Influence of concentration of zinc ions on electrocrystallization process of zinc [①]

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Abstract: Cyclic voltammetry, chronoamperometry and scanning electron microscopy were employed to study the influence of Zn^{2+} ion concentration in electrolyte solutions on zinc electroplating process. The results show that, at high overpotentials, the nucleation of zinc is instantaneous, and nuclear density increases with the overpotentials increasing. While at low overpotentials, the zinc may be preferentially electrodeposited on surface inhomogeneities such as emergence points of edge, screw dislocations, atomic disorder, kink sites, or monoatomic steps, and no distinguished nucleation current can be observed. The major dissolution peak in cyclic voltammogram drifts positively due to the change of the rate-determining step of zinc electroplating processes from diffusion to the electrochemical reaction with the increase of Zn^{2+} ion concentration.

Key words: zinc electroplating; nucleation; growth; mechanism

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1 INTRODUCTION

The electrodeposited coatings of zinc and its alloys have been widely used as protective films of metals, and electrodeposition of alloys is widely used in the production of new materials with specific chemical and physical properties, such as nanocrystalline magnetic thin films and functional multilayers[1-5]. As far as the electroplating process is concerned, the nucleation kinetics and the growth mechanism of the first metallic nuclei formed on the initial substrate are critical, which determine the physicochemical properties of the electrodeposited materials[6, 7] and are, therefore, crucial points to be understood and controlled.

On the other hand, the different electrocrystallization nucleation and growth processes of zinc will result in different electrodeposited layer morphologies, such as compact, spongy or dendritic surfaces[8].

The aim of this paper is to investigate the influence of Zn^{2+} ions concentration on the nucleation and growth mechanism of zinc, detect the relationship between the structure of deposit layer and the reaction of rate determining steps during zinc electroplating process, and provide the basis reference for further studying on the nucleation and growth mechanisms of zinc-base alloys.

2 EXPERIMENTAL

The experimental electrolyte was prepared with AR grade reagents and twice distilled water according to the basic compositions listed in Table 1. A three-electrode system consisting of cycloidal polycrystalline brass electrode with an area of 0. 502 7 cm^2 exposed which was used as working electrode(WE), saturated calomel electrode(SCE) as reference electrode and a large bright platinum foil as counter electrode, was employed. Before measurements, the exposed surface of WE were polished with silicon carbide papers from 3 through 1 to 0. 5 μm and velvet, rinsed with the twice distilled water, washed in acetone, rinsed with the twice distilled water again and then dried in air. The experimental temperature was (25 ±1) ℃ controlled by thermostat water tank.

Table 1 Basic electrolyte compositions for electroplating zinc electrodeposits （g/ L）

$ZnCl_2$	$Na_3C_6H_5O_7 \cdot 2H_2O$	EDTA-2Na	H_3BO_3	KCl
20 - 90	12	4	40	100

Cyclic voltammetry and chronoamperometry measurements were performed with a commercial electrochemical analyzer/ workstation (Model 660A, US). After experiments, scanning electron microscopy(SEM, HITACHI S-570, Japan) was

used to observe the morphologies of the electrode-posited layers.

