Electrodeposition and Twinning Structures of the Cadmium Dendrites in Aqueous Cadmium Chloride Solutions

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Abstract

The morphology and structures of cadmium dendrites electrodeposited from aqueous cadmium chloride solutions were investigated by means of a scanning electron microscopy and an X-ray diffractionmetry using transmission Laue photographs. The dendrites were electrodeposited on the polyhedral precursor formed after epitaxial growth. The time required for the formation of dendritic crystal became short along with an exponential increase in cathodic overvoltage as expected from the kinetics theorem of dendritic growth proposed by J'O'M. Bockris. All of the dendrites were reflection twins under all electrolytic conditions and they were classified into the following two types. The one had the $(0\ 1\ \bar{1}\ 2)$ co-plane as the twinning plane. This twin was a needle-like dendrite growing in the $\langle 1\ 0\ 0 \rangle$ direction and the crystal phase was the $(0\ 0\ 0\ 1)$ basal plane. The other had the $(\bar{1}\ 2\ \bar{1}\ 2)$ co-plane as the twinning plane. The whole shape of this crystal was sword-like and the striations formed with both the $(0\ 0\ 0\ 1)$ planes and the $(1\ 0\ \bar{1}\ 2)$ planes were seen symmetrically in reference to the $\langle 0\ \bar{1}\ 1 \rangle$ growth direction.

1 Introduction

P. B. Price et al. reported that the cadmium dendrites prepared from vapor phase were twinning crystal which agreed with the Coincident Site Lattice model¹⁾ (CSL model²⁾). T. Kobayashi reported similarly with respect to the snow crystal that the twinning occurred in the twelve-rayed crystals which made pairs of six-rayed crystals with a relative rotation of 70.3° on the basal plane³⁾. We also reported that the tin dendrites electrodeposited from stannous chloride solutions were rotating twins around the $\langle 1\ 0\ 0 \rangle$ co-axis according to the CSL model⁴⁾. The dendritic growth often seen by the electrolysis in aqueous solution has been hitherto interpreted by the T.P.R.E (Twinning Plane Re-entrant Edge) mechanism⁵⁾. As zinc belongs to the same crystal system as cadmium and snow crystal, it is expected that a zinc dendrite is also the similar twin. However the zinc dendrite electrodeposited from aqueous solution was a single crystal^{6), 7)}. The dendrite of a single crystal was found out in the electrocrystallization of lead and tin under particular electrolytic conditions⁴⁾. Therefore, the growth of dendrites can not be explained only by the T.P.R.E. mechanism. Then we interpreted the growth of the single crystalline lead dendrite by the mechanism of the continuous occurrence of two-dimensional nuclei⁸⁾. The purpose of the present paper is to examine the presence of the dendrite having the structures of the CSL model and the single crystalline dendrite. In addition, an attempt was made to clarify the relationships between the structures of dendrites and the electrolytic conditions such as the current density, the deposition time and the overvoltage.

2. Experimental

2.1 The electrodeposition of cadmium dendrites

In order to observe the occurring process of dendrites, the electrodeposition was carried out in a cylindrical cell on the polycrystalline cadmium disk cathode prepared by casting granular cadmium metal with the purity of 99.99% in a stream of argon. Before each electrodeposition, the cathode was polished by emery papers and by the buff immersed with a suspension of alumina particles of ca. $1\ \mu\text{m}$ in diameter. Furthermore, in order to obtain the

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cathode having a more flat surface, the electropolishing was carried out in 10% sulfamate solution with a pulse electrolysis using the square pulse wave (width 10ms, height: 2.5V). The electrode of the same material as that of the cathode and a saturated calomel electrode (SCE) were used for the anode and for the reference electrode, respectively. The electrodepositions were carried out under potentiostatic conditions in cadmium chloride solutions acidified by hydrochloric acid having the various composition. Since the cadmium dendrites obtained by this method were too small to examine the structure of dendrites, a conical platinum cathode with a working area of 0.26cm² was used in such cases. Prior to each electrodeposition, the electrodeposits on the cathode were dissolved with anodic polarization in 2M HCl solution. The instruments used for carrying out the electrolysis were a potentiostat (NICHIA, type NP-G1000E), a function generator (NICHIA, type K-3T) and an X-Y recorder (YOKOGAWA, type 3056).

