CRYSTAL MORPHOLOGY AND MECHANISMS OF GROWTH

OF α-Fe₂O₃ WHISKERS ON IRON

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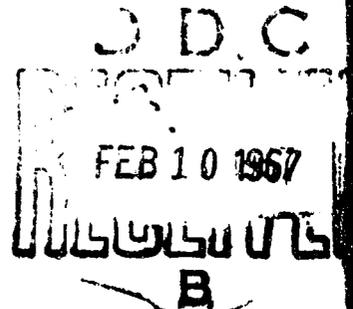
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ABSTRACT

The morphology of α-Fe$_2$O$_3$ whiskers formed on iron at 400° to 500°C in dry oxygen was studied. Diffraction patterns of individual whiskers and texture patterns of oxidized surfaces showed the whisker axis to be $[\bar{1}\bar{1}20]$. The axial rotation indicated by the pattern is that resulting from an axial twist. This is good evidence that the most simple oxide whiskers have a single axial screw dislocation. Arguments are presented for the view that growth of the whisker occurs by diffusion of iron atoms or ions through the dislocation and reaction with oxygen at the tip.

INTRODUCTION

When iron is heated in oxidizing atmospheres, localized oxide growths form on the oxidized iron surface.[1,2,3] The crystal habit of these oxide growths and the extent of oxide growth depend upon many factors, including temperature, time of reaction, internal or external stress, impurities in the metal, pre-treatment of the metal, and the composition of the oxidizing atmosphere.[3]

Oxide whiskers formed on pure annealed iron at 400°C to 500°C in dry oxygen have diameters of about 150 Å or more, lengths up to 4×10^5 Å, and whisker densities on the surface up to $10^8/cm^2$.[3] Electron diffraction studies show that the most simple whiskers are single crystals of $\alpha\text{-Fe}_2O_3$.

This paper will present: (1) new selected area electron diffraction studies on single iron oxide whiskers formed during the oxidation of iron in dry oxygen, (2) morphological evidence for screw dislocations in oxide whiskers, and (3) a growth mechanism for oxide whiskers on iron.

EXPERIMENTAL

A large file of carefully oxidized pure iron wires were available from earlier studies.[3] Before oxidizing, the iron wires had been carefully annealed and cleaned. The iron wires were then oxidized in dry and purified oxygen under controlled temperature and time conditions.

An RCA EMU-3D electron microscope with selected area diffraction was used at 100 kV electron energy. The relative rotation of the selected area electron diffraction pattern was determined by use of the selected area images and the selected area diffraction patterns of asbestos fibers.

STRUCTURAL INFORMATION

A. α-Fe$_2$O$_3$ Crystal Structure

Pauling and Hendricks[4] determined the crystal structure to be trigonal or rhombohedral, space group R $\bar{3}$ C. This structure was confirmed by Blake et al.[5] in 1966. The latter authors give the following structural hexagonal dimensions: $a = 5.038 \pm 0.002$ Å, $c = 13.772 \pm 0.012$ Å, and $c/a = 2.733 \pm 0.015$. We have calculated the corresponding structural rhombohedral dimensions to be $a = 5.469$ Å and $\alpha = 55°13.9'$.

B. Unit Cells and Indices

Figure 1 shows top and front views and dimensions for the unit cells for α-Fe$_2$O$_3$ and its isomorphs. Four unit cells are in common use. The conventional structural hexagonal and rhombohedral unit cells are shown at the left. Four indices are used to describe a set of lattice planes in terms of the hexagonal cell. The conventional morphological rhombohedral unit cell is shown at the right. The face-centered rhombohedral F unit cell has an a value of twice that for the conventional morphological rhombohedral unit cell. This cell is shown at the center. The rhombohedral F cell angle α is nearly 90°. It is this relationship to the face-centered cubic cell which makes the rhombohedral F cell

convenient for indexing. Directions are nearly normal to lattice planes with the same indices. This cell is used in indexing all of our selected area diffraction patterns, and is referred to wherever the unit cell is not identified. Conventional structural hexagonal and rhombohedral indices will also be given.

