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Citation: The Journal of Chemical Physics **27**, 1349 (1957); doi: 10.1063/1.1744006 View online: http://dx.doi.org/10.1063/1.1744006 View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/27/6?ver=pdfcov Published by the AIP Publishing

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Crystal Growth of Silver Metal. Mechanism and Kinetics

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The crystal growth of silver-metal whiskers and "ferns" occurring in the reduction of Ag(I) with Fe(II)from aqueous perchlorate solution was directly observed under the microscope. Whiskers frequently grew at well-defined angles to the previous direction and occasionally stopped growing abruptly although nearby whiskers continued to grow. In fern growth, short spikes grew in a regular manner from only one side of a parallel-sided main stem. Linear growth rates of whiskers were essentially independent of an estimated eightfold variation in supersaturation, but the growth rate of a whisker occasionally increased abruptly in approximately integral ratios. Whisker and fern growth are qualitatively attributed to perfect and twinned screw dislocations, respectively, but no explanation is offered for the formation of whisker and fern habits. It is shown that an interpretation of growth habit will require the Burton, Cabrera, and Frank treatment of infinite surfaces to be extended to the edges and corners of a crystal. Limited kinetic data suggest that the size of the critical surface nucleus was independent of supersaturation, which is contrary to the classical theory of crystal growth. A possible explanation for constant-sized critical surface nuclei is offered.

INTRODUCTION

HEORIES of the mechanism of crystal growth can be divided into surface nucleation and dislocation viewpoints. The classical nucleation mechanism¹ proposes that fresh layers of atoms deposit on a closepacked crystal surface by the slow formation of a twodimensional nucleus and the rapid lateral growth of the nucleus to the edges of the surface. The dislocation mechanism, suggested by Frank² and extended by Burton, Cabrera, and Frank³ (BCF), proposes that deposition occurs at the self-perpetuating surface steps caused by a screw dislocation emerging from the crystal surface.

Experimental studies of the kinetics of crystal growth indicate that most crystals are imperfect and grow by a dislocation mechanism.3 Observations of spiral growth patterns⁴ and abrupt changes in growth rates^{5,6} appear to be direct evidence for a dislocation mechanism. Sears⁷ attributed the formation of a whisker habit at low supersaturation to a crystal having a screw dislocation in a single direction, i.e., one surface is screwdislocated and the lateral surfaces are perfect, closepacked surfaces.

This paper presents experimental observations of the whisker and "fern" growth of silver-metal crystals. Whisker and fern growth are qualitatively attributed to different types of dislocation mechanisms. However, a quantitative interpretation of these growth habits will require the BCF treatment of the equilibrium behavior

- ² F. C. Frank, Discussions Faraday Soc. 5, 48 (1949). ³ Burton, Cabrera, and Frank, Trans. Roy. Soc. (London) A243, 299 (1951).
- 4 A. R. Verma, Crystal Growth and Dislocations (Academic Press, Inc., New York, 1953). ⁵ C. W. Bunn, Discussions Faraday Soc. 5, 132 (1949).
- ⁶G. C. Krueger and C. W. Miller, J. Chem. Phys. 21, 2018 (1953)
- ⁷G. W. Sears, Acta Met. 3, 361 (1955).

of crystal surfaces to be extended to the edges and corners of a crystal. Limited kinetic results suggest that the critical surface nucleus has a constant size independent of supersaturation.

BCF THEORY

Since the present results will be compared with the BCF theory of crystal growth, the BCF theory will be reviewed briefly. Recent reviews were also given by Vermilyea⁸ and Hirth and Pound.⁹

For an infinite vapor-solid interface, BCF showed that a surface step contains an appreciable equilibrium concentration of kinks but that a fully grown, closepacked surface is atomically smooth at ordinary temperatures. Therefore, with perfect crystals a stepped surface would readily grow at low supersaturation to form close-packed surfaces, but a close-packed surface would grow only at high supersaturation by a nucleation mechanism. With an imperfect crystal, the screw-dislocated surface would continue to grow at low supersaturation because the surface step is self-perpetuating.

The linear rate of growth of a dislocated surface is given by the number of surface steps passing a given point per unit time multiplied by the step height. With moderate supersaturation the dislocation step develops into a spiral, and BCF showed that the steady state rate of growth of a dislocated surface, \mathbf{R}_{BCF} , is given by

$$\mathbf{R}_{\mathrm{BCF}} = \frac{\mathbf{H}}{4\pi (1 + 3^{-\frac{1}{2}})\rho_c} \cdot \mathbf{h} \cdot \mathbf{v}, \qquad (1)$$

where **H** is the dislocation "strength" of the surface, ρ_c is the radius of the critical surface nucleus, **h** is the step height, and v is the rate of advance of the step across the surface.

