

01 Jan 1970

Etch Patterns On Zone-Refined Fe

M. E. Straumonis

Chang-Soo Kim

Missouri University of Science and Technology, ckin@mst.edu

Follow this and additional works at: https://scholarsmine.mst.edu/ele_comeng_facwork



Part of the [Electrical and Computer Engineering Commons](#), and the [Metallurgy Commons](#)

Recommended Citation

M. E. Straumonis and C. Kim, "Etch Patterns On Zone-Refined Fe," *Journal of the Electrochemical Society*, vol. 117, no. 4, pp. 517 - 519, The Electrochemical Society, Jan 1970.

The definitive version is available at <https://doi.org/10.1149/1.2407558>

This Article - Journal is brought to you for free and open access by Scholars' Mine. It has been accepted for inclusion in Electrical and Computer Engineering Faculty Research & Creative Works by an authorized administrator of Scholars' Mine. This work is protected by U. S. Copyright Law. Unauthorized use including reproduction for redistribution requires the permission of the copyright holder. For more information, please contact scholarsmine@mst.edu.

Etch Patterns on Zone-Refined Fe

To cite this article: M. E. Straumanis and C. D. Kim 1970 *J. Electrochem. Soc.* **117** 517

View the [article online](#) for updates and enhancements.

You may also like

- [Maskless convex corner compensation technique on a \(1 0 0\) silicon substrate in a 25 wt% TMAH water solution](#)
Mile M Smiljani, Vesna Jovi and Žarko Lazi
- [Fracture behavior of lithium single crystal in the framework of \(semi-\)empirical force field derived from first-principles](#)
Sébastien Groh and Masud Alam
- [Tuning critical resolved shear stress ratios for bcc-titanium Ti21S via an automated data analysis approach](#)
Kaustubh Venkatraman, Meriem Ben Haj Slama, Vincent Taupin et al.

Etch Patterns on Zone-Refined Fe

M. E. Straumanis* and C. D. Kim

Graduate Center for Materials Research and Department of Metallurgical Engineering of the University of Missouri-Rolla, Rolla, Missouri

ABSTRACT

Upon dissolution of zone-refined Fe in strong acids, mainly three kinds of corrosion patterns were observed in the crystallites of the sections. Regardless of the acids, the {110} plane always appeared on the three patterns in the form of smooth and even steps, ledges, or facets. The {112}, {122}, and {123} planes were also developed but to a much lesser degree. The {100} and {111} planes were not observed because grains of the respective orientation were missing on the sections. Attempts were made to explain the formation of the planes by taking into consideration the reticular density of the planes and the frequency of their appearance. The theoretical relative corrosion rates of the separate crystallographic planes were estimated. The trend obtained agreed with the observed rates.

Zone-refined iron is attacked only slightly even by strong acids. As a result, in contrast to a previous investigation where a fine crystalline Fe was used (1), characteristic etch patterns appeared on the polycrystalline sample, each grain showing an array of steps, ledges, and facets. The surface was also highly resistive to atmospheric corrosion.

Etch patterns on single Fe crystals (2, 3), kinetics of dissolution of Fe whiskers (4), potentials (5), and anodic dissolution rates of separate crystal planes (6) were investigated previously. However, no reports on angular measurements between the ledges produced on single crystallites of an iron sample by the action of strong acids could be found. The aim of this study was, therefore, to determine the indices of the faces developed on separate grains during corrosion of zone-refined Fe in several acids and to compare the results with those of other investigators who worked, *e.g.*, with single crystal spheres and plates (2,3,6).

The luster of the etched samples originates not only from the strongly reflecting ledges on each grain, but also from other, usually weaker reflecting step systems. If these systems are within the same crystallographic zone, the angles between them can be measured with an optical goniometer. As the wide and shiny steps (see *e.g.*, Fig. 4) are easily indexed (see below), the indices of the other faces of the same zone can be determined from the angles optically measured, the bright steps serving as reference planes.