RESULTS AND DISCUSSION

Figure 2 shows a selected area electron diffraction pattern from an iron oxide whisker measuring 1.5 microns in the selected area image. Indexing was made using the rhombohedral F unit cell. The orientation of the projection of the axis of the whisker lies normal to the layer lines of the pattern shown in Figure 2, i.e. in the $[\bar{2}20]$ direction. This whisker axis is $[\bar{1}\bar{1}20]$ and $[\bar{1}01]$ in the conventional structural hexagonal and structural rhombohedral indices, respectively.

An analysis of the diffraction spots in Figure 2 shows two nets, the first is a net normal to the $[111]$ direction and the second is a net normal to the $[\bar{1}10]$ direction. The angles between rows of spots are within $1°$ of the angles between rows of index points in the reciprocal lattice of α-Fe_2O_3. The sections of whisker giving the two reciprocal lattice nets lie at $32.4°$ to one another.

Both nets of Figure 2 include the origin, $\bar{2}20$, and $2\bar{2}0$. We conclude, therefore, that the rotation axis of the pattern is $[\bar{2}20]$. The same conclusion results from the fact that the spots of each layer line are indexed by points in a corresponding reciprocal lattice net normal to $[\bar{2}20]$.

Two additional oxide whiskers which have been studied satisfactorily by selected area electron diffraction are of interest. In one, two new nets of spots, normal to the [001] and [II2] directions, respectively, were found. The rotation axis of the oxide whisker was [Ž20]. The whisker axis was proved to be the rotation axis as follows: The whisker axis lies in a plane normal to the pattern of the second oxide whisker different from the plane of the whisker axis for the whisker giving the pattern shown in Figure 2. These two planes intersect in the [Ž20] rotation axis. If the whisker axis is the same in the two cases, it is [Ž20].

For the third indexed pattern, the same rotation axis was found, but not close to 90° to the beam direction. Again the projections of the whisker and rotation axes coincide in the pattern. This is a more common type of diffraction pattern than that shown in Figure 2. Bent, kinked, and apparently multiple whiskers introduce further complications.

The three different selected area patterns which were indexed include very weak extra anomalous diffraction spots on the layer lines. Some of the spots correspond in position in the pattern to the systematically absent diffraction from planes of the form $\{11\overline{1}\}$, but most of the spots could not be indexed. The anomalous spots were also found by Takagi.[2]

Since the whisker axis and the rotation axis coincide we are led to hypothesize that the whisker is twisted. This is consistent with the diffraction patterns of individual whiskers, in that they show a limited rotation by including diffraction represented by appropriately limited sectors of the reciprocal lattice. Since no grain boundaries are commonly revealed by diffraction contrast

in the micrographs, any grain boundaries which may exist must be such that the contrast is difficult to observe. The probability that a small number of untwisted crystals might lie in the special orientations in the beam indicated by the diffraction patterns of individual whiskers is negligible.

In addition to evidence in the selected area diffraction patterns of individual whiskers, we find evidence of axial twist in the electron diffraction patterns of whiskers growing from a surface. These patterns contain long, straight streaks which include elongated spots on arcs of several rings of the pattern between 400 and $4\bar{2}0$, ($02\bar{2}4$ and $12\bar{3}2$ in structural hexagonal indices).

The angles of the streaks on the pattern and the positions of the spots on the streaks show that each streak is the second layer line for limited rotation about the whisker axis. That is, the streaks correspond to diffraction represented by the plane of the reciprocal lattice normal to the whisker axis, $[\bar{2}20]$, and passing through $\bar{2}20$ (or $2\bar{2}0$). The rotation of the crystal about $[\bar{2}20]$ is evidenced further by the continuity of the streaks, as follows: the intensity between the spots results from integration over the sector of the reciprocal lattice plane by rotation through the reflecting sphere.