H arises from the interaction of dislocations on a

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ginia. ¹W. Volmer, *Kinetik der Phasenbildung* (T. Steinkopf, Dresden and Leipzig, 1939). ¹D. C. Frenk, Discussions Faraday Soc. 5, 48 (1949).

⁸ D. A. Vermilyea, J. Chem. Phys. 25, 1254 (1956). ⁹ J. P. Hirth and G. M. Pound, J. Chem. Phys. 26, 1216 (1957).

dislocated surface.¹⁰ Crudely, **H** is essentially equal to one with a singly dislocated surface or with a multiply dislocated surface if the dislocations are greater than $2\rho_c$ apart, for all of these surfaces possess roughly the same step density although the configurations of the steps on the surface will vary. However, if two (or more) dislocations of similar type are closer together than $2\rho_c$, they produce a pair of nonintersecting growth spirals and **H** will equal two. Therefore, **H** is essentially a small integer.

Following nucleation theory, BCF assumed that the free energy of formation of a circular monolayer nucleus is given by

$$\Delta F = 2\pi\rho\gamma - \pi\rho^2 k \mathbf{T} \ln\alpha, \qquad (2)$$

where ρ is the radius of the nucleus, γ is the macroscopic surface free energy of the interface, k is the Boltzmann constant, **T** is absolute temperature, and α is the supersaturation ratio. Maximizing ΔF with respect to ρ gives a critical radius of

$$\rho_c = \frac{\gamma}{k \Gamma \ln \alpha},\tag{3}$$

where ρ_c is the radius of the surface nucleus which has the maximum free energy for the given supersaturation. Substituting Eq. (3) in Eq. (1) gives

$$\mathbf{R}_{\mathrm{BCF}} = \frac{\mathbf{Hh}k\mathbf{T}}{4\pi(1+3^{-\frac{1}{2}})} \cdot \frac{1}{\gamma} \cdot \ln\alpha \cdot \mathbf{v}. \tag{4}$$

The rate of advance of the surface step depends upon the kinetics of the sequence of transport and chemical reactions involved in crystal growth. BCF discussed several alternatives for these kinetics.

Frank ¹⁰ also noted that a dislocated surface would grow only if the distance on the dislocated surface between the emerging dislocation line and the edge of the crystal is greater than $2\rho_c$. If this distance is equal to $2\rho_c$ the dislocated surface stops growing.

EXPERIMENTAL

The dendritic crystal growth of silver metal occurring during the chemical reduction of Ag(I) with Fe(II)from aqueous perchlorate solution was directly observed with the optical microscope at ambient conditions. The chemical reaction was

$$\operatorname{Ag}(I) + \operatorname{Fe}(II) = \operatorname{Ag}^{\circ} + \operatorname{Fe}(III).$$

Runs were made by mixing Ag(I) and Fe(II)perchlorate stock solutions in a 10-ml test tube. Polyhedral silver-metal particles formed in the test tube over several hours. Microscopic examination of a typical sample of the reacting mixture at first showed triangular and hexagonal metal platelets whose sizes ranged from 1 to 20μ . However, in 30% of the microscope slide samples whisker and "fern" types of crystal growth began after an induction period in the slide mount varying from 2 min to 4 hr with increasingly dilute reagent solutions. Although growth on the glass surfaces of the slide occurred occasionally, only growth from the bulk solution, as evidenced by observation of particles both above and below the dendrite, is reported. Ordinary microscope slides and cover glasses were used. The microscope slide temperature corresponded to ambient temperature. Dendrites did not grow in a test tube kept at ambient temperature but did grow in a test tube when the reacting mixture was heated to 50°C.

Linear growth rates of whiskers were measured in the slide mount with an eyepiece micrometer and stop watch. Reagent concentrations in a slide mount during the growth of dendrites were crudely estimated by comparison of initial reagent concentrations with numbers and sizes of metal crystals in the slide. Size and number counts were made from four photographs of the slide taken within eight minutes after the growth rate was measured. All metal crystals in a photograph were counted and their silhouette sizes measured. Volume of metal was calculated assuming whiskers and ferns to have circular cross sections and platelets to have thicknesses of 2μ except when actually measured with the vertical scale on the microscope. Height of liquid in the slide mount was measured with the vertical scale and was usually about 40μ . Error in the change in concentration (i.e., initial concentration minus the calculated concentration) was estimated to be less than 20%. A Polaroid Land Camera was used for photomicrography.