3   RESULTS AND DISCUSSION

3. 1   Voltammetric study

The influence of the concentration of Zn^{2+} ions in the electroplating solution on zinc deposition process was first investigated by cyclic voltamme-try. The sweep potential range was set from open circuit potential to -1.5 V and always initiated in the negative direction. Fig. 1 shows the typical vol-tammograms obtained in electroplating solution with different Zn^{2+} ion concentrations. All voltam-mograms presented here are obtained during the first cycle with a scanning rate of 10 mV/s. It can be seen that there are two distinct current peaks in each voltammogram. The cathodic peak is associat-ed with Zn^{2+} ions reduction process(electrodeposi-tion); while the anodic peak with the Zn dissolu-tion process from the cupro-zinc substrate. Mean-while, in the anodic branches of the zinc deposi-tion, the major dissolution peaks are located at dif-ferent potentials, which implies that different zinc phases are involved.
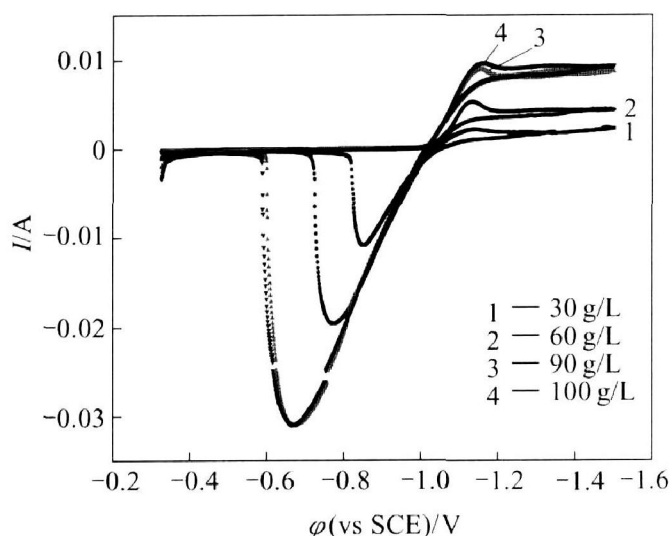

Fig. 1   Cyclic voltammograms for brass electrode in basic electrolyte(pH = 4. 0) containing different Zn^{2+} ion concentrations
(Cathodic current is taken as positive one)

From Fig. 1, it can be seen that the cathodic current peak intensity increases with the concen-tration of Zn^{2+} ions, indicating that the zinc depo-sition is controlled (limited) by the diffusion process of Zn^{2+} ions as far as the investigated con-centration range concerned[7]. However, SEM ob-servation of the layers obtained in different Zn^{2+} ion concentrations contained electrolyte solution ($J_k = -1.5$ A/dm^2) shows that, under an identi-cal electroplating current density, the morphology of zinc electrodeposits changes from dentritic to the

compact with the increase of Zn^{2+} ion concentra-tion (Figs. 2 ～ 4). Because the electroplating process under diffusion control favors the forma-tion of less compact deposits, such as spongy and dentritic coatings, the rate determining step may change from diffusion process of Zn^{2+} ions through
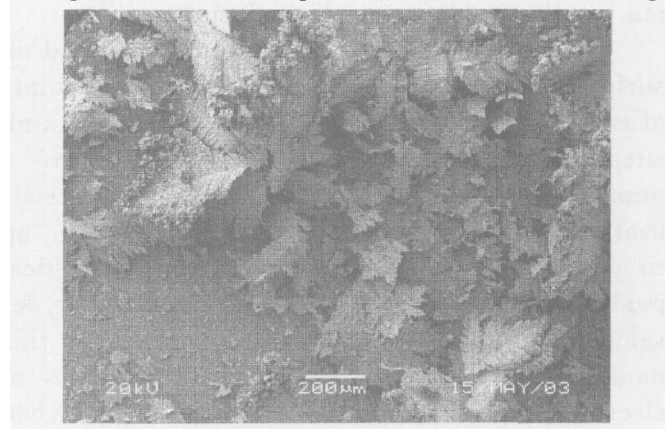

Fig. 2   SEM morphology of zinc electrodeposit obtained in electrolyte containing 30 g/L Zn^{2+} ions
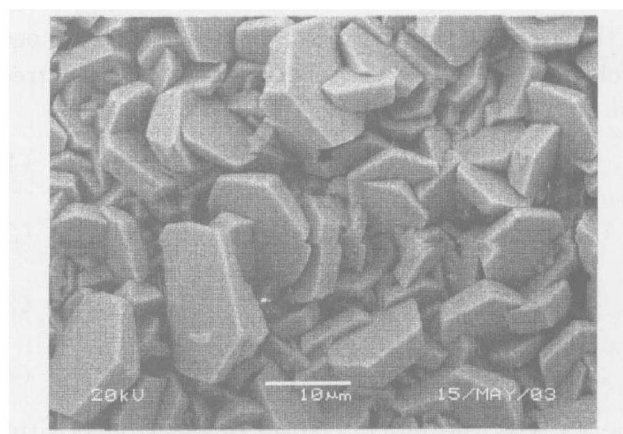