AXIAL TWIST CALCULATIONS

The axial twist α can be calculated from an equation given by Eshelby,[7] $\alpha = K\, b/A$. Here b is the length of the Burgers vector, A is the cross section area, and K is a constant which depends on the shape of the cross section. $K = 1$ for an elliptical cross section with central dislocation. If we approximate the cross sectional area A with the area of a circle of the whisker image diameter, we can calculate the axial twist

and compare this with the observed twist. The full length of whisker in the
selected area image for the pattern of Figure 2 was 1.5 μ. The diameter,
including contamination, was about 300 Å. Assuming the smallest Burgers vector,
i.e. the minimum repeat distance along the whisker axis, 5.03 Å, the axial twist
is calculated to be 41° per micron. The sections of whisker giving the two
reciprocal lattice nets of Figure 2 are at 32.4° to one another by rotation
about the whisker axis. If at most these two sections lie at the ends of the
1.5 μ whisker section, the axial twist is not less than 22° per micron; thus
the 5.03 Å Burgers vector is likely.

There are many reasons for a discrepancy between the calculated and
observed axial twist. (1) Both the cross section and the axial twist were
difficult to determine, (2) the elastic anisotropy of α-Fe_2O_3 may be important
and should be included in the theory, (3) the dislocation strain may have a
planar character which would alter the strain distribution near the core,
(4) the discrete atomic structure and the decreased stress at high strain near
the dislocation may result in a smaller twist than that calculated by the simple
formula of Eshelby,[7] and (5) surface stresses may decrease the axial twist.

COMPARISON WITH PREVIOUS MORPHOLOGICAL STUDIES

Miyake[8] reported in 1937 a preferred orientation in the electron
diffraction pattern of α-Fe_2O_3 formed on an oxidized iron specimen. He stated
that the (10$\bar{1}$) structural rhombohedral plane was parallel to the surface.
Apparently, lack of knowledge of the existence of oxide whiskers precluded a
complete interpretation. The (10$\bar{1}$) structural rhombohedral plane given by
Miyake is normal to the whisker axis we have determined.

Takagi[2] determined the growth axis of localized α-Fe$_2$O$_3$ growths using diffraction patterns of individual growths. That Takagi's work preceded the general recognition of axial twist apparently explains his failure to recognize the rotation pattern. Takagi oxidized pure iron in flowing dry oxygen, but not so dry as to prevent the formation of oxide platelets. He observed that whiskers and sometimes smaller blades grew from broken bases of blades. This and other observations suggested that growth is from the top. Takagi postulated a screw dislocation mechanism for the localized growths. He considered surface diffusion to provide the transfer of metal.

Bigot[9] and Talbot and Bigot[10] failed to correctly analyze their selected area electron diffraction patterns of α-Fe$_2$O$_3$ whiskers and platelets. They give no indexing for their whisker rotation patterns. Instead they determine the whisker axis on the basis that the most intense spots are aligned parallel to the smallest dimension of the crystal. They give incorrectly the structural hexagonal direction $[10\bar{1}0]$ as the whisker axis without supporting data. The most intense arc in the fiber texture pattern for whiskers on an oxidized iron surface is at 90° to the surface in the $11\bar{2}0$ ring. This results from the preferred orientation of the $(11\bar{2}0)$ planes, which are normal to the $[11\bar{2}0]$ whisker axis. Thus, the most intense arc is on a normal to the $[10\bar{1}0]$ direction, but this is not the whisker axis.

THE TRANSPORT MECHANISMS OF WHISKER GROWTH

Three mechanisms have been put forward for the growth of oxide whiskers: (1) surface diffusion to the tip of the whisker, (2) extrusion from the oxide, and (3) growth by internal diffusion in a hole or screw dislocation.

The possibility that α-Fe_2O_3 whiskers result from some extrusion process seems unlikely because the growths are so uniform and are apparently of high crystalline perfection.

It is also unlikely that α-Fe_2O_3 whiskers could grow by a surface transport mechanism as suggested by Takagi[2] from a surface with competing α-Fe_2O_3 surface growth mechanisms. The hypothesis of a surface growth mechanism would require that other growth mechanisms or the existence of α-Fe_2O_3 crystals growing by only mechanisms other than the mechanism of whisker tip growth be very limited. The existence of species and mechanisms for surface transport of iron sufficient to produce the rapid growth rates and the extreme lengths of the α-Fe_2O_3 whiskers is not known and is unlikely because of the stability of the Fe_3O_4 from which the iron would be transported. Furthermore, the nucleation of α-Fe_2O_3 on Fe_3O_4 is a common phenomenon and involves only a change from cubic close-packing to a distorted hexagonal close-packing of oxygen in the α-Fe_2O_3 lattice together with a change in the iron positions. One cannot readily propose that the driving force for rapid diffusion to the α-Fe_2O_3 whisker tips can be provided by high concentrations of iron species mobile on the Fe_3O_4 surface.