Whisker and fern growth were observed using variously prepared reagents with initial concentrations of 0.07-0.7M AgClO₄, 0.05-0.5M Fe(ClO₄)₂, < 0.02-0.1M $Fe(ClO_4)_3$, and 0.05–0.5M HClO₄, but they were not observed using lower initial Ag(I) or Fe(II) concentrations. Dendrites were not observed using sulfate solutions. Silver-perchlorate stock solutions were prepared by dissolving commercial Ag₂CO₃, freshly prepared or commercial Ag₂O, and commercial AgClO₄ in dilute HClO₄. Ferrous perchlorate solutions were prepared by dissolving commercial $Fe(ClO_4)_2$ in dilute $HClO_4$ and by metathetical synthesis using ferrous sulfate solution containing HClO₄ and barium perchlorate solution with 10% molar excess of barium ion. Reagent grade chemicals and distilled water were used. Analyses used Mohr's method for Ag(I), potentiometric titration with Cr_2O_7 for Fe(II), and potentiometric titration with Sn(II) for Fe(III). Analysis of Fe(III) concentrations less than 0.02 molar was unsatisfactory, but lack of time prevented further work on this important aspect.

The equilibrium for the reaction was briefly studied in aqueous perchlorate solution at ambient temperature. In four runs equal volumes of 1.4M Ag(I) and 1.0MFe(II) perchlorate stock solutions were mixed in an Erlenmeyer flask. Two runs were made approaching the equilibrium from the reverse side by using 0.4M Fe(III)

¹⁰ F. C. Frank, Z. Elektrochem. 56, 429 (1952).

perchlorate solution and Ag-metal particles from the above work. Periodic samples were filtered through a sintered glass funnel, the filter washed, and the filtrate plus wash water analyzed. Results corresponded to

$$\mathbf{K}_{c} = \frac{\left[\operatorname{Ag}(I)\right]\left[\operatorname{Fe}(II)\right]}{\left[\operatorname{Fe}(III)\right]} = 0.11 \pm 0.02,$$

where brackets indicate molar concentrations. The present work used a salt concentration considerably greater than previous studies of the equilibrium constant.^{11,12}

RESULTS

Whiskers (Fig. 1) grew to over 1000μ in length with parallel sides (at $1940 \times$ magnification), unknown cross sections, and widths usually between 0.4 and 1.5μ . Growth on the lateral surfaces of a whisker was never observed. A whisker stopped growing by either (a) abruptly stopping although nearby whiskers continued



FIG. 1. Silver-metal whiskers grown by the reduction of Ag(I) with Fe(II) from aqueous solution. The whisker entering the microscope field at the left grew from left to right before angling. Original magnification of 1940× increased to 2200× in reproduction.

growing, (b) forming either a "fern" or a hexagonal platelet at its tip, or (c) hitting a glass surface and stopping. Whiskers grew with either a triangular-tip silhouette or an apparently flat tip perpendicular to the whisker axis. A growing whisker frequently changed its direction of growth abruptly, and its width appeared to remain unchanged during angling. A typical whisker went through the focal plane of the microscope, but forty angles occurring in the focal plane were distributed as seven of 30°, twenty one of 60°, four of 70°, and eight of $120^{\circ}\pm5^{\circ}$, where the angle was measured between the new direction and the extension of the old direction.

Fern growth (Figs. 2 and 3) consisted of short spikes growing at regular angles from only one side of a main stem. The stem had parallel sides, was between 0.5 and 1μ wide, and grew with a plane tip perpendicular to the stem axis. Cross sections were unknown. A spike often



FIG. 2. Silver metal fern. Direction of growth was left to right. Note the reversal of spiked growth when the main stem angled. Original magnification of $1940 \times$ increased to $2200 \times$ in reproduction.

"presumed the responsibility" for further stem growth, the hitherto stem then becoming a spike. Spikes then continued to grow from the new stem but only from the side opposite to previous spike growth. This reversal was repeated over five times on four ferns.