Fig. 3   SEM morphology of zinc electrodeposit obtained in electrolyte containing 60 g/L Zn^{2+} ions
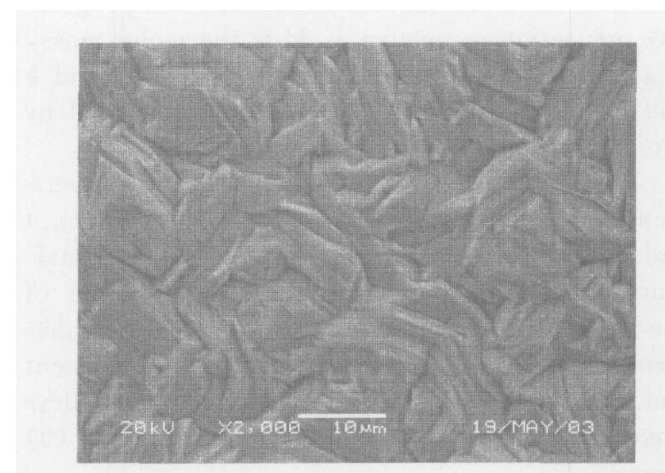

Fig. 4   SEM morphology of zinc electrodeposit obtained in electrolyte containing 90 g/L Zn^{2+} ions

the bulk electrolyte solution to the cathodic surface to electrochemical reaction with the increase of Zn^{2+} ions concentration.

3. 2　Chronoamperometric study

In order to clarify the discrepancy between the results of cyclic voltammetry and SEM technique, zinc nucleation process is characterized in more detail by chronoamperometric analysis.

Generally, nuclei are preferentially formed on surface inhomogeneities, such as emergence points of edge, screw dislocations, atomic disorder, kink sites, or monoatomic steps. And there are a number of literatures describing the electrocrystallization process mathematically[9-16], however, up to date, the most widely employed theoretical model for electrochemical nucleation is the one developed by Hills and his colleagues[17]. In this model[12-15], the authors describe the kinetics of electrolytic phase formation at early stages when diffusion of the electroactive species from bulk solution to the interface is the rate determining step, and the growth of nuclei is considered to be 3D when taking into account of overlap of diffusion zones. According to this model, the rising portion of the current transient can be described, respectively for the instantaneous nucleation and progressive nucleation by

$$I_i = \frac{nD^{1/2}c}{\pi^{1/2}t^{1/2}}[\,1 - \exp(-\,N\pi kDt\,)\,] \qquad (1)$$

$$k = \left[\frac{8\pi cM}{\rho}\right]^{1/2} \qquad (2)$$

$$I_p = \frac{nD^{1/2}c}{\pi^{1/2}t^{1/2}}\left|\,1 - \exp\left|\frac{-N_{A,\infty}\pi k'Dt^2}{2}\right|\,\right| \qquad (3)$$

$$k' = \frac{4}{3}\left[\frac{8\pi cM}{\rho}\right]^{1/2} \qquad (4)$$

where n is the molar charge of electrodepositing species, D the diffusion coefficient, c the bulk concentration of the zinc species, N is the number of nuclei, N_∞ and $N_{A,\infty}$ are the total number of active sites for instantaneous nucleation and progressive nucleation respectively, M is the molar mass, ρ is the density of the deposited material, and k and k' are the numerical constants determined by the experimental conditions.

