TECHNICAL REPORT NO. 4

TO THE OFFICE OF NAVAL RESEARCH

CONTRACT NONR 3925(00)

THE ACTION OF ADSORPTIVE INHIBITORS IN SOME CORROSIVE SYSTEMS

by

M. B. Ives

Department of Metallurgy and Metallurgical Engineering
McMaster University
Hamilton, Ontario, Canada

October 1964

34/p

"Reproduction in whole or in part is permitted
for any purpose of the United States Government"

CLEARINGHOUSE FOR FEDERAL SCIENTIFIC AND TECHNICAL INFORMATION CFSTI
DOCUMENT MANAGEMENT BRANCH 410.11

LIMITATIONS IN REPRODUCTION QUALITY

ACCESSION # AD608121

☒ 1. WE REGRET THAT LEGIBILITY OF THIS DOCUMENT IS IN PART UNSATISFACTORY. REPRODUCTION HAS BEEN MADE FROM BEST AVAILABLE COPY.

☐ 2. A PORTION OF THE ORIGINAL DOCUMENT CONTAINS FINE DETAIL WHICH MAY MAKE READING OF PHOTOCOPY DIFFICULT.

☐ 3. THE ORIGINAL DOCUMENT CONTAINS COLOR, BUT DISTRIBUTION COPIES ARE AVAILABLE IN BLACK-AND-WHITE REPRODUCTION ONLY.

☐ 4. THE INITIAL DISTRIBUTION COPIES CONTAIN COLOR WHICH WILL BE SHOWN IN BLACK-AND-WHITE WHEN IT IS NECESSARY TO REPRINT.

☐ 5. LIMITED SUPPLY ON HAND: WHEN EXHAUSTED, DOCUMENT WILL BE AVAILABLE IN MICROFICHE ONLY.

☐ 6. LIMITED SUPPLY ON HAND: WHEN EXHAUSTED DOCUMENT WILL NOT BE AVAILABLE.

☐ 7. DOCUMENT IS AVAILABLE IN MICROFICHE ONLY.

☐ 8. DOCUMENT AVAILABLE ON LOAN FROM CFSTI (TT DOCUMENTS ONLY).

☐ 9.

PROCESSOR: P. McLean

TSL-107-10/64

ABSTRACT

A review will be made of the proposed mechanics of adsorptive inhibitors on crystalline surfaces, as substantiated by experimental activity in recent years. In particular, detailed consideration will be given to the profound effects that can be wrought by small quantities (ppm) of suitable ions in aqueous solution on the dissolution of alkali halide crystals. Radio-tracer experiments have been performed in order to deduce adsorption isotherms for iron adsorbed on lithium fluoride surfaces from dilute solutions of ferric chloride. The results support the concept of inhibitor control by action at the "kink" sites in an otherwise close-packed crystal surface, and the etch morphologies obtained may be successfully related to such a concept.

It is proposed that the theories may be extrapolated to cases of metallic corrosion controlled by inhibitors which act by means other than the creation of a continuous "passive" film. Some of these examples are being studied.

It is intended in this paper to review some of the recent dissolution studies involving the action of specific surface-active adsorbates which profoundly modify the dissolution kinetics of some crystalline materials. At present, we are concerned with understanding the detailed kinetics of the dissolution processes and this is being done by considering the basic atomic structure of a crystal surface, instead of depending on any macroscopic phenomenological concept. Such an approach has recently been recommended to the Chemical Engineering industry by Parr(1). Further, it should be realized that the studies are confined to surfaces of <u>single</u> crystal material, which are less applicable technologically, and give results which at first encounter may appear too dramatic to the user of normal polycrystalline material of commercial purity.

The use of inhibitors in corrosive systems is, of course, not a new concept - for example, metallurgists have used etches to reveal the structure of metals and alloys for centuries and these, although prepared by cook-book and trial-and-error methods, almost invariably necessitate the inclusion of a quantity of some ingredient other than the solvent. This agent will be referred to here as an "inhibitor" and we shall be restricting any general remarks only to systems where the inhibitor does <u>not</u> form a "passive" protective film on the surface. It should be emphasized that the ideas expressed herein are in their infancy and only a few systems have been directly studied. However, thorough understanding of the mechanisms involved in this type of dissolution may well lead to important technological application at some future date.

Experimental Facts

Considerable experimental effort has been expended on the study of $\{100\}$ cleavage surfaces of single crystal lithium fluoride dissolved in aqueous solutions. Gilman, Johnston and Sears (2) have concluded that for an etchant to produce uniform crystallographic etch features in this material, there must be present a few parts per million (p.p.m.) of inhibitor ion. Furthermore, of some thirty cations investigated, only Fe^{+++} and Al^{+++} were found effective in this respect. These workers(2) have suggested that three conditions must be fulfilled for successful inhibition. The cation must be of similar ionic radius to that of the cation of the lattice; there must be a stable fluoride complex of the cation; the metal fluoride should be relatively insoluble in water. The standard etchant for lithium fluoride is now an aqueous solution containing 3 to 4 p.p.m. Fe^{+++} as ferric fluoride or ferric chloride (acidified to a $p_H \sim 3$ to prevent precipitation of ferric hydroxide). This etchant is primarily used in order to study the mechanical properties of lithium fluoride, by revealing the sites of dislocation intersection with the crystal surface through the formation of an etch pit. Figure 1 demonstrates, using interference microscopy, the range of such pit shapes that are produced by varying the ferric ion content of the etchant. The small concentrations involved emphasize the effectiveness of this inhibitor.

Of more direct technological significance than the shape of etch features is the rate of dissolution and its dependence on the presence of inhibitor.

Measurements of the normal dissolution rate of the general (unpitted) surface of lithium fluoride as a function of bulk concentration of ferric ions produces the curves of Figure 2. There is good reason to believe(3) that the absolute values of dissolution rate are dependent on the impurity content of the crystals, but for our present purposes the significant observation is the considerable reduction of etch rate produced by small quantities of ferric ion. Another effect of inhibitor presence is demonstrated in Figure 3 whe the curves represent the effect of percentage saturation of lithium fluoride in solution on (a) the general surface dissolution (3) and (b) the rate of dislocation etch pit widening(4). In both cases the solutions contained 4 p.p.m. ferric ions, and this is sufficient to reduce the rates to immeasurable values at only a fraction of the saturated condition. It is hard to justify this on the basis of a change in equilibrium conditions affecting solubility, and one is therefore forced to an explanation involving a modification of the etch kinetics. Again, the effects of small concentrations of inhibitor are considerable.*

---

*It should be emphasized that neither of the parameters shown in Figure 3 to be modified by Fe^{+++} are intrinsic parameters of the crystal itself. Dissolution, in both cases, is nucleated at defects in the surface(4). A variation in these lead to discrepancies of absolute value from crystal to crystal.