Angled growth of whiskers allowed only intermittent rate measurements which were treated as mean linear growth rates for the periods when rates were measured. Growth rates of a typical whisker are given in Fig. 4. Two hundred growth rates measured on 35 whiskers from 15 slide mounts were almost uniformly distributed from 0.3 to 1 μ /sec. There was no correlation between the growth rate of a whisker and angling, the whisker width or length, exposure to artificial or natural light, initial reagent concentrations, or reagent preparation. As noted in Table I, six whiskers had roughly similar growth rates despite a tenfold variation in actual reagent concentrations as estimated by the counting technique. These similar growth rates were observed despite a twenty-fold variation in J_c/K_c and an eightfold variation in $\ln(\mathbf{J}_c/\mathbf{K}_c)$, where $\mathbf{J}_c = \lceil \operatorname{Ag}(I) \rceil \lceil \operatorname{Fe}(II) \rceil / \lceil \operatorname{Fe}(III) \rceil$ with concentrations being those actually in the slide mount and J_c/K_c is the supersaturation ratio. Ten fern stems grew with rates distributed within the range observed for whiskers. Error in rate measurement was estimated to be less than 10%.

DISCUSSION

A. Mechanism

1. Dislocation Mechanisms

With whisker growth, abrupt stoppage of growth and discontinuous growth rates can be readily explained assuming a dislocation mechanism with an axial screw dislocation emerging at the whisker tip.



¹¹ A. A. Noyes and F. F. Brann, J. Am. Chem. Soc. **34**, 1016 (1912).

¹² E. J. Shaw and M. E. Hyde, J. Chem. Educ. 8, 2065 (1931).

Initial concentration m/l Ag(I) Fe(II) Fe(III)			Estimated concentration* m/l Ag(I) Fe(II) Fe(III)			Ta	Ie/Ke	ln(Ic/Kc)	Observed growth rate µ/sec
0.70	0.50	0.02 ^b	0.65 0.63 0.35	0.45 0.43 0.15	0.07 0.09 0.37	4.2 3.0 0.14	38 27 1 3	3.64 3.30 0.26	0.37 0.51 0.67
0.70 0.070 0.070	0.50 0.50 0.050	0.10 0.02ь (0.002)	0.39 0.023 0.060	0.19 0.45 0.040	0.41 0.067 0.01	0.14 0.18 0.15 0.24	1.3 1.7 1.4	0.53 0.34	0.56 0.41 0.39

TABLE I. Whisker growth rates.

Estimated by counting technique.
 ^b Maximum concentration.

The abrupt stoppage of growth of a whisker despite the continued growth of nearby whiskers indicates the accidental poisoning of a single dislocation source at a whisker tip by the adsorption of one or several impurity molecules.¹³ If whiskers grew by a nucleation mechanism at the tip, the high concentration of impurity required to poison the entire tip should also affect the growth rate of a nearby whisker.

The growth rate of a dislocated surface could, by its dependence upon **H** (Eq. 1), vary abruptly by integral ratios. The intermittent kinetic data in the present work are only suggestive, but the fifteen observed increases in growth rates of whiskers could all be interpreted within the experimental error as either abrupt twofold or $\frac{3}{2}$ increases, suggesting singly, doubly, and triply dislocated whiskers. In Fig. 4 the first increase suggests an abrupt twofold increase. The second increase could be interpreted as either an abrupt twofold or $\frac{3}{2}$ increase although a $\frac{3}{2}$ increase would indicate that the whisker initially had a single dislocation but gained a second and third dislocation.

The growth of a whisker habit also suggests a dislocation mechanism, with an axial screw dislocation and perfect lateral surfaces.⁷

Fern growth implies that the stem contains an axial screw dislocation plus a self-perpetuating edge disloca-



FIG. 4. Variation in the linear growth rate of a whisker. Horizontal lines indicate experimental data. Angled growth is noted by \angle .

tion along one lateral surface. A mechanism for fern growth in contrast to whisker growth might be the formation of a twinned rather than perfect screw dislocation. With a face-centered cubic material such as silver metal, a dislocation line in the $\langle 110 \rangle$ direction can result in either a perfect or a mirror-twinned lattice orientation across two parallel {111} planes.² A surface having a perfect screw dislocation can grow perpendicular to itself with perfect lateral surfaces [Fig. 5(a)], which presumably corresponds to whisker growth. However, a twinned screw dislocation always leads to a twinned edge dislocation in an adjacent lateral surface [Fig. 5(b)].

The surface steps from both the twinned screw and the twinned edge dislocations will behave in a similar manner and are self-perpetuating to a degree. An atom depositing at a kink on either the top or lateral surface makes 5 and 7 bonds in alternate layers of atoms at the twinned row and 6 bonds in the following rows, as compared with 6 bonds for a perfect dislocation. Deposition at the twinned rows will require a moderate supersaturation or a time delay for statistical fluctuation at the twinned row.² Therefore, with a twinned dislocation and sufficient supersaturation the screw-dislocated surface and the lateral edge-dislocated surface would both grow, and a crystal with a twinned screw dislocation would grow like a whisker and also grow on one side—which corresponds to fern growth.