Figs. 5 – 7 show the relationship of the experimental non-dimensional variables between (t/t_{max}) and (I/I_{max})^2, where I_{max} and t_{max} are the maximum current transient values. Determination of the nucleation process involved is achieved by analyzing the rising section of the current transient and then comparing the curve to the dimensionless theoretical curves obtained from Eqns. (1) and (3) respectively.

From Figs. 5 – 7, it can be seen that, each of the "I –t" curves consists of an initial spike(within the first 0. 02 s) due to the charging of the electro-
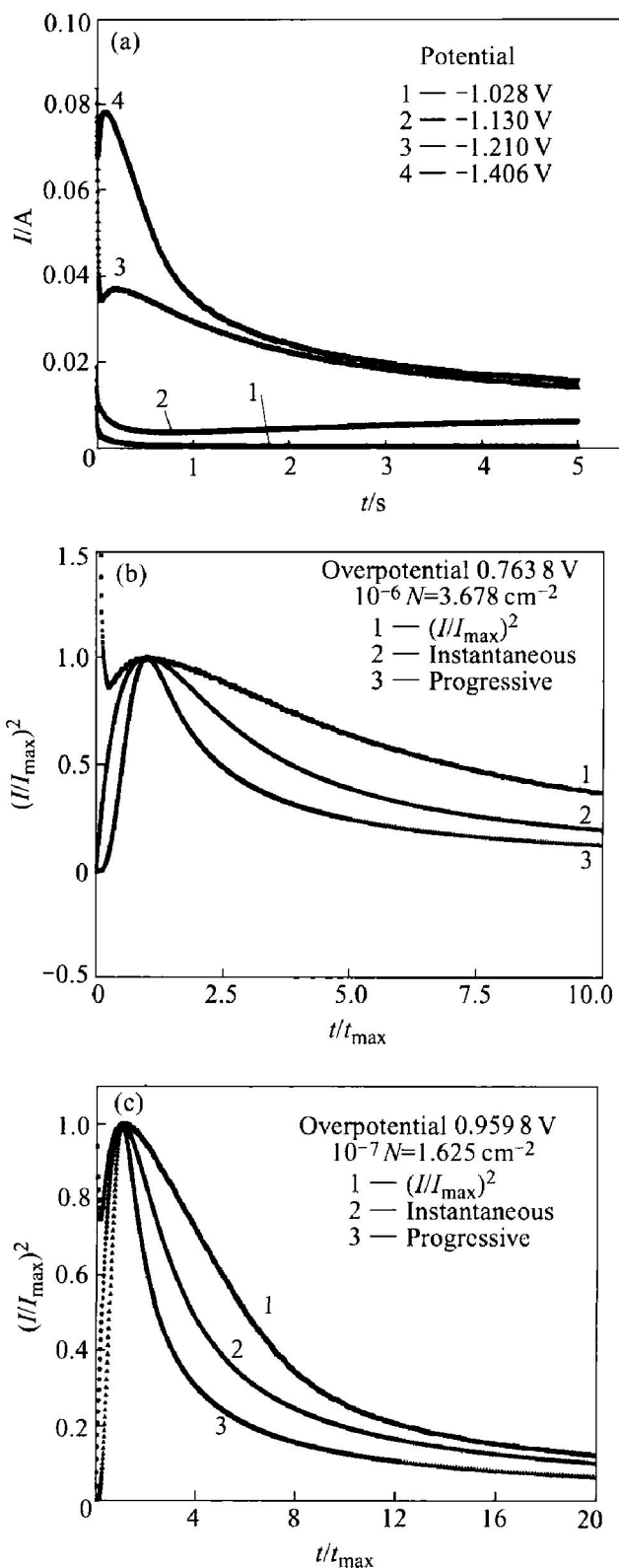