2.2 Observation and X-ray diffractometry of cadmium dendrites

After the cadmium dendrites were washed subsequently with distilled water and pure ethanol, these dendrites were placed into a vacuum evaporator in order to remove the washings. The whole shapes of the dendrites were observed with a microscope (NIHON KOUGAKU, type SMZ) and a scanning electron microscope (SHIMAZU, type EMX-SM). The angle among the facets well-developed on the dendrites was measured with a gonio-microscope (Union KOUGAKU, type GM-5). The cross sections of some dendrites were polished by the method used for a standard metallographic practice. The etch figure of the cross section of cadmium dendrite was observed by a scanning electron microscope. The transmission Laue photographs of some dendrites were taken by an X-ray diffractometer (RIGAKU DENKI, type DS). A specimen was attached to an X-ray goniometer having a device for adjusting a crystal. This adjustment is based on two arc motions and one rotary motion. Until a high symmetric transmission Laue photograph was obtained, the position of the specimen was adjusted by the X-ray goniometer. The analysis of the Laue photographs was carried out by comparing these with the Laue patterns calculated by a personal computer (NEC, type PC-9801VM2). On the basis of the angle data obtained during the crystal adjustment, the determination of crystal orientation was carried out by using a stereographic projection technique on the Wulf net.

3 Results and Discussion

3.1 Dependence of overvoltage on the occurrence of dendrites

The only epitaxial growth occurred on the cadmium disk cathode at the initial stage of the electrodeposition under the potentiostatic condition. The epitaxial growth layers were formed by the electrodeposits inheriting an orientation of a crystal grain in the substrate

Fig.1 SEM photographs of the electrodeposits obtained on the polycrystalline cadmium disk cathode under the potentiostatic electrolysis in 2M CdCl₂ + 2M HCl solution.

- a) Epitaxial growth layer
- b) Needle-like dendrites electrodeposited on the polyhedral precursors

of the disk cathode (Fig.1a). At the next stage, the polyhedra formed mainly by the (0001) basal planes were electrodeposited on the epitaxial growth layers. The grain boundary of polycrystalline substrate disappeared and the needle-like dendrites were electrodeposited on the polyhedra at the final stage (Fig.1b).

Therefore, it can be presumed that the polyhedra are regarded as the precursors for the dendritic growth. The current density increased linearly with to the electrolytic time when the epitaxial growth and/or the formation of the polyhedron occurred mainly. When only the dendritic growth occurred, the current density increased linearly with the square of the electrolytic time. The inducement time (τ) for the occurrence of the dendrites corresponded to the time required for the formation of precursors. The $\log(\tau)$ decreased linearly with an increase in the cathodic overvoltage, and the dendritic growth occurred in a shorter time with an increase in the concentration of cadmium chloride as shown in Fig.2. The following equation was derived from the Bockris's theorem⁹⁾ on the kinetics of dendritic growth under the potentiostatic condition.

$$\ln(\tau) = \ln(K) + (\alpha F/RT)\eta$$

where α is a transfer coefficient, η is cathodic overvoltage, K is a constant, and other variables have an ordinary meaning. The transfer coefficient α calculated from slopes of these straight lines was in the range from 0.4 to 0.8. As these values were smaller than one, it was presumed that the dependence of overvoltage on the inducement time for the occurrence of dendrites followed the kinetics of a dendritic growth.

3.2 Relationship between morphology of dendrites and electrolytic conditions

The shape of the cadmium dendrites was confined to be needle-like and sword-like. The dendrite which was made of the hexagonal platelet, as reported by Price¹⁾, was not observed.

Fig.2 Dependence of the overvoltage on the inducement time (τ) for the occurrence of cadmium dendrites during the potentiostatic electrolysis on the polycrystalline cadmium disk cathode.

Δ : 0.25M CdCl₂ + 1M HCl
 $\circ$: 1M CdCl₂ + 2M HCl
 $\square$: 4M CdCl₂ + 2M HCl

Fig.3 SEM photographs of the typical morphology of the cadmium dendrites electrodeposited in the cadmium chloride solutions acidified by hydrochloric acid.