2. Dislocation Directions

In the literature $\langle 110 \rangle^{14,15}$ and $\langle 211 \rangle^{15}$ directions are reported for silver-metal dendrites.

In the present work, direct attempts to identify whisker axes by x-ray diffraction techniques were unsuccessful. Electron diffraction in the electron microscope was not attempted because previous experience indicated that metal whiskers of this size melted in the electron beam. However, when a whisker degenerated into a hexagonal platelet, the whisker was essentially coplanar with the large {111} surface and joined to a

¹³ F. C. Frank, Discussions Faraday Soc. 5, 189 (1949).

¹⁴ J. H. Howey, Phys. Rev. 55, 578 (1939); S. Tsuboi, Mem. Coll. Sci. Kyoto Imp. Univ. 11, 271 (1928) (Chem Abstr. 23, 2083).

¹⁵ Schenck, Fricke, and Brinkmann, Z. physik. Chem. A139, 32 (1928).

vertex. In two cases the whisker was collinear with the platelet "diameter" and in three cases it was collinear with an adjacent platelet side. This orientation corresponds to a (110)-directed whisker with no lattice disorder across the juncture. (In five cases the whisker ended at the center of the platelet.)

A (110)-directed whisker (i.e., a perfect (110) dislocation) which angled with perfect crystal orientation in a different (110) direction would account for the observed 60° and 120° whisker angles. A 90° whisker angle also is permitted but was not observed. A $\langle 110 \rangle$ -directed whisker which twinned during angling would give 33° and 71° angles and would account for the 30° and 70° whisker angles.

A twinned (110) dislocation which twinned during angling could again give 33° and 71° angles and would account for the observed 30° angle between stems in fern growth.

3. Growth Habit

In the present section we reconsider the earlier suggestion that a whisker habit occurs because one surface of a crystal has a perfect screw dislocation and the lateral surfaces are perfect, close-packed surfaces.

With a face-centered cubic material such as silver metal the close-packed surfaces are $\{100\}$ and $\{111\}$ surfaces. For the present solution-solid interface, a close-packed surface may be atomically rough at equilibrium because of hydration energies.⁸ If the equilibrium surface is rough an atom could deposit at any point on the surface. However, we conclude later that the rate-controlling reaction in whisker growth is a surface reaction which depends upon the number of surface steps at the whisker tip. This in turn implies that the close-packed surface at the tip is actually atomically smooth under the present experimental conditions, although it is uncertain whether {100} and {111} surfaces are both smooth or whether only one type of surface is smooth.

Close-packed lateral surfaces for (110)-directed silver





whiskers could be {111} or {111} plus {100} surfaces.† Consider a silver-metal crystal with a perfect dislocation on the {111} surface and with perfect {111} and {100} lateral surfaces [Fig. 5(a)]. For whisker growth to occur, the new layers of atoms must grow across the dislocated surface to continue the original lateral surfaces. However, a new layer of atoms will first form embryonic low index surfaces one-atom-layer wide at several of the edges, and the original lateral surfaces are continued only if the edge rows of atoms are deposited. With the example given in Fig. 5(a) a new layer first forms a $\{100\}$ surface at the $\{111\}-\{111\}$ edge marked A, a $\{111\}$ surface at the $\{111\}-\{010\}$ edge marked B, and a $\{001\}$ surface at the $\{111\}-\{11\overline{1}\}$ edge marked C.

The edges and corners of an actual crystal will be rounded with an equilibrium curvation of ρ_c , and the corresponding surface steps will be kinked. Whether the new layer stops at the embryonic surface at an edge or over-runs it and continues the original lateral surface, thereby permitting whisker growth, will depend upon (a) the comparative equilibrium stabilities of embryonic and completed edges under the given experimental conditions and (b) any kinetic problems in the formation of the equilibrium edge. An appreciable delay in overrunning an embryonic edge would soon lead to the formation of a well-defined, perfect, close-packed surface which, if smooth under the experimental conditions, would grow only at high supersaturation by a nucleation mechanism.

Therefore, an interpretation of growth habit first requires the BCF treatment of the equilibrium behavior of infinite surfaces to be extended to edges and corners, and it is not immediately obvious that the whisker growth of a face-centered cubic material is due to the growth behavior of dislocated and perfect surfaces. If {111} surfaces are smooth but {100} surfaces are rough with the present experimental conditions, the problem of edge behavior would again occur. Although Sears⁷ attributed the whisker growth of mercury to an axial dislocation and perfect close-packed lateral surfaces, mercury has a face-centered cubic structure with compression along one three-fold axis of symmetry,¹⁶ and the above discussion of edge effects would also apply.