Fig. 5　Potentiostatic I –t transients(a) and non-dimensional I/I_{max} vs t/t_{max} plot for electrodeposition of zinc from electrolyte containing 30 g/ L ZnCl$_2$(b, c)

chemical double layer, a subsequently rising portion due to the nucleation process and a posterior decreasing portion due to the diffusion process. The rising section appears to reach its maximum in increasingly shorter time with more negative overpotential steps. The maximum in the current tran-
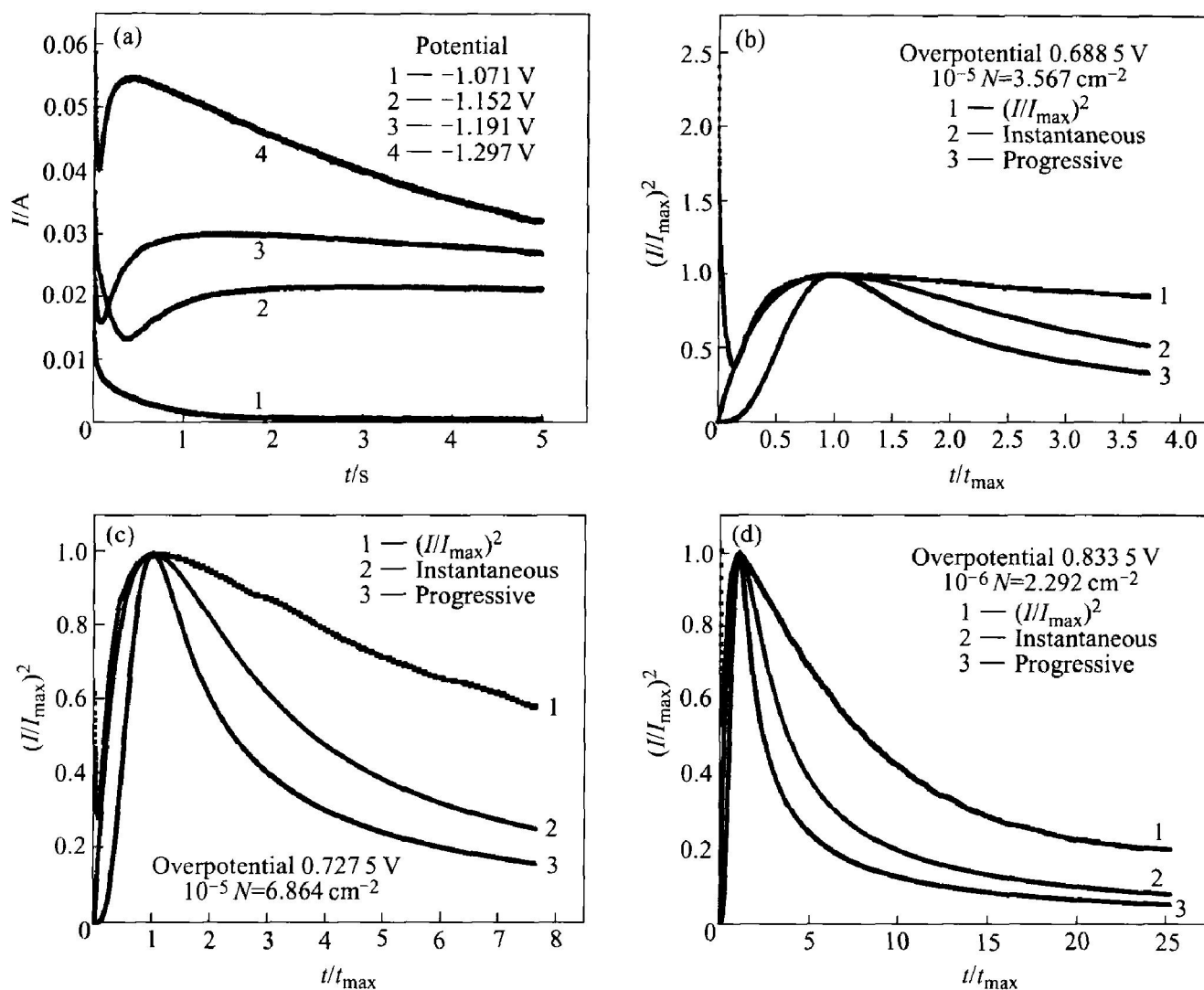
(a)