a) Surface structure of the sword-like dendrite
 b) Needle-like dendrites

The morphology of cadmium dendrites changed from sword-like to needle-like with the passage of electrolytic time. The needle-like dendrites were electrodeposited at the lower current density compared with the case for the deposition of sword-like dendrites. Consequently, as the current density was lower at the center of the disk cathode than near the periphery for the sake of the first order current distribution, two kinds of dendrites were observed simultaneously. Also, the dendrites became fine with an increase in overvoltage. Although the use of a disk cathode was favorable to observe the occurring process of the dendrites, the cadmium dendrites were too small to examine the structure of dendrites and it was difficult to form only a kind of dendrite. This problem could be solved by the use of a conical cathode. Since most of the total current concentrated on the top of the cathode according to the secondary current distribution, the area of the dendritic growth may be restricted to such a place. Figure 3 shows the needle-like dendrites and the surface structure of the sword-like dendrite electrodeposited on the conical platinum cathode. Table 1 shows the morphology of cadmium dendrites electrodeposited on the conical platinum cathode during the galvanostatic electrolysis for 1h. It was found that the morphology of the cadmium dendrites changed from sword-like to needle-like with an increase in the concentration of cadmium chloride.

Table 1 morphology of cadmium dendrites electrodeposited on the conical platinum cathode during galvanostatic electrolysis in various cadmium chloride solutions acidified by 2M HCl.

Concentration of CdCl ₂ (M)	Current density (mA/cm ²)	Morphology of dendrite
1	54.1	Sword
	135	Sword
	243	Sword
2	54.1	***
	108	Needle
	243	Needle
3	54.1	***
	108	***
	216	Needle
	243	Needle

Electrolytic time: 1h

*** : No appearance of dendrite

3.3 Structures of cadmium dendrites

3.3.1 Structure of sword-like dendrite

The ridge-valley structures on the surface of the sword-like dendrite looked symmetrical with respect to the striation elongated to the growth direction of the dendrite as shown in Fig.3a. The edge of the ridge-valley intersected the striation by the angle of 60°. From this morphology, it was obviously presumed that the sword-like dendrite was a reflection twinning crystal rather than a rotating twinning crystal as reported by Price¹⁾. It was found by the goniomicroscopy that the angle among the elongated facets observed on the sword-like dendrite was about 49°. The angle between the (0001) plane and the (1012) plane calculated from the values of the lattice parameter ($a=2.9793\text{\AA}$, $c=5.6181\text{\AA}$) was 47.4°. As this calculated angle was approximately equal to the observation value mentioned above, the ridge-valley structure was considered to be formed by the (0001) plane and the (1012) plane. Figure 4 shows the Laue photographs obtained from the sword-like dendrites by the X-ray radiation toward the well developed crystal planes placed at the position on which the growth direction of the sword-like dendrite was set upward. The Laue photograph shown in Fig.4a was obtained from the left side and the one shown in Fig.4b was obtained from the right side, respectively. The Laue photograph shown in Fig.4c was obtained from the center part and this Laue pattern coincided with the pattern obtained by overlapping Fig.4a and Fig.4b. From this result, it was confirmed that the sword-like dendrite was a twinning crystal. The crystal position on which the photographs of Fig.5 were taken was adjusted by the X-ray goniometer until a high symmetric transmission Laue photograph was obtained. The Laue photograph (Fig.5a) taken after the adjustment completely agreed with the theoretical patterns (Fig. 5b) calculated for the (1010) plane of a cadmium single crystal. A stereographic projection on the (1010) plane was made by using the angle data of the X-ray goniometer. Figure 6 shows the pole figure of crystal planes calculated by a personal computer on the assumption that the sword-like dendrite was the

Fig.4 Transmission Laue photographs taken by an X-ray radiation perpendicular to the well developed crystal plane of the sword-like cadmium dendrite.

- a) Left side with respect to the twin boundary
- b) Right side with respect to the twin boundary
- c) Center part including the twin boundary

a)

b)

Fig.5 Comparison of the laue photograph taken for the sword-like dendrite with the calculated Laue pattern.

- a) The transmission laue photograph obtained on the $(10\bar{1}0)$ plane after the crystal position was moved by an X-ray goniometer
- b) A theoretical transmission laue pattern calculated on the $(10\bar{1}0)$ plane of the cadmium single crystal and the arrows indicating the azimuth on the $(10\bar{1}0)$ plane

Fig. 6 Stereogram on the sword-like dendrite having the $(\bar{1}2\bar{1}2)$ twinning plane with the stereographic projection plane parallel to the well developed crystal facet. The orientation of twin is indicated by the symbol of an accent.