It is perhaps of interest to speculate on the resulting growth habit if the edge rows of atoms were not deposited in the example given in Fig. 5(a). In this case, the new layers of atoms also extend only to the bounding close-packed surfaces, the area of the dislocated surface decreases, and an edge of the surface approaches the emerging dislocation line (Fig. 6). When the dislocation line is $2\rho_c$ from an edge, the dislocated surface would stop growing despite a moderate supersaturation in the

[†] A closed path around the (110) direction could not be obtained

¹⁶ L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, 1948), second edition, p. 411.



parent phase. The resulting crystal has a polyhedral habit and whisker growth would not be permitted.[‡]

Since a whisker habit is actually observed, either the embryonic close-packed surfaces at the edges are overrun because of equilibrium reasons or some other aspect is important. An alternate explanation for whisker growth might be that an impurity induces the growth of lateral surfaces. Habit modification with impurities is well known, and the dendritic growth of silver metal has been attributed to sulfur-containing^{17,18} and organic¹⁸ compounds. However, it seems somewhat unlikely that such impurities would be in the present Ag(I)-Fe(II) system, in the whisker growth of Hg from the vapor,⁷ and also in the whisker growth of copper metal (facecentered cubic structure) in the reduction of Cu(II)from aqueous $CuSO_4 - H_2SO_4$ solution by H_2 at 150°C and 500 psig H₂ partial pressure.¹⁹

The present work poses numerous other problems in growth behavior for which no satisfactory explanation can be offered here. For example, whisker growth via either a plane or triangular tip perhaps suggests dislocation lines in two different crystallographic directions. Dislocation movement is probably involved when whiskers and fern stems undergo their angled growth, but a closer description is of course desired and the angling mechanism must preserve the original width. The lack of growth at re-entrant surfaces suggests that the lateral surfaces are poisoned and supports the impurity mechanism noted above. However, the addition of excess Fe(III) to previously formed whiskers resulted in corrosion at the angle junctures but not at the whisker tips, indicating a poisoned tip and unpoisoned (or less poisoned) surface irregularities at the junctures.

B. Kinetics

The kinetic results in this work are limited because of uncertainities in the number of dislocations in each whisker and in the determination of actual reagent concentrations by the counting technique. However, the similarity in growth rates of whiskers despite the tenfold variations in concentrations noted in Table I suggests that a whisker growth rate, R_{Ag} , was essentially independent of reagent concentrations, or that

$$\mathbf{R}_{Ag} = \text{constant.}$$
 (5)

Krueger and Miller⁶ investigated the crystal growth of Na₂S₂O₃·5H₂O with a more direct experimental technique and similarly observed that the growth rate of a crystal surface could be constant despite large changes in reagent concentration in the bulk solution. The following discussion is given principally to suggest an explanation for their zero-order growth kinetics and presumes that the present silver whiskers also grew with zero-order kinetics.

The immediate problem is to decide whether the BCF theory of growth kinetics given by Eq. (4) could account for the similarity of growth rates of whiskers despite the eightfold variation in $\ln(J_c/K_c)$ noted in Table I. A fourfold variation is obtained using the most favorable concentrations within the estimated error. For the present Ag(I)-Fe(II) system, Eq. (4) becomes

$$\mathbf{R}_{\mathrm{BCF}} = K' \cdot \ln \alpha \cdot \mathbf{v}, \tag{6}$$

where $K' = \mathbf{h} \mathbf{H} k \mathbf{T} / 4\pi (1 + 3^{-\frac{1}{2}}) \gamma$ and is essentially independent of reagent concentrations since a change in concentrations would probably affect J_c and v much more than γ . Therefore, if the classical theory of ρ_c is applicable to the present system, the concentration dependence of v must essentially cancel the $\ln(\mathbf{J}_c/\mathbf{K}_c)$ factor in Eq. (6).

Abrupt increases in growth rates of whiskers imply that the rate-controlling reaction in growth is a surface reaction which depends upon an abruptly varying density of "active" sites at the whisker tip. A varying site density is difficult to explain unless the sites are at the BCF surface steps because a varying dislocation density gives a varying step density. Decreasing growth rates (Fig. 4) are attributed to unknown impurities poisoning the steps at the whisker tip and would account in part for the variation in observed rates. An alternate explanation of oscillating growth rates could be the disrupting of a rate-controlling bulk diffusion of ions by irregular currents in the solution near the whisker tip because of thermal gradients or density gradients due to the change in solution density with chemical reaction.²⁰ However, similar ranges in growth rates would not be expected with a tenfold change in concentrations if the growth rate of a whisker were limited by bulk diffusion.