Potential
1 — -1.071 V
2 — -1.152 V
3 — -1.191 V
4 — -1.297 V

I/A

0.06
0.05
0.04
0.03
0.02
0.01
0

t/s

(b)

Overpotential 0.688 5 V
$10^{-5} N$=3.567 cm^{-2}
1 — $(I/I_{max})^2$
2 — Instantaneous
3 — Progressive

$(I/I_{max})^2$

2.5
2.0
1.5
1.0
0.5
0

t/t_{max}

(c)

1 — $(I/I_{max})^2$
2 — Instantaneous
3 — Progressive

$(I/I_{max})^2$

1.0
0.8
0.6
0.4
0.2
0

Overpotential 0.727 5 V
$10^{-5} N$=6.864 cm^{-2}

t/t_{max}

(d)

Overpotential 0.833 5 V
$10^{-6} N$=2.292 cm^{-2}
1 — $(I/I_{max})^2$
2 — Instantaneous
3 — Progressive

$(I/I_{max})^2$

1.0
0.8
0.6
0.4
0.2
0

t/t_{max}

Fig. 6   Potentiostatic $I \rightarrow t$ transients(a) and non-dimensional I/I_{max} vs t/t_{max} plot for electrodeposition of zinc from
electrolyte containing 60 g/L ZnCl$_2$(b, c, d)

sient at high overpotential and short time corre-sponds to the maximum surface area, i. e. the point at which hemi-spherical nuclei are on the point of collision. Meanwhile, it can also be seen that, in the case of high overpotentials, the experi-mental $I \rightarrow t$ curves follow closely the theoretic in-stantaneous nucleation curve. However, at low overpotential, no distinguished nucleation current is observed because the practical electrode sub-strate surfaces usually possess many defects such as plateau edges, kinks, vacancies and emergent screw dislocations, at which crystal growth can oc-cur without nucleation.

In order to clarify the influence of the concen-tration of zinc ions on the zinc electroplating process deeply and clearly, the nuclear densities (N) at different concentrations of zinc ions are cal-culated according to the theoretical Eqn. (5) [11-14] and illustrated in Figs. 5 - 7.

$$I_{max} = 0.638\ 2\ nDc(kN)^{1/2} \quad\quad (5)$$

With the comparison of Figs. 5 - 7, it can be

seen that the nuclear densities (N) increase with overpotential, and the overpotential for nucleation current obviously decreases with the increase of the concentration of zinc ions, which indicates that the zinc electroplating process in electrolyte solution containing less Zn^{2+} ions is mainly controlled by diffusion processes, which coincides with the above SEM results.

Because the rate-determining step of the zinc electroplating process is changed from diffusion process to activation reaction with the increase of zinc ions concentration, the structure of the electrodeposited zinc is changed from spongy to compact(Figs. 2 - 4), resulting in the positive drift of the major dissolution peak in cyclic voltammo-gram with the increase of zinc ions concentration (Fig. 1).