Fig. 7 The atomic arrangement on the $(10\bar{1}0)$ plane perpendicular to the twinning plane of the sword-like dendrite and the atomic gliding motion required to form a reflection twin. The dashed circles indicate the atoms before a gliding motion.

reflection twinning crystal with respect to the $(\bar{1}2\bar{1}2)$ plane. The inclination angle of the ridge to the twinning line was 63° and this angle agreed with the observation angle measured with a goniomicroscope. It was confirmed from this result that the sword-like dendrite was the reflection twinning crystal with respect to the $(\bar{1}2\bar{1}2)$ plane and that the growth direction was toward the $\langle 011 \rangle$ direction. Figure 7 shows the atomic arrangement on the $(10\bar{1}0)$ plane perpendicular to the twinning plane. If the reflection symmetry with regard to the $(\bar{1}2\bar{1}2)$ plane appeared in the atomic arrangement around the twin boundary, atoms should glide to the $\langle 01\bar{1} \rangle$ direction as shown in Fig. 7. Generally speaking, this gliding motion of atoms is caused by the deformation of crystal. In the case of an electrocrystallization, it is presumed that this phenomenon occurred by the stress of the strains when the adatoms were present in excess on the electrode surface. It is considered that such a phenomenon is apt to occur at a place where a local current density is greatly enhanced, such as a tip of the dendrite.

3.3.2 Structure of needle-like dendrite

The needle-like dendrite shown in Fig. 3b was made of two flat crystal facets and the shape of its cross section perpendicular to the growth direction was like a letter of "L". It was observed by the goniomicroscopy that the angle between the two flat facets was 87° . The Laue photograph shown in Fig. 8a was obtained from the flat facets. This pattern agreed with the theoretical transmission Laue pattern (Fig. 8b) calculated on the basis of the assumption that the X-ray was radiated perpendicular to the (0001) basal plane. It was determined from this result that the well developed crystal facet was the (0001) plane. Furthermore, the twinning line was observed on the cross section of the needle-like dendrite. It is well known that the deformed twinning crystal is the reflection twin in regard to the $(01\bar{1}2)$ plane¹⁰⁾. Then, Fig. 9 and Fig. 10 show the stereographic projection which coincided with the relationship between the twinning mentioned above and the atomic arrangement on the $(2\bar{1}\bar{1}0)$ plane perpendicular to the $(01\bar{1}2)$ twinning plane, respectively. The angle

Fig.8 A comparison of the Laue photograph obtained for the needle-like dendrite with the calculated Laue pattern.

- a) The transmission Laue photograph taken by an X-ray radiation perpendicular to the well developed facet of the needle-like dendrite.
 b) A theoretical transmission Laue pattern calculated on the (0001) plane of the cadmium single crystal and the arrows indicating the azimuth on the (0001) plane.

Fig.9 Stereogram on the needle-like dendrite having the $(01\bar{1}2)$ twinning plane with the stereographic projection plane perpendicular to the growth direction of the dendrite. The orientation of twin is indicated by symbols with an accent.

Fig.10 The atomic arrangement on the $(2\bar{1}\bar{1}0)$ plane perpendicular to the twinning plane of the needle-like dendrite and the atomic gliding motion required to form a reflection twin. The dashed circles indicate the atoms before a gliding motion.

between the two (0001) planes calculated by using a matrix of the twinning transformation was 81° and this value agreed with an angle between the two facets determined as the (0001) basal plane by the Laue photographs. It was confirmed from these results that the needle-like dendrite was the reflection twinning crystal with respect to the $(01\bar{1}2)$ plane and the growth direction was toward the $\langle 100 \rangle$ direction. In this case, the direction of atomic gliding motion was toward the $\langle 12\bar{1} \rangle$ direction.

Conclusions

- 1) The inducement time was required to bring about the dendritic growth and it became shorter with an exponential increase in cathodic overvoltage according to the dendritic growth theorem derived from Bockris et al.
- 2) The twinning crystal which coincided with the CSL model was not found in the cadmium dendrites electrodeposited from the aqueous cadmium chloride solution acidified by hydrochloric acid.
- 3) The typical morphology of cadmium dendrites was classified into the needle-like crystal and the sword-like crystal. The former was the reflection twinning crystal with respect to the $(\bar{1}2\bar{1}2)$ plane and developed toward the $\langle 100 \rangle$ direction. Similarly, the latter was the reflection twinning crystal with respect to the $(\bar{1}2\bar{1}2)$ plane and developed toward the $\langle 0\bar{1}1 \rangle$ direction.
- 4) As the twinning structure agreed very closely with that of the deformation twinning, the origin of the twin was considered to be due to the strain with a stress induced during the electrodeposition.

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