Since whisker growth rates depended upon step density, the slow reaction in growth must have been at or

[‡] Extending the present argument, a dislocated {100} surface initially bound by {100} surfaces would form {111} surfaces at the corners during growth. A face-centered cubic crystal for which all surfaces except one are dislocated would soon assume a polyhedral habit and then soon stop growing because the area of the perfect nabit and then soon stop growing because the area of the perfect surface would increase, an edge would approach a dislocation on an adjacent surface, and the dislocated surfaces would successively stop growing. If all surfaces are dislocated or if surface nucleation occurs, a polyhedral habit would again be obtained. ¹⁷ H. D. Keith and J. W. Mitchell, Phil. Mag. 44, 877 (1953). ¹⁸ Compton, Arnold, and Mendizza, Corrosion 7, 365 (1951).

¹⁹ W. G. Courtney (unpublished data).

²⁰ H. A. Laitinen and I. M. Kolthoff, J. Am. Chem. Soc. 61, 3344 (1939).

adjacent to a surface step. Possible alternatives for the slow reaction were considered to be either surface diffusion to the step or adsorption, chemical reaction, deposition, or desorption at sites at the step. Even brief consideration§ of these alternatives^{3,21} indicates that the concentration dependence of v would be either zero or a positive kinetic order in Ag(I) and/or Fe(II) and would never essentially cancel the dependence of **R** upon ρ_c which is predicted by nucleation theory. It is therefore concluded that the classical viewpoint that ρ_c varies with reagent concentrations is not applicable to the Ag(I)-Fe(II) system within the experimental range studied here.

The similarity in growth rates with varying reagent concentrations suggests that both v and ρ_c are independent of the moderate changes of concentrations used in the present work.

Slow desorption of Fe(III) or solvent molecules from sites at the surface step would, for example, account for v being independent of concentrations.

If ρ_c is independent of concentrations, the size of the critical surface nucleus is constant despite a variation in supersaturation. Constant-sized critical nuclei are contrary to nucleation theory, which predicts that the critical nucleus varies with supersaturation according to Eq. (3). However, the kinetics of the 3-dimensional nucleation of solid materials from aqueous solution are frequently interpreted in terms of constant-sized critical nuclei,²²⁻²⁷ although nucleation theory again predicts variable-sized nuclei.

Constant-sized critical nuclei can be rationalized in terms of the excess energy of small nuclei. The free energy change in the formation of a surface nucleus can be represented by

$$\Delta F = 2\pi\rho(\gamma + \gamma') + \epsilon_s(\rho) - \pi\rho^2 k \mathbf{T} \ln\alpha - \epsilon_v(\rho), \quad (7)$$

where γ is the surface free energy per atom area of the pure, infinite interface, $\| \epsilon_s(\rho)$ is the excess surface energy in a nucleus at the pure interface due to excessive bond dissymmetry in the nucleus, γ' is any excess surface energy per atom area due to preferential adsorption or other reasons, and $\epsilon_v(\rho)$ represents any variation in the volume free energy due to impurities being incorporated in the nucleus (i.e., dilution). The standard surface free energy is thus chosen to be the macroscopic surface energy. With a pure, simple system,

$$\Delta F = 2\pi\rho\gamma + \epsilon_s(\rho) - \pi\rho^2 k \mathbf{T} \ln\alpha. \tag{8}$$

Quantitative evaluation of the excess surface free energy, $\epsilon_s(\rho)$, is difficult. For an ionic crystal Benson and Shuttleworth²⁸ calculated that the surface energy of a surface nucleus containing 13 atoms is about 15% greater than for the infinite interface. For silver metal a quantum-mechanical approach such as employed by Taylor, Eyring, and Sherman²⁹ in their calculation of the stabilities of 3-dimensional metal nuclei will be required.

The classical nucleation theory assumes that the excess surface energy of a nucleus is negligible compared to the macroscopic surface energy for an infinite interface. It is generally accepted that the nucleation theory is useful only for large nuclei because of this assumption.30

However, a small nucleus which contained less than, say, ten atoms has an appreciably greater bond dissymmetry than the infinite interface and therefore has an appreciable excess surface energy. Furthermore, a small nucleus of a certain size will have a particularly unstable bond configuration, i.e., a particularly high excess surface energy. If the excess surface energy of this nucleus is sufficiently high, this nucleus would have a free energy considerably greater than all other sized nuclei and would thus be the constant-sized critical surface nucleus.