4   CONCLUSIONS

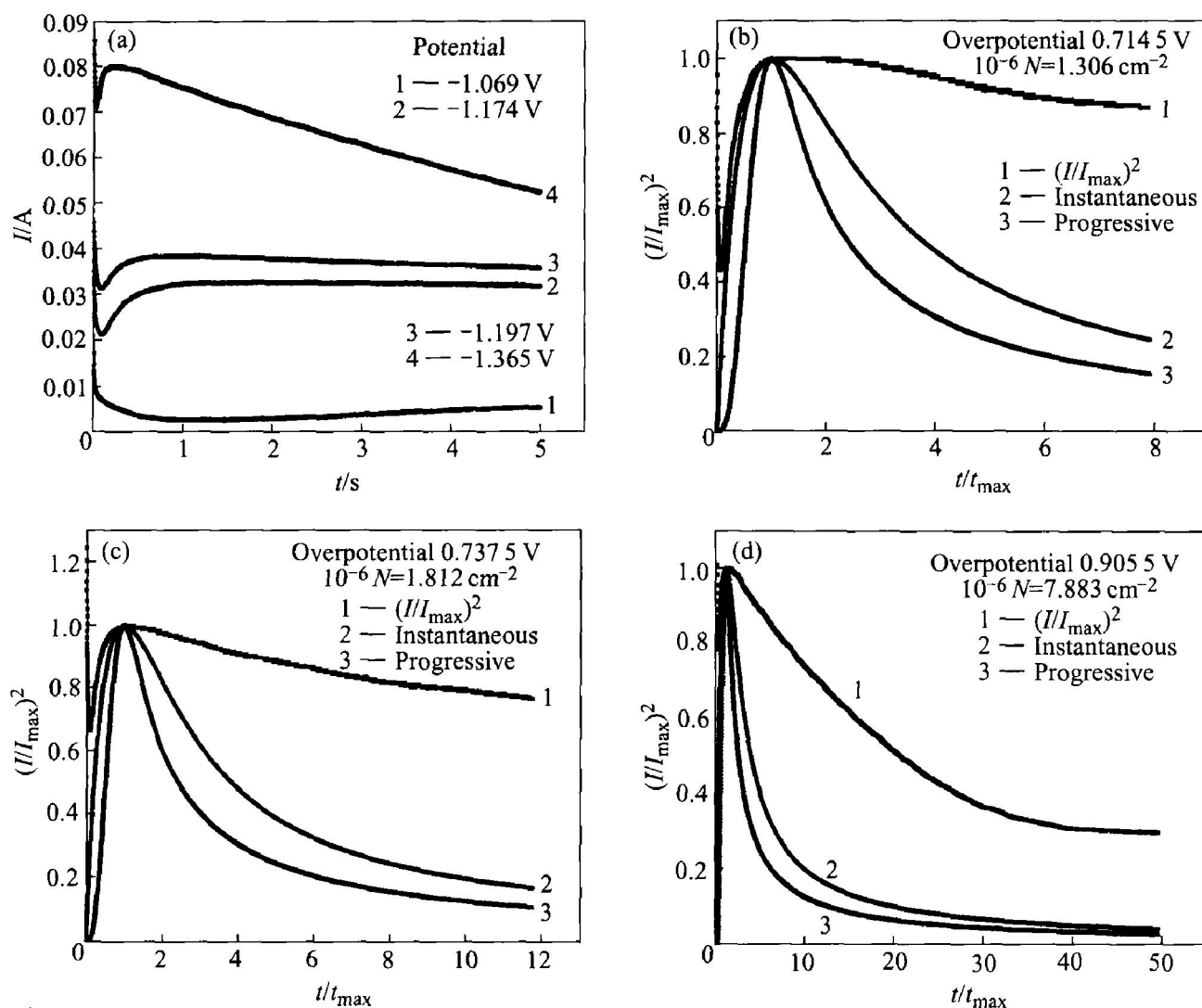1) Zinc electroplating processes are controlled

Fig. 7　Potentiostatic I —t transients(a) and non-dimensional I/I_{max} vs t/t_{max} plot for electrodeposition of zinc from electrolyte containing 90 g/L $ZnCl_2$(b, c, d)

by diffusion of Zn^{2+} ion from bulk solution to cathodic surface. However, SEM and chronoamperometric results clearly show that the rate determining step of zinc electroplating process changes from diffusion to the electrochemical reaction with the increase of Zn^{2+} ion concentration.

2) At high overpotentials, the nucleation of zinc is instantaneous, and the nuclear densities N increase with increase of the overpotentials. While at low overpotentials, the zinc electrodeposits may be preferentially formed at surface inhomogeneities such as emergence points of edge, screw dislocations, atomic disorder, kink sites, or monoatomic steps, and no distinguished nucleation current can be observed.

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