm 0.13) \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ , was found to be in good agreement with Kim's<sup>[2]</sup> and Wu's<sup>[3]</sup> work.

**Table 2** The  $AN_0$ ,  $N_s$ ,  $D_{ez}$ , and  $T_s$  at different overpotential,  $\eta$   
 ( $S=0.0113 \text{ cm}^2$ ,  $T=301 \text{ K}$ ,  $\text{ZnCl}_2$  content : 65 g/l)

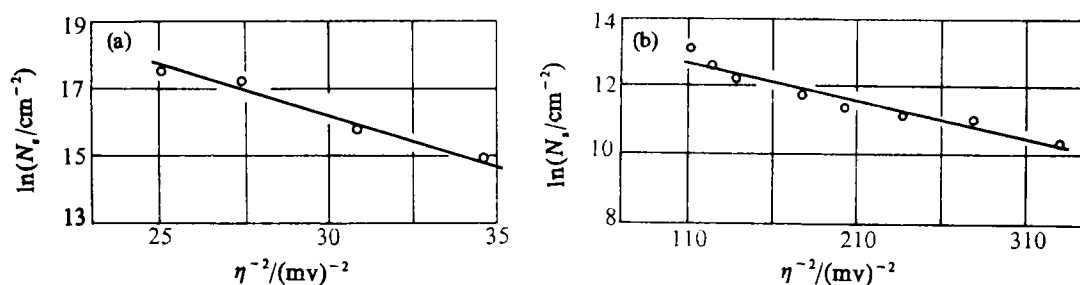
With brightener					Without brightener				
$\eta$	$AN_0 \times 10^{-6}$	$N_s \times 10^{-7}$	$D_{ez} \times 10^4$	$T_s$	$\eta$	$AN_0 \times 10^{-6}$	$N_s \times 10^{-7}$	$D_{ez} \times 10^4$	$T_s$
/mV	/cm <sup>-2</sup> s <sup>-1</sup>	/cm <sup>-2</sup>	/cm	/s	/mV	/cm <sup>-2</sup> s <sup>-1</sup>	/cm <sup>-2</sup>	/cm	/s
200	3.97	8.02	1.1	0.20	95	32.9	4.77	1.4	0.15
190	3.20	7.20	1.2	0.23	90	12.8	2.97	1.8	0.23
180	0.173	1.68	2.4	0.97	85	6.21	2.07	2.2	0.33
170	0.029	0.68	3.8	3.00	75	2.40	1.29	2.8	0.54
					70	1.05	0.85	3.4	0.81
					65	0.71	0.70	3.8	0.99
					60	0.49	0.58	4.2	1.19
					55	0.14	0.31	5.7	2.23

The corresponding data for experiments without brightener are also listed in Table 2 (right).

Table 2 shows that in the presence of the brightener the saturated nucleus number densities are found to be 2 orders of magnitude higher, and nucleation rates 3 orders of magnitude higher than those in the absence of the brightener at a difference in overpotential about 100 mV.

It can be also seen from Table 2 that in presence of the brightener nucleation rate is increased 3 orders of magnitude and saturated nucleus number density 2 orders of magnitude when overpotential is increased by 30 mV. In the case without brightener the increases of the corresponding quantities is almost the same orders of magnitude for an increase of 40 mV in overpotential.

Such a huge increase in nucleus number density, or grain refinement should be considered as a important effect of the brightener.



**Fig. 4** The dependences of  $N_s$  on  $\eta$  for experiments (a) with brightener and (b) without brightener

From the values of  $N_s$ , the mean diameters of exclusion zones for nucleation were calculated, giving values of a few micrometers in the case with brightener. these values should be the limits of the grain sizes at corresponding values of overpotential. The surface irregularities of the electroplates would be smaller than the grain sizes, say, 1 micrometer or smaller, so that the electroplates obtained by using brightener CT-2 should be very bright, of uniform grain size and of very few defects.

The sharp change of saturated nucleus number density with the overpotential could be explained by classic theory for nucleation, i.e.,  $\ln N_s$  vs  $\eta$  should be linear as shown in Fig.4.

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## 光亮剂 CT-2 对氯化钾镀锌的影响

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**摘要** 光亮剂 CT-2 是锌沉积的强阻化剂, 使阴极极化增大约 100 mV, 阴极峰电流降低到 1/20; 但它也是成核的强促进剂, 使核数密度增大两个数量级, 所以使用这种光亮剂应得到晶粒细, 表面光亮平滑, 缺陷很少的高质量镀层.

**关键词** 镀锌/ 光亮剂, 阻化作用, 成核

**中图分类号** TQ153.15