SUMMARY

1. The crystal growth of silver metal whiskers and ferns was observed during the chemical reduction of Ag(I) with Fe(II) from aqueous solution.

2. Whiskers and ferns appeared to grow by dislocation mechanisms, with new metal depositing at an axial screw dislocation emerging from the growing tip of the crystal. Qualitatively, whiskers and ferns are attributed to perfect and twinned screw dislocations, respectively. Indirect evidence suggested that the dislocation lines were in the (110) direction.

3. No explanation is offered for the growth of whisker and fern habits. It is shown that an interpretation of growth habit for a pure system requires the Burton, Cabrera, and Frank treatment of infinite crystal surfaces to be extended to the edges and corners of a crystal. Impurities may be important in the present work.

[§] It was assumed that the equilibrium concentration of each ionic species adsorbed at the interface could be related to its bulk concentration by a Langmuir-type adsorption isotherm or one of its extremes throughout all concentration ranges of interest. This model is similar to that adopted by O. Stern [Z. Elektrochem. 30, 508 (1924)] in his treatment of adsorption.

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4. Limited kinetic data suggest that the linear rate of growth of a whisker was independent of supersaturation. This implies that the size of the critical surface nucleus was independent of supersaturation, which is contrary to the classical theory of crystal growth. A possible explanation for constant-sized critical surface nuclei is suggested.

ACKNOWLEDGMENTS

The author is pleased to acknowledge the advice of Dr. H. M. Hulburt, Dr. F. A. Schaufelberger, and numerous colleagues at Experiment Incorporated and the Stamford Research Laboratories, American Cyanamid Company. Particular thanks are due to Mr. J. J. Shaw, who performed most of the experimental work.

THE JOURNAL OF CHEMICAL PHYSICS

DECEMBER, 1957

Neighbor Interactions and Symmetric Properties of Polyelectrolytes

VOLUME 27, NUMBER 6

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The grand partition function of polyelectrolyte molecules, considered as linear Ising chains, is studied with respect to certain symmetry properties of these systems. The degree of ionization and the buffering capacity are shown to possess a symmetry with respect to the point of half neutralization. Equations for the pH, the degree of ionization, and the buffering capacity are derived explicitly for a model in which only the interactions between first- and second-neighbors are taken into account. The results are compared with those of the theory of first-neighbor interactions, and graphs of titration and buffering-capacity curves are given. The properties of the maxima and minima occurring in the buffering-capacity curves are discussed. It is found that the form of buffering-capacity curve provides information on the order of non-negligible interactions.

1. INTRODUCTION

ELECTROSTATIC interactions between the ion-izable groups of a polyelectrolyte molecule are known to have a pronounced influence on many properties of polyelectrolyte solutions. Recently, special attention was focused on the interaction between closeneighbor groups. On the one hand these contribute a significant part of the total interaction-energy because of the rapid decrease of interaction with distance; on the other hand, neighbor interaction is amenable to exact statistical treatment similar to that of the Ising model¹ of ferromagnetism. Marcus,² Harris and Rice,³ and Steiner⁴ were the first to apply this model to the study of polyelectrolytes. Katchalsky, Mazur, and Spitnik⁵ found that neighbor interaction dominates the behavior of polyelectrolyte solutions even at very high ionic strengths, provided that the adjacent ionizable

groups are close enough as, for example, in polyvinylamine. Hill⁶ reported some applications of the method to statistical problems concerning linear molecules. Lifson⁷ applied it to association phenomena in polyelectrolytes and to polyampholytes and other electrolytic copolymers of periodic structure. Rice and Harris⁸ considered second-neighbor interactions in their study of equimolar polyampholytes of regularly alternating structure.

The justification for considering neighbor interactions independently from all other factors affecting the behavior of polyelectrolyte solutions rests on certain assumptions which we wish to state explicitly.

(a) The macromolecule is considered as a separate phase which maintains thermal and chemical equilibrium with the rest of the solution. This implies that the free energy of the whole solution is approximately the sum of the free energy of the macromolecule and that of the rest of the solution. The interaction between the two phases is represented by an average electrostatic potential difference between the immediate vicinity of the macromolecule and the bulk of the solution⁹; it is assumed that the average local concentration

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⁴ After submitting the paper for publication our attention has here with the two processes.

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