In order to better understand the action of the ferric ions in these systems, radiotracer experiments, using Fe^{59}, by Rosenblatt and Ives(5) and Baskin and Ives(6) have established adsorption isotherms for iron chemisorbed onto the surfaces during etching. A typical isotherm is represented in Figure 4. The significance of its shape will be discussed later. The striking initial result, however, is that the mean coverage of ferric ions in the optimum range is equivalent to only a fraction (1/25) of a monolayer. This further emphasizes the considerable power of the inhibitor, and, as we shall see, provides a valuable clue to the understanding of the mechanics of the inhibited action.

Examples of other systems, which have received much less direct experimental attention, will be the subject of extrapolated hypotheses in a later section.

Theoretical Concepts

In order to apply an atomistic approach to crystal dissolution, it is convenient to adopt a model of the crystal surface which was first proposed by Kossel(7). Any surface of a crystal can be thought of as being composed of low-index (close-packed) facets separated by ledges of monomolecular height. The ledges consist of segments lying in close-packed directions, separated by kinks of monomolecular offset. Figure 5 represents such a model for a cubic crystal, and in the case of lithium fluoride, the close-packed facets correspond to the $\{100\}$ cleavage planes. With a suitable mean concentration of ledges and kinks any macroscopic crystal surface may be represented in this way. For a real surface at a finite temperature, however, lattice thermal energy will cause the nucleation of a certain concentration of double kinks (such as 'a' in Figure 5) which will be dependent on absolute temperature and effective undersaturation at the surface. Such kink pairs will not affect the macroscopic orientation of the surface.

When such a surface dissolves, ions will be lost preferentially from the kinks, where binding is weakest, and effect a motion of the kinks along the ledges. By travelling the length of a ledge, a kink can produce an overall motion of that ledge by an amount equal to the offset of the kink (henceforth considered monatomic).

Because the kinks are the primary dissolution sites, a true analysis of a dissolving surface may be made only in three dimensions. However, some interesting theoretical considerations with important practical implication have been made for the case of a two-dimensional crystal section, dissolving by the motion of ledges. The macroscopic situation may be related to two atomistic parameters; viz., the flux of ledges, q, passing a point on the surface, and the density of ledges, k, about the point. It then follows that the mean velocity of one ledge, $v = q/k$. Also q is proportional to the dissolution rate normal to the close-packed surface, and k is a measure of the slope, tan α, of the surface with reference to the close-packed. These parameters are defined in Figure 6. If it is supposed that etch rate is only dependent on crystallographic surface orientation then a complete summary of the etch characteristics of any system will be represented by the relationship between q and k. We can conceive of two general forms of this relationship (Figure 7), which depend on whether $\frac{d^2q}{dk^2} < 0$ (Type I) or $\frac{d^2q}{dk^2} > 0$ (Type II). Analysis of the kinetics of ledge motion subject to these functional relationships was shown by Frank(8) to be exactly equivalent to the analysis of Lighthill and Whitham applied to the flow of traffic on long straight highways(9) (Type I) and flood waters on rivers(10) (Type II). For the former, it is only necessary to equate ledges with automobiles and the solutions are obtained. One particular aspect of such analyses is applicable to our present considerations. This concerns the prediction of the progress of a traffic hump (section of steeper slope) in an otherwise uniform distribution of vehicles (ledges). Figure 8 shows the results of the analyses for the two types of q-K relationship. The two cases differ in that the discontinuity of slope (edge) is developed at the trailing edge of the increase for Type I (consistent with the motorist's familiar experience of suddenly meeting the "shock wave" on a road, and accelerating slowly through it) and at the leading edge for Type II (analogous with the sudden rise of flood waters as in a river 'bore'). Both types of ledge kinetics can be expected in dissolving systems and it has been proposed that Type I kinetics are applicable to dissolution situations where the interaction between ledges is purely diffusion-controlled, as in the case of a pure solvent. (Quantitatively visualized by the Type I condition that ledge velocity, v, decreases when k increases - ledges move faster when farther apart). Type II kinetics apply when well-defined etch features are required, and these systems are known to need an inhibitor.* Consquently, the shape of a dissolving step on a crystal surface would be a direct indication of the type of control conditions which prevail in a given situation. Figure 9 shows an interference micrograph of a Type II case (dissolution of lithium fluoride). The observation of a Type I ledge (Figure 8) is still unreported. This is probably due to the fact that a Type I bunch is more quickly dispersed than the other form - and also because dissolution is much faster in uninhibited systems. A more useful criterion is, therefore, that macroscopic ledge formation is stabilized in Type II only, and that if Type I conditions hold no pile-up is stable and smooth dissolution features are observed. This is suggested by the recent work of Young and Hulett(11) on the electrolytic dissolution of copper crystals in electrolytes containing HCl and HBr. Type I conditions and morphologies (smooth surfaces) prevail at high current densities and low Br^- concentrations, and Type II (macro-ledges) are stable at low current and high Br^- concentrations. It is possible to cause the ledges to appear and to disappear as the current conditions are switched. These results are consistent with the previous concepts if one accepts that Br^- ions are inhibitors and that current density controls the effective under-saturation of the solution.

It is, however, the detailed atomistic studies which have been most rewarding in assisting with the understanding of the mechanics of inhibitor action and its control of etch morphologies. The direct

---

*The mechanics of this type of kinetics, which requires ledges to move faster when closer together is less readily visualized, but is not of direct importance to this review.

radioisotope studies of Ives et al (5,6), have permitted hypotheses which adequately explain the observed effects. With the refined techniques of autoradiography (β-track counting of fine emulsions), it was quickly established that the ferric ion adsoprtion is independent of macroscopic surface morphology and, in particular, etch pit density. This is considered to be due to the fact that the whole general surface is also dissolving (by nucleation of dissolution at impurity sites, etc.) and is subject to the same conditions as those at the pits. Consequently, after dissolution the whole surface is presumably composed of identical facets to those at the pits, but they are not in general resolvable, since they are never able to attain sufficient size due to the lack of a constant dissolution source. (In many instance, there is a suggestion of a surface mottle, which could represent such facets.) Due to the uniformity of inhibitor coverage, it was possible to use a low-background counter technique, calibrated with known standards, for more accurate measurement (6).

Adsorption studies on dissolving surfaces immersed in <u>dilute</u> etchants are not truly amenable to equilibrium thermodynamics, due to the kinetic situation existing and also to the difficulty of measuring the total surface area of a sample when roughened by the etch. Consequently, the best information concerning the kinetics of the inhibitor adsorption is derived from samples immersed in <u>saturated</u> solutions of lithium fluoride containing varying amounts of ferric ion. A typical isotherm from such a system is shown in Figure 4. Another significant consequence of this curve, in addition to revealing the overall low values of the coverage, is that there is an inflection at a bulk Fe^{+++} concentration corresponding to the "optimum" condition for good, plane-sided square pyramidal pits.