Gulbransen[11] has proposed a model for the growth of oxide whisker assuming the whiskers are hollow or contain a screw dislocation at the center. The essential feature of this model is that this internal defect allows rapid

diffusion of iron to occur compared to normal lattice diffusion. The

morphological studies presented demonstrate that oxide whiskers are single

crystals of high crystalline perfection and show axial twist. The latter property

is strong evidence for a screw dislocation at the center of the whisker.

Figure 3 shows a model for the whisker growth on iron. The whisker

contains an internal hole or screw dislocation where grain boundary or internal

surface diffusion of iron occurs along a gradient in chemical potential.

Most of the growth occurs by reaction with oxygen atoms or ions at the

tip of the whisker. Since the diameter is nearly uniform during growth it follows

that cationic mobility is much smaller in the lattice than along the dislocation.

Good measurements of the growth rates of oxide whiskers are not yet

available. Pease and Ploc[12] have observed initial growth rates at 500°C of

over 0.2 μ/min., an average rate over five minutes. Takagi[2] observed growth

rates up to 2 μ/min. at 700°C in the first minute. Whether the growth observed

in these cases should be classified as whiskers or platelets cannot be determined

from the information given.

The structures of the sections where the cation diffusion rate is

high cannot be given at this time. It may be that information on these structures

is contained in the anomalous diffraction. The structure in the immediate

vicinity of the screw dislocation must show ions either displaced by the strain

into some distortion of the α-Fe_2O_3 structure, or otherwise positioned, possibly

in some disordered structure. In either type of structure, diffusion coefficients

would be expected to be different from those in the much less distorted

structure of more than half of the cross section of the whisker. This outer

region probably exhibits the bulk or lattice ionic diffusion coefficients.

REFERENCES

(1) G. Pfefferkorn, Naturwiss. $\underline{40}$, 551 (1953).

(2) R. Takagi, J. Phys. Soc. Japan $\underline{12}$, 1212 (1957).

(3) E. A. Gulbransen and T. P. Copan, Faraday Society Discussions, No. 28, 229 (1959).

(4) L. Pauling and S. B. Hendricks, J. Am. Chem. Soc. $\underline{47}$, 781 (1925).

(5) R. L. Blake, R. E. Hessenick, T. Zoltai, and L. W. Finger, American Mineralogist $\underline{51}$, 123 (1966).

(6) ASTM X-ray Powder Data File, Card 13-534 (1964), Aravindakshan and Ali.

(7) J. D. Eshelby, Phil. Mag. $\underline{3}$, 440 (1958).

(8) S. Miyake, Inst. of Phys. and Chem. Res. (Japan) $\underline{31}$, 161 (1937).

(9) J. Bigot, Mem. Sci. Rev. Met. $\underline{60}$, 5 (1963).

(10) S. Talbot and J. Bigot, Mem. Sci. Rev. Met. $\underline{62}$, 261 (1965).

(11) E. A. Gulbransen, Rev. Metallurg. $\underline{67}$, 253 (1965).

(12) R.F.W. Pease and R. A. Ploc, Trans. Met. Soc. A.I.M.E. $\underline{233}$, 1949 (1965).

FIGURES AND FIGURE CAPTIONS

Figure 1 - α-Fe_2O_3 Unit Cells.   Dwg. 747A966

Figure 2 - Selected area electron diffraction. α-Fe_2O_3 RM 35096

whisker. 1.5 μ long, 10^{-15} g. Indexed with a

face-centered rhombohedron, α = 85.7°. Nets

normal to [111] and [110] included.

Figure 3 - Model of whisker growth during oxidation of   Dwg. 294B898

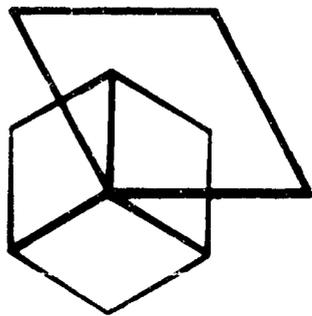iron, 400°C, dry O_2.