Samples and Technique

High-purity zone-refined Fe was obtained from Battelle Memorial Institute. The main impurities in ppm were: Ni, 20; Al, 15; Ca, 10; Si, 10; C, 9; P, 9; Cu 7; and other elements in still smaller amounts. The Fe rods were sliced into pieces of about 5 mm thick, and each slice was ground and polished. The specimens, 1-5 cm² in surface area, were deeply etched using as solutions concentrated HCl, 1.5N HNO₃, 2N H₂SO₄, aqua regia (25%), and concentrated HF (48%). Two hours produced an etch pattern in concentrated HCl, whereas several days were required to obtain the same pattern in 2N H₂SO₄. Etching in each solvent was continued until the grain boundaries were clearly resolved.

As the Fe rods consisted mainly of large crystallites (2-5 mm in diameter), their orientation could be determined from Laue back-reflection patterns (Fe radiation, sample-to-film distance, 3 cm). The strong reflections were read with the aid of the respective Greninger (-Bond) chart, plotted into Wulff's stereonet and the indices found in the usual way (7, 8).

To determine the indices of the brightest, most reflective planes developed by etching (Fig. 4) on each grain of the sample, the latter was mounted on the head of an optical goniometer and so adjusted that the

reflective steps of the grain became perpendicular to the goniometer vertical circle axis, which, in turn, was parallel to the x-ray beam.

With the goniometer head and the adjusted sample now in the Laue camera, the indices of the surface of the parallel steps could easily be found. Minor optical reflections, *e.g.*, the sides of the steps with larger area, were determined in the same way. This procedure of investigating grain after grain was continued on several sections of the polished and etched Fe samples.

Results

Figure 1, representing a unit triangle of a standard (001) stereographic projection, shows a random orientation distribution of the grains.

The etch patterns on each grain were similar to each other although various etchants were used. However, only concentrated HCl produced very clean surfaces with a shining metallic luster. Samples treated with H₂SO₄ and HF were covered with a layer of whitish-gray salts, and those etched with HNO₃ and aqua regia partly exhibited a brown oxide film. Nevertheless, the surface structure of all the grains on the sections was generally similar.

Three major corrosion patterns could be distinguished: (i) a set of grooves running nearly parallel across the grains (Fig. 2); (ii) triangles or pyramids (Fig. 3); and (iii) irregular but shiny ledges running roughly parallel to each other (Fig. 4). Evidently the formation of these etch patterns depended on the degree of inclination of some crystallographic planes within the grains to the surface of the sample.

All of the Laue patterns obtained from the larger area facets of different grains, etched with various

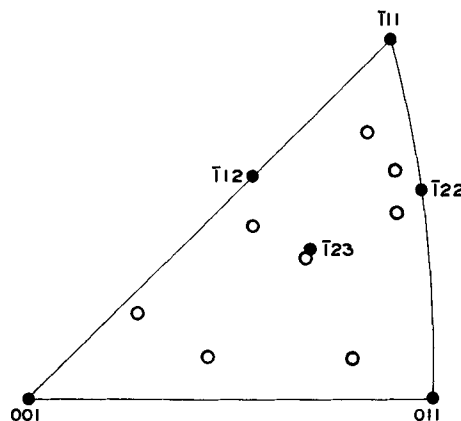


Fig. 1. Surface orientation of 8 large grains on a sample of zone-refined Fe.

* Electrochemical Society Active Member.



Fig. 2. Crystallite of zone-refined Fe. Etchant: conc. HCl, 12 hr. 150X.

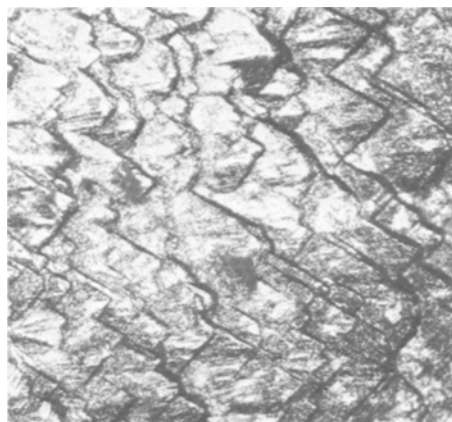


Fig. 3. Ditto. Triangles and set of parallel short dark lines on another grain. 150X.

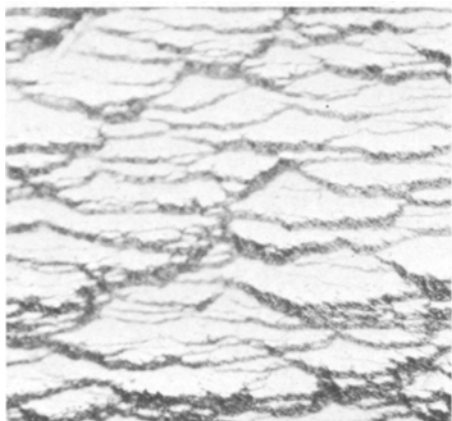


Fig. 4. Ditto. Irregular ledges roughly parallel to each other. 320X.

acids, were indexed. The orientation of these facets is shown by their projections (Fig. 5).

In HF the grains were covered with a layer of corrosion products too thick for goniometric examination. No attempts were made to study these specimens.

Figure 5 clearly shows that the indices of the larger reflecting areas were (in HCl): 6 close to (011), 4 to $\bar{1}22$, and one to $\bar{1}23$. In aqua regia: 6 close to (011), 1 to $\bar{1}22$. In H₂SO₄: 5 close to (011), and in HNO₃: 5 close to (011) and 2 to $\bar{1}22$. The planes mentioned are not in the ideal positions of (011), $\bar{1}22$, and $\bar{1}23$ because the planes formed due to corrosion are never smooth and large enough to produce sharp signals from each crystallite in the goniometer during the setting procedure.

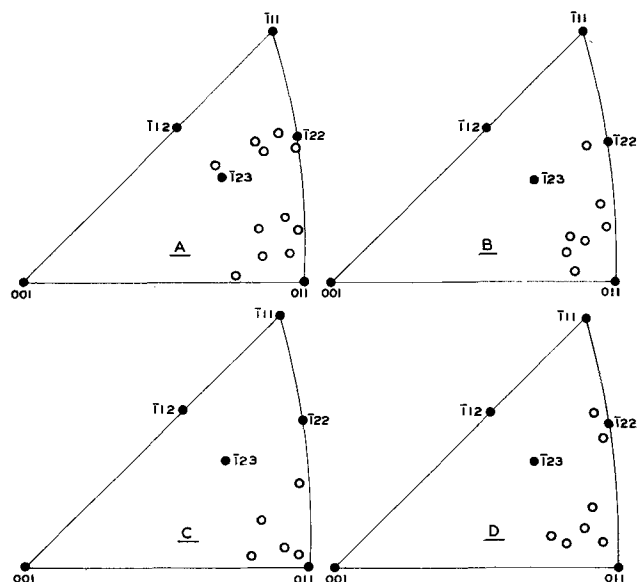


Fig. 5. Orientations of the best defined facets on the grains of Fe samples etched with various acids: A, conc. HCl (10 grains); B, 25% aqua regia (7 grains); C, 2N H₂SO₄ (5 grains); D, 1.5N HNO₃ (7 grains); full circles, ideal planes; open circles, planes determined.

In addition, there were a series of other weaker optical reflections, the respective planes inaccessible to the x-ray technique. The optical goniometer was a useful tool here.

The angles between the reflections on crystallites showing the etch pattern, Fig. 2, were measured normal to the striations. Surprisingly enough, no new planes were found (Fig. 6).

To obtain as many reflections as possible on grains with etch pattern, Fig. 3, the vertical circle (carrying the sample) was also rotated: at each 5° interval the corroded surface of a certain grain was scanned by turning the horizontal circle. However, the reflecting planes were all the same, but in addition there were weak reflections from {112} and {123}.

Etch pattern 3 (Fig. 4) was investigated in the same way. Very strong reflections from the {011} planes and weak ones from {122} were obtained.

Generally, only the {110} plane appeared as a main facet on the corrosion patterns of zone-refined Fe; the other planes were much smaller in extent and dissolved faster in the acids used.

Discussion

Since the Fe used for the etching experiments was very pure, no significant local corrosion ensued. The corrosion patterns observed are, therefore, a consequence of the reaction of the acids with the body centered structure of crystalline Fe. Such a possibility is deduced from the very slow attack of carbonyl Fe by acids (1) and by the recent facts that the four acids in agreement with Buck and Leidheiser (2, 3), produced in essence the same corrosion patterns (see Fig. 2, 3, and 4) and the planes

$$\{110\}, \{112\}, \{122\}, \text{ and } \{123\} \quad [1]$$

This corrosion form of Fe can be compared with that calculated for a body centered crystal (in equilibrium with its vapor) by Kossel and Stranski (9-12)

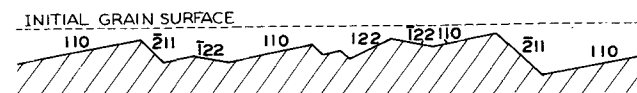


Fig. 6. Planes measured on a crystallite of Fig. 2 with striations within the vertical axis of the horizontal circle of the optical goniometer. Section perpendicular to the striations.

{110}, {100}, {112}, and {111} [2]

whereby the appearance of other planes is not excluded.

The explanation as to why in series [1] the {100} and {111} planes are missing is that none of the grains on the sections were close to these orientations (Fig. 1). On the other hand the {110}-planes are not mentioned, e.g., by Buck and Leidheiser. Thus, there are considerable differences between the theoretical equilibrium form [2] and the corrosion form obtained with Armco Fe or L-steel (2, 3), but there are minor ones between [2] and [1].

However, series [2] can also be obtained, if one assumes that the most stable planes in a homopolar crystal are those with the highest reticular density. The sequence of planes with decreasing relative density, s , is then

(110), (100), (112), (111), (123), (122) [3]

s , as listed in Table I, was obtained from both purely geometrical considerations and by calculation from

$$s \sim 1/(h^2 + k^2 + l^2)^{1/2} \quad [4]$$

where h , k , and l are the x-ray indices of a body-centered structure (13).

Thus, the experimental corrosion form [1], would agree with the theoretical form [2] or [3] if the {001} and {111} planes had been in the section areas of the Fe samples.

A further question is which of the planes of form [3] would appear as dots and which would produce larger areas during attack by strong acids? Only estimates can be made, and for this purpose the frequency of appearance of various planes (multiplicity factor, m , in x-ray analysis) has to be considered. Assume that the {001}-plane of some crystallites is inclined to the surface of the sample and an etchant is applied. The latter will remove the atoms from the surface and penetrate into the depth of the respective crystallite. But on its way, before reaching the next sound {001}-plane it will meet one of the high reticular density {101}-planes which occur more frequently ($m = 12$, see Table I) than the {100}-planes with $m = 6$.

The corrosive process, therefore, will be blocked by such planes and penetrate laterally and parallel to them to produce a stairlike structure across the grains with {110} as main broad faces and with {112}, {221}, and others as narrow lateral ones (see, e.g., Fig. 4 and 6). Even the {hkl} planes, such as {123} will appear. However, if a {001}-plane is parallel to the sample surface, it may remain during corrosion. The same pertains to the {111}-plane, which is corroded, according to Buck and Leidheiser (2, 3), faster than {001}, evidently because of the lower reticular density (Table I).

The relative velocity of corrosion, V , of various crystallographic planes can also be estimated, assuming that the rate is proportional to the multiplicity, m , of the respective dissolving planes and inversely proportional to the reticular density s . This operation

Table I. Relative reticular density, s , of some planes of b.c. metals. Multiplicity factor, m , and relative corrosion rates, m/s

Plane	s	m	m/s	m/s^*	$m/s \text{ exp.}^{**}$
100	1.000	6	6	1	1
110	1.412	12	8.5	1.42	2.41
111	0.577	8	13.9	2.32	3.51
112	0.816	24	29.4	4.90	—
122	0.334	24	71.9	11.96	—
123	0.535	48	89.7	14.96	2-4.8†

* Corrosion rate of {100} is assumed to be 1.