The detailed mechanics of inhibitor action in producing the observed morphological changes has recently been proposed by Baskin and Ives(6). It was originally suggested by Gilman, Johnston and Sears(2), that the most suitable site for the incorporation of Fe^{+++} ions into a lithium fluoride surface would be at a kink position where it could be surrounded by neighbouring F^- ions of the crystal (As at 'B' in Figure 10). Baskin and Ives have preferred, however, to consider the 'A' kink-pairs as the principal sites for adsorption. Accepting the established concepts of physical chemistry, it would seem appropriate therefore to relate the inflection in the isotherm to the filling of these preferred kink sites by the iron – a condition which is described as "monokink" coverage. Consequently, since the values of surface excess, Γ', are known absolutely, a figure for the density of these sites is also available (viz., ~1/25 monolayer). This concentrations of kinks is consistent with theoretical calculations(12) of the equilibrium configuration of a ledge containing kinks produced by thermal fluctuations in the lattice at finite temperatures. Furthermore, the preponderance of 'A' kinks is sufficient to cause the dissolution features to macroscopically appear composed of only "ledge-surface",*

---

*"Ledge-surface" has been defined(13) as any surface belonging to the zone of the close-packed direction – it can, therefore, be represented as a parallel array of straight ledges containing no (nett) concentration of kinks. Any other surface is a "kink-surface".

as they do at optimum inhibitor concentration (Figure 1 (c)).

Accepting the monokink coverage concept at the optimum inhibitor concentration, the variation in microstructure may be rationalized.

At inhibitor coverages less than monokink, kinks will be unequally inhibited. Consequently, some kinks will quickly traverse their ledges until annihilated by kinks of opposite sense, while others will be held up by inhibitor. Such a situation will lead to irregular surfaces, but exhibiting ledges only in the close-packed directions, due to 'pile-ups' of kinks into multi-kinks, as uninhibited kinks catch up with inhibited ones. (Figure 11).

At monokink coverage, all kinks are equally constrained and uniform dissolution occurs. This will favour the maintenance of straight close-packed ledges, in that salient ('B') kinks will more readily strip the ledge than a new kink pair will break away from configurations such as 'A' (Figure 10). This condition also explains the profound effect of the inhibitor on dissolution rate up to the 'monokink' condition (Figure 2). Once all the kinks are filled, the surface mechanisms are controlled. To explain the barrelling of the etch features and their approach to a conical shape at inhibitor concentrations in excess of the optimum, Baskin and Ives(6) have shown the need for diffusion control - as distinct from surface control - as an increasingly important constraint on the dissolution rate and morphology. Due to the obviously greater relative stability of configurations such as 'A' (Figure 10), it is not easy to conceive of a mechanism whereby increased direct adsorption of inhibitor will cause 'A' kinks to move more readily than 'B' kinks and thereby produce the nett kink-surfaces that are observed. It is proposed(6) therefore, that once 'monokink' coverage of iron is attained at the surface, the rate of formation of ferric ion complexes in solution (in the stagnant boundary layer or loosely associated with the surface) becomes comparable to that of attachment of ferric ions at other surface sites (such as "at-ledge") and the solution contains additional species (exact form unknown) which increase the barrier to diffusion of solute away from the surface. When dissolution is subject to diffusion control, the dissolution sites interact through the diffusion fields centred on the sites(12,14) and they therefore 'repel' each other. In particular, this condition gives rise to kink 'pile-ups' and the stabilizing of kink-surface which is observed in the barrelling (Fig. 1 (d)) and the eventual attainment of conical features (Figure 1 (e)) - a condition corresponding to complete diffusion control, since all crystallographic features have been eliminated. The form of the observed increase in surface excess, Γ , at conditions greater than monokink is, from this explanation, of no direct significance, since it represents contributions not only from the ions chemisorbed at higher energy surface sites but also from solution complexes which equilibrate with the surface as it is removed from the solution. The thermodynamics of this contribution are not presently known.

The above example has been described in some detail in order to demonstrate the atomistic properties of surfaces and some of the concepts to be considered when describing their dissolution.

Other examples

The concepts evolved from the study of lithium fluoride in dilute aqueous solutions of ferric ions may, in company with the kinematic theory of dissolution, be applied to the tentative prediction of parallel conditions existing in other dissolving systems.

Etchants for most other alkali halides produce morphologies which have a similar dependence on the concentration of a specific inhibitor(15,16), and it is probable that similar kinetics apply to these cases.

The etching of metals to produce crystallographic dissolution features is much less documented, and it is only possible here to suggest systems that *may* be amenable to the conclusions drawn for lithium fluoride. In aqueous environments, the dissolution of copper in the presence of Br^- ions(11,17,18) suggests an inhibitive effect of the bromine. There is a possibility that mercury ions play a part in sharpening etch features in both silicon(19) and germanium(20). Etch pits in germanium have also been enhanced by the presence of potassium(21) and silver(22) ions. General reviews of etchants for many materials have been prepared by Regel et al.(23) and by Lovell et al.(24), and these may be consulted for other possible applications to liquid solvents.

It is also possible that similar specific inhibitive effects can be produced by impurities present during thermal etching of materials. Here, however, the surfaces are usually subject to considerably greater ranges of undersaturation than is general in liquids, and consequently there is likely to be greater variation of dissolution (evaporation) morphology. The following suggestions are thus even more tentative. It seems most probable that the morphologies produced by Suzuki(25) on copper crystals annealed close to the melting point under conditions of relatively low undersaturation were subject to specific inhibition. Figure 12 shows a $\{100\}$ surface produced in that study, containing square pits and macroscopic ledges with a preference to be kinked in the $\langle 100 \rangle$ directions. In this case, the low evaporation rate allows better inhibition by impurities from the atmosphere or released from the crystal itself as it evaporates. Microstructures of zinc(26), titanium(27) and iron(28) suggest macro-ledge morphologies that are subject to partial inhibition. It is, however, necessary to study the shapes of monatomic ledges in order to directly apply the theory. This can be done by electron microscopy of decorated surfaces as developed by Bassett(29), and Figure 13 is an example of its application by Bethge(30,31). The figure shows evaporation spirals of monatomic and diatomic ledges, centred at dislocations on sodium chloride, decorated by gold nuclei. The shapes of the ledges are well defined.*

---

*This technique is presently being develped by the author for studying etched surfaces of lithium fluoride crystals, in order to substantiate the current theories at the atomistic level.

The existence of a balance between diffusion and interface control in evaporating systems is suggested by the tendency to depart from crystallographic morphologies when the surface temperature is raised, as exemplified by studies on the alkali halides(32,33), germanium(34), and diamond(35).

In the work of Kern and Pick(32) on evaporation of some alkali halides, the surfaces exhibit the types of morphologies discussed herein for lithium fluoride in aqueous environment. Low surface temperatures favour the maintenance of close-packed kinked macro-ledges (Figure 11), while more rounded features appear at higher temperatures.

Future Possibilities

Work is in progress(36) to apply the adsorption concepts to evaporating surfaces of zinc crystals in well controlled and monitored atmospheres, with the aim of identifying possible effective inhibitors. For possible practical application to corrosion control the most likely useful effect is that produced by specific inhibitors present at "monokink" coverage. The study also suggests the relative wastefulness of adding inhibitor in excess of this. It will be some time before these mechanisms have such economic importance, but we are certainly becoming aware of their possibilities. This review has been an attempt to increase this awareness.