Dwg. 747A966

Fig. 1 — α-Fe$_2$O$_3$ unit cells
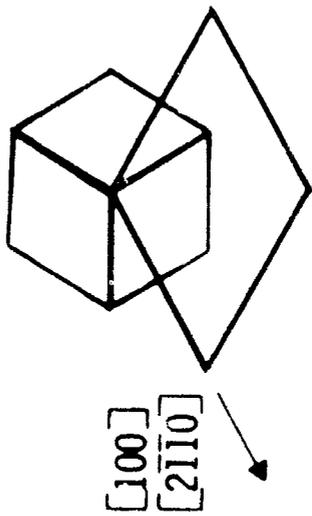
Conventional
Structural
a = 5.4228 Å, α = 55.273°
a = 5.0317 Å, c = 13.737 Å

[100]
[2$\bar{1}\bar{1}$0]

[0001]

[100]
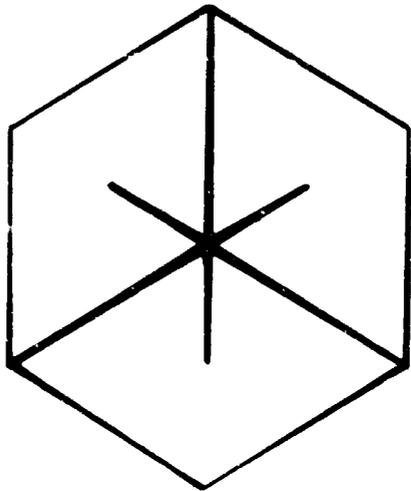
Rhombohedral F
Structural
a = 7.3976 Å
α = 85.715°

[100]

Conventional
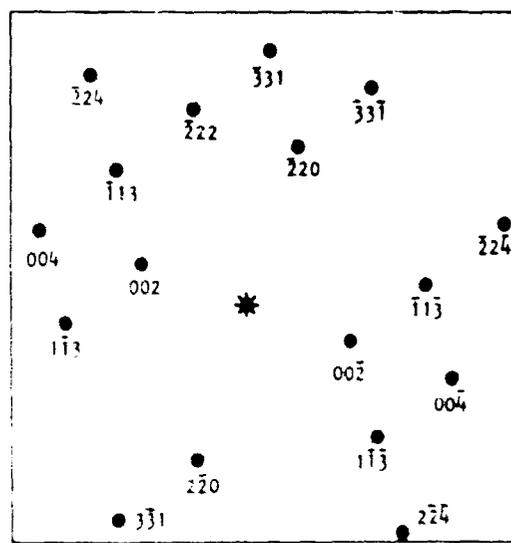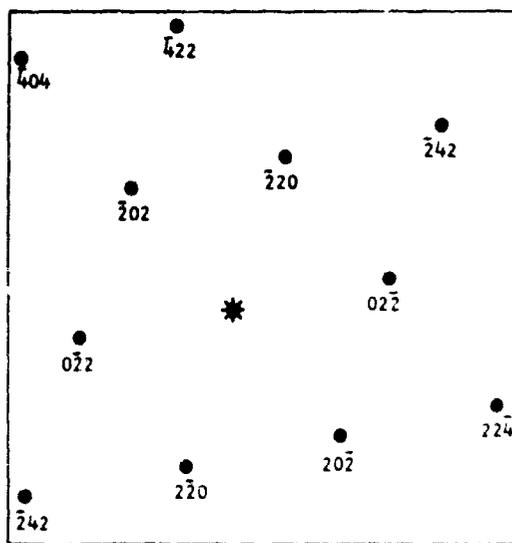Morphological
a = 3.6988 Å
α = 85.715°
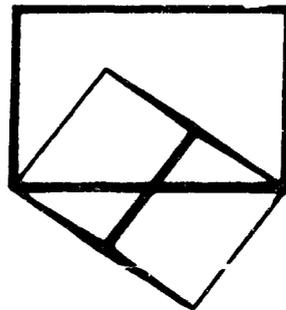