** According to Shemenski *et al.* (4) for Fe whiskers in 1N H₂SO₄ + 0.2N K₂S₂O₈.

† Buck and Leidheiser (3) for steel in boiling 0.2M citric acid.

will also reduce the corrosion rates of the various planes to the same surface area

$$V = km/s \quad [5]$$

Thus a plane will dissolve faster, the more equivalent directions available to the etchant: the corrosion process on a {001}-plane spreads in 5 directions (or 6, if undermining occurs); on a {110}-plane—in 6 to 12 directions and on {123} or generally {hkl}—in at least 24 directions (up to 48 during undermining), etc. The latter face will, therefore, produce a much higher corrosion rate than {100}. This statement is confirmed by the results of Buck and Leidheiser (3). No extensive faces will be developed, only small dots, because of the various inclinations of the {123} planes to the sample surface. A development of larger {123} reflecting planes thus becomes impossible: due to the increased rate of dissolution, corrosion resistive planes, e.g., {101} will be reached soon and steps will develop as already described.

The theoretical maximum m/s values are summarized in Table I, the next column showing the relative rates. In the last column rate ratios, as obtained with Fe whiskers by Shemenski *et al.* (4), are given for comparison. Although objections can be raised against this method of calculating rate ratios, the trend does agree with the experimental data obtained by several authors for various kinds of Fe in different solvents (2, 3, 4, 6). Calculated rate ratios for the {hhl} and {hkl} planes are too high because the highest m values were taken. Furthermore, ion diffusion rates would limit the velocity of corrosion. On the other hand oxidizers, such as K₂S₂O₈ would increase the low rates. The presence of impurities in appreciable amounts would distort the over-all picture. Taking these factors into consideration, the agreement between the theoretical and experimental rate ratios for various crystallographic planes should be regarded as very satisfactory, explaining why the corrosion rate depends on the crystallographic direction, at least for pure Fe.

Acknowledgments

Thanks are expressed to the Office of Naval Research for the funds provided, to Dr. W. J. James, Director of the Graduate Center for Materials Research, and to Dr. A. A. Khan for useful discussion.

Manuscript submitted June 27, 1969; revised manuscript received November 21, 1969. This paper is Contribution 68 from the Graduate Center for Materials Research.

Any discussion of this paper will appear in a Discussion Section to be published in the December 1970 JOURNAL.

REFERENCES

1. M. Centnerszwer and M. E. Straumanis, *Z. physik. Chem.*, **A162**, 94 (1932).
2. W. R. Buck and H. Leidheiser, Jr., *Z. Elektrochem.*, **59**, 748 (1955).
3. W. R. Buck and H. Leidheiser, Jr., *This Journal*, **104**, 474 (1957).
4. R. M. Shemenski, F. H. Beck, and M. G. Fontana, *J. Appl. Phys.*, **36**, 3909 (1965).
5. F. N. Speller, "Corrosion, Causes and Prevention," p. 79, McGraw Hill Book Co., New York (1926).
6. H. J. Engell, *Arch. Eisenhüttenw.*, **26**, 393 (1955).
7. A. B. Greninger, *Z. Krist.*, **91**, 424 (1935); *Trans. Met. Soc. AIME*, **117**, 61 (1935).
8. See, e.g. B. D. Cullity, "Elements of X-ray Diffraction," Addison-Wesley, Reading, Mass. (1956).
9. W. Kossel, *Nachr. Ges. Wiss. Göttingen, Mathphysik. Klasse* **1927**, 135.
10. I. N. Stranski, *Z. physik. Chem.*, **A136**, 259 (1928).
11. I. N. Stranski and R. Kaischew, *Z. Krist.*, **78**, 373 (1931).
12. B. Honigmann, "Gleichgewichts- und Wachstumsformen," pp. 10 and 116, D. Steinkopff, Darmstadt (1958).
13. F. C. Phillips, "An Introduction to Crystallography," p. 245, J. Wiley & Sons, Inc., New York (1966).