ACKNOWLEDGMENT

This review, and much of the author's research described herein, has been possible through the support of the National Research Council of Canada, and the United States Office of Naval Research. The material was originally prepared for presentation at the 14th Chemical Engineering Conference of the Canadian Institute of Chemistry.

REFERENCES

1 Farr, J. G., Chem. Eng. 71 no. 14 160 (July 6, 1964)

2 Gilman, J. J., Johnston, W. G., and Sears, G. W., J. Appl. Phys. 29 747 (1958)

3 Ives, M. B. and Plewes, J. T., J. Chem. Phys. in press

4 Ives, M. B. and Hirth, J. P, J. Chem. Phys., 33 517 (1960)

5 Rosenblatt, G. and Ives, M. B., J. Electrochem. Soc. 110 1088 (1963)

6 Baskin, M. S., and Ives, M. B., to be published

7 Kossel, W., Nachr. Ges. Wiss. Göttingen 135 (1927)

8 Frank, F. C., "Growth and Perfection of Crystals" (John Wiley and Sons, New York, 1958) p. 411

9 Lighthill, M. J. and Whitham, G. B., Proc. Roy. Soc. 229A 317 (1955)

10 Lighthill, M. J. and Whitham, G. B., Proc. Roy. Soc. 229A 281 (1955)

11 Young, F. W. Jr., and Hulett, L. D., to be published

12 Burton, W. K., Cabrera, N., and Frank, F.C., Phil. Trans. Roy. Soc. 243A 299 (1951)

13 Ives, M. B., J. Phys. Chem. Solids, 24 275 (1963)

14 Hirth, J. P., and Pound, G. M., J. Chem. Phys. 26 1216 (1957)

15 Moran, P. R., J. Appl. Phys. 29 1768 (1958)

16 Johnston, W. G., Prog. Ceram. Sci. 2 1 (1962)

17 Lovell, L. C., and Wernick, J. H., J. Appl. Phys. 30 590 (1959)

18 Livingston, J. D., J. Appl. Phys. 31 1071 (1960)

19 Vogel, F. L., Jr., and Lovell, L. C., J. Appl. Phys. 27 1413 (1956)

20 Wehner, G. K., J. Appl. Phys., 29 217 (1958)

21 Billig, E., Proc. Roy. Soc., 235A 37, (1956)

22 Schell, H. A., Z. Metallk. 47 614 (1956)

23 Regel, V. R., Urusovskaya, A. A., and Kolomiichuk, V. N., Soviet Physics - Crystallography, 4 895 (1959)

24 Lovell, L. C., Vogel, F. L., Wernick, J. H., Metal Progress 75 no. 5 96 (1959)

25 Suzuki, H., J. Phys. Soc. Japan, 10 981 (1955)

26 Ruff, A. W., to be published

27 Evans, P., Acta Met., 5 342 (1957)

28 Sewell, P. B., Brewer, E. G. and Cohen, M., J. Phys. Chem. 67 2008 (1963)

29 Bassett, G. A., Phil. Mag. 3 1042 (1958)

30 Bethge, H., Phys. Stat. Solidi, 2 1, (1962)

31 Bethge, H., Surface Science, 1 in press

32 Kern, E., and Pick, H., Z. Physik., 134 610 (1953)

33 Grinberg, A., Phys. Stat. Solidi. 3 1369 (1963)

34 Denda, S., J. Phys. Soc. Japan 13 533 (1958)

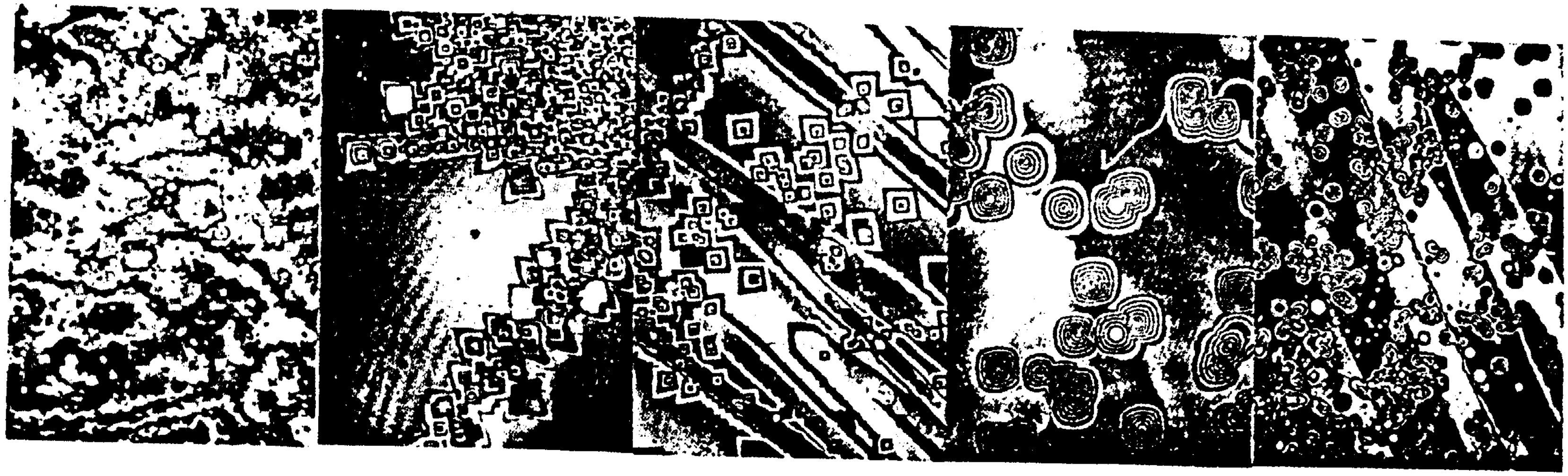
35 Tolanski, S., and Patel, A. R., Phil. Mag. 2 1003 (1957)

36 Terni, P., and Ives, M. B., unpublished research

CAPTIONS TO FIGURES

Figure 1	Interference micrographs of etch pits on lithium fluoride etched for 2 minutes at 23°C in solutions of ferric chloride containing (a) 0.2 ppm, (b) 1.7 ppm, (c) 2.5 ppm, (d) 10 ppm, (e) 200 ppm Fe^{+++}.
Figure 2	$\{100\}$ surface dissolution rate, as a function of ferric ion content (ppm Fe^{+++}) in etchant (after Ives and Plewes).
Figure 3	Effect of undersaturation of lithium fluoride in solutions of "optimum" ferric ion concentration on (a) $\{100\}$ surface dissolution rate, (after Ives and Plewes) and (b) etch pit widening rate (after Ives and Hirth).
Figure 4	Typical adsorption isotherm for ferric ions adsorbed on lithium fluoride surfaces (from saturated solutions).
Figure 5	Kössel model of a crystal surface, showing close-packed $\{100\}$ surface, ledges and kinks.
Figure 6	Two dimensional model of a general surface represented by an array of ledges. k is the concentration of ledges necessary to produce a macroscopic surface mis-oriented by α degrees from the close-packed surface. v is a mean ledge velocity and is therefore related to the dissolution rate in the region.
Figure 7	Ledge flux-concentration curves for the two cases — Type I, where $\frac{d^2q}{dk^2} < 0$ and Type II where $\frac{d^2q}{dk^2} > 0$.

Figure 8	Surface profiles arising from step bunches with (a) Type II ledge kinetics and (b) Type I.
Figure 9	Type II ledges on etched lithium fluoride surface (interference micrograph).
Figure 10	Two types of kinks in a surface ledge, which may be host to inhibitor ions (filled circles).
Figure 11	Electron micrograph of kinked ledges on $\{100\}$ surfaces of sodium chloride, thermally etched 4 hours in air at 710°C (after Kern and Pick).
Figure 12	$\{100\}$ surface of copper after annealing close to melting point under conditions of limited undersaturation (after Suzuki).
Figure 13	Thermally etched sodium chloride surface with monatomic and diatomic ledges revealed by decoration with gold nuclei (after Bethge).



(a) (b) (c) (d) (e)

Figure I

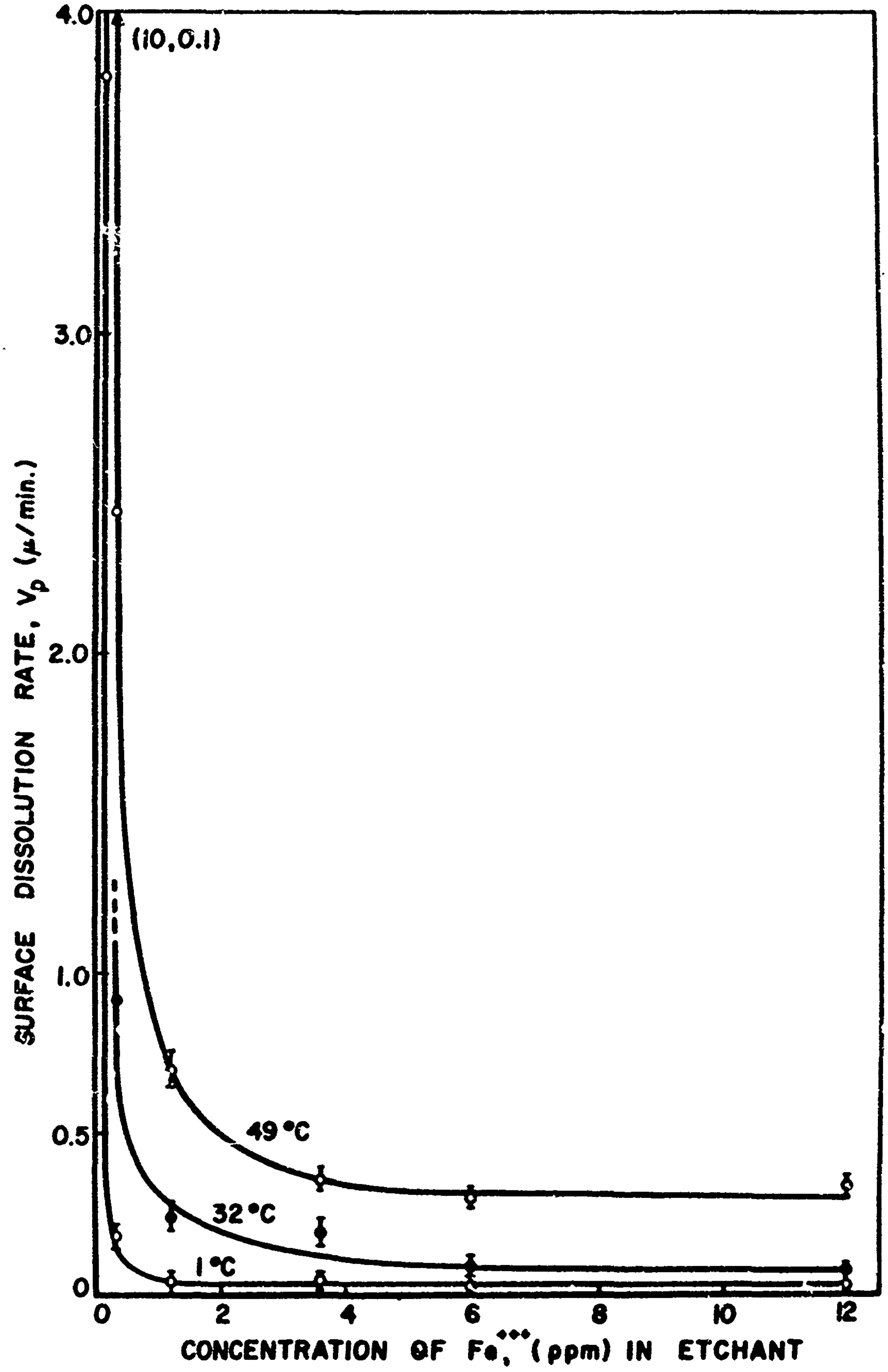

4.0
3.0
2.0
1.0
0.5
0
(10,0.1)
49 °C
32 °C
1 °C
0
2
4
6
8
10
12
SURFACE DISSOLUTION RATE, V_p (μ/min.)
CONCENTRATION OF Fe^{+++}, (ppm) IN ETCHANT

Figure 2

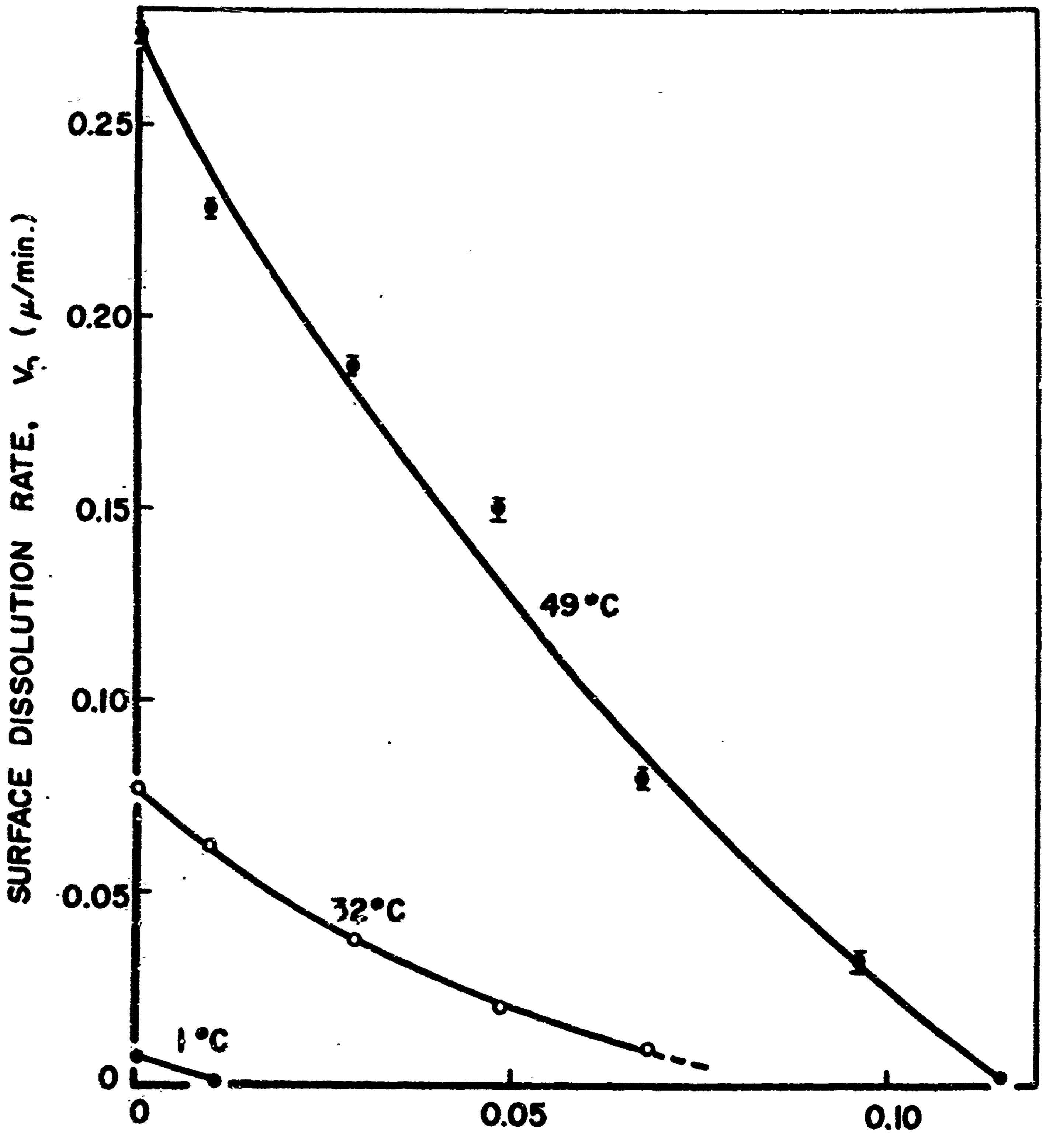
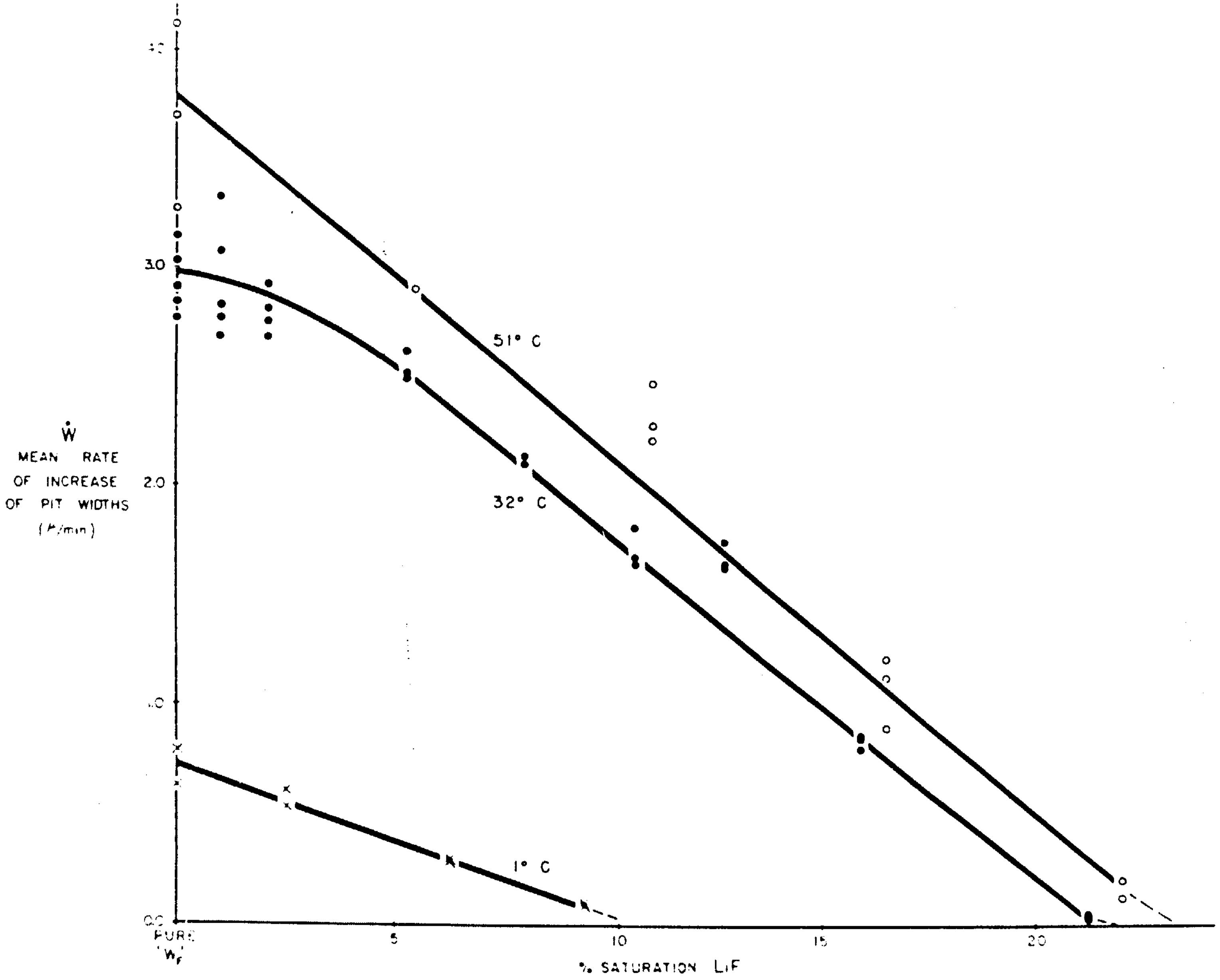


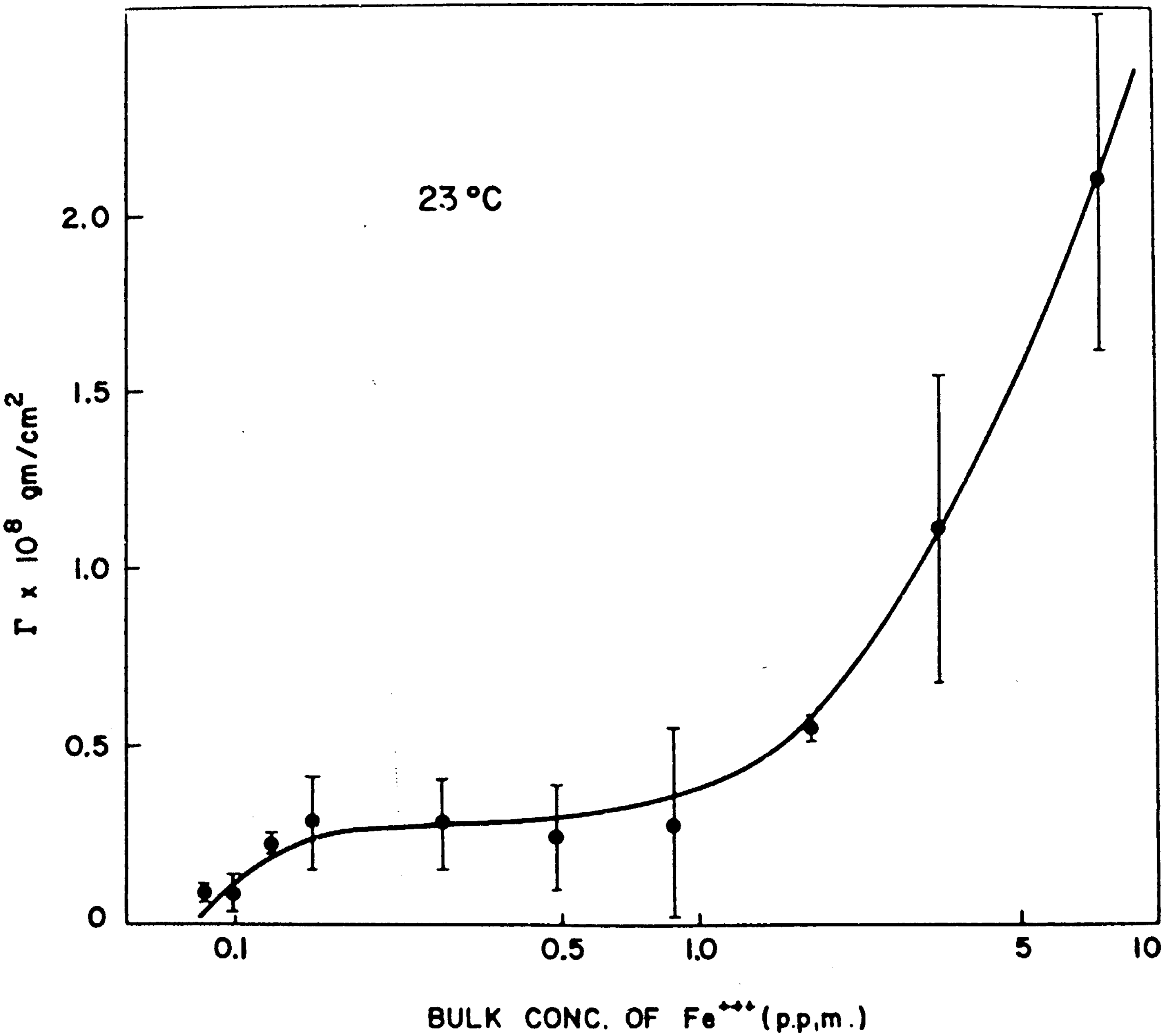
Figure 3 (a)

Fig. 3b Rate of Increase of Pit Width as a Function of Saturation of LiF in W$'_F$ Etchant

% SATURATION LiF


$\dot{W}$
MEAN RATE OF INCREASE OF PIT WIDTHS
(μ/min)
4.0
3.0
2.0
1.0
0.0
PURE W_f
5
10
15
20
% SATURATION LiF
51° C
32° C
1° C

[illegible]



23 °C
2.0
1.5
1.0
0.5
0
$\Gamma \times 10^8$ gm/cm^2
0.1
0.5
1.0
5
10
BULK CONC. OF Fe^{+++} (p.p.m.)

Figure 4

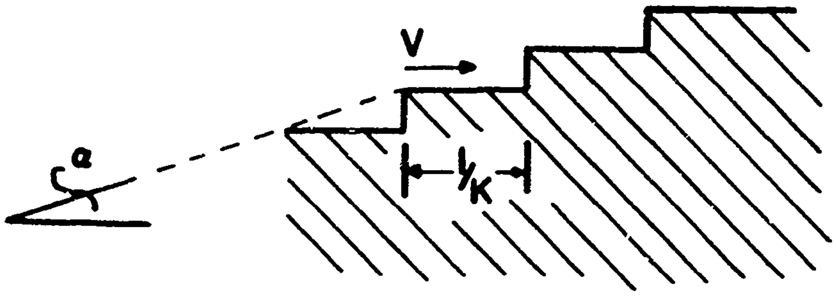


Figure 6

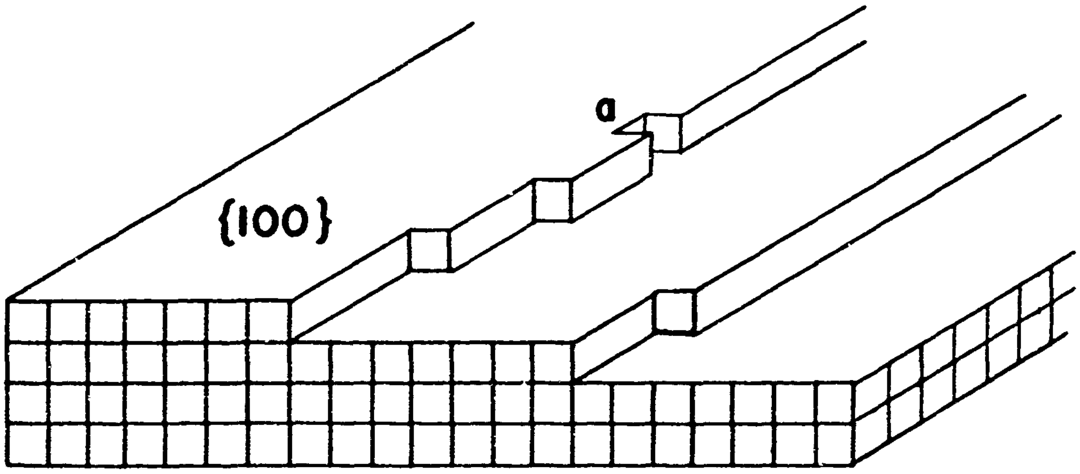


Figure 5

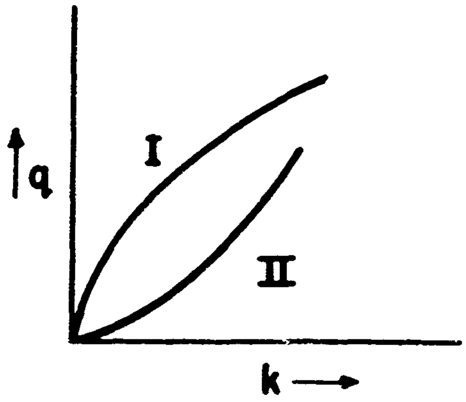


Figure 7

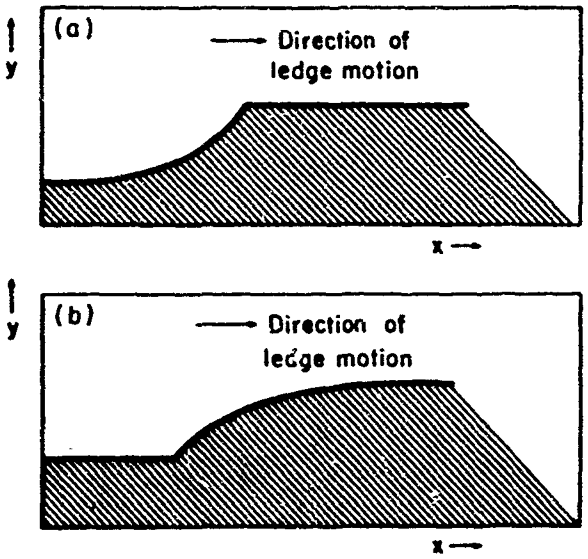

(a)
Direction of ledge motion
y
x
(b)
Direction of ledge motion
y
x

Figure 8

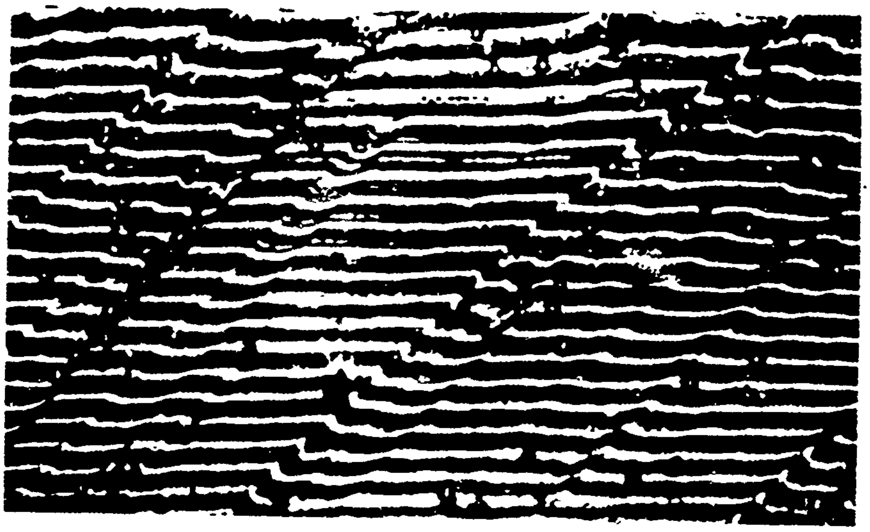


Figure 9

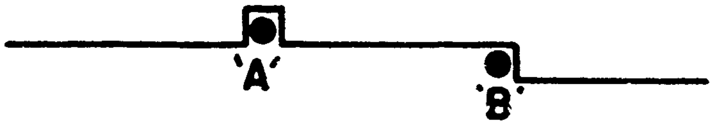


Figure 10

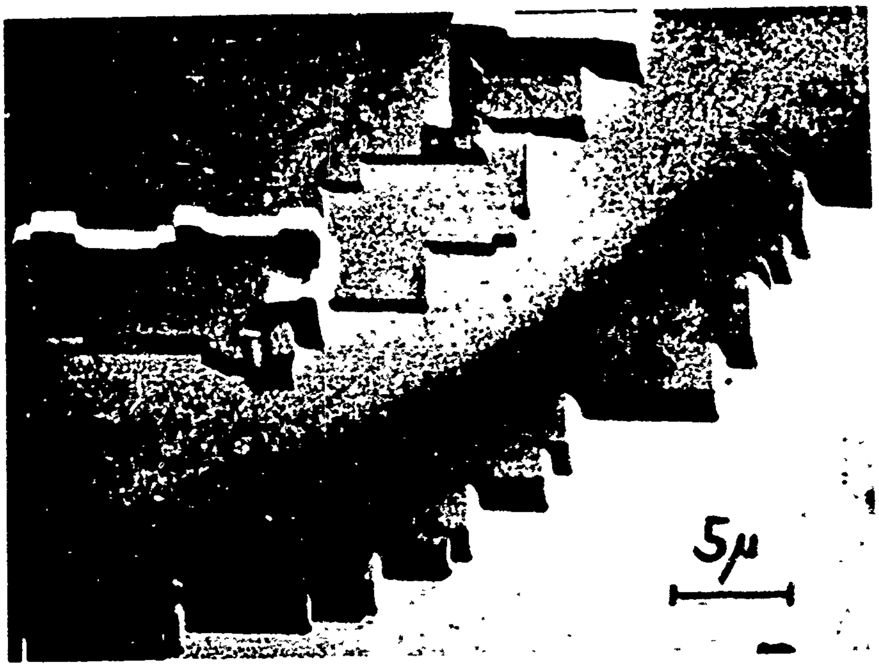


Figure 11

Figure 12

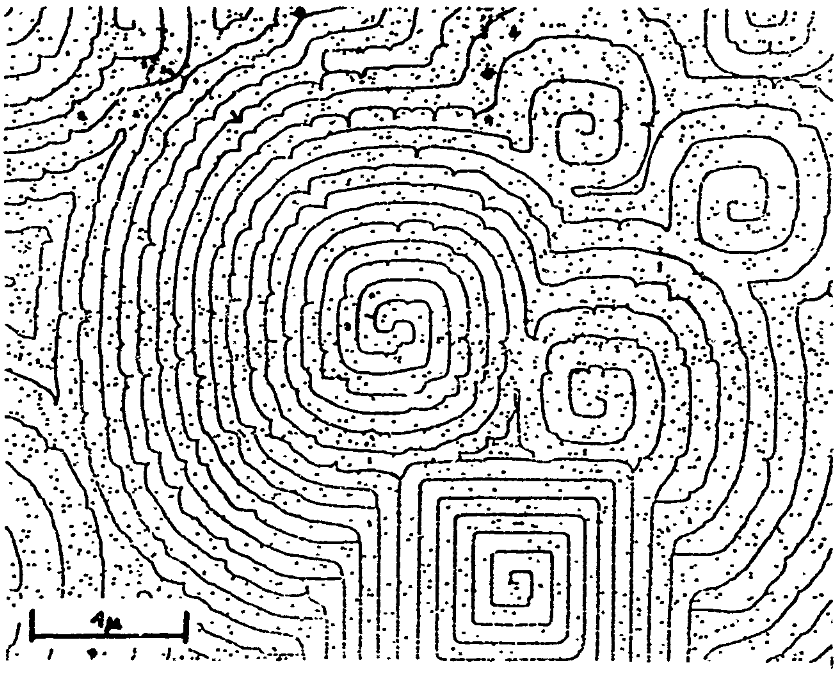


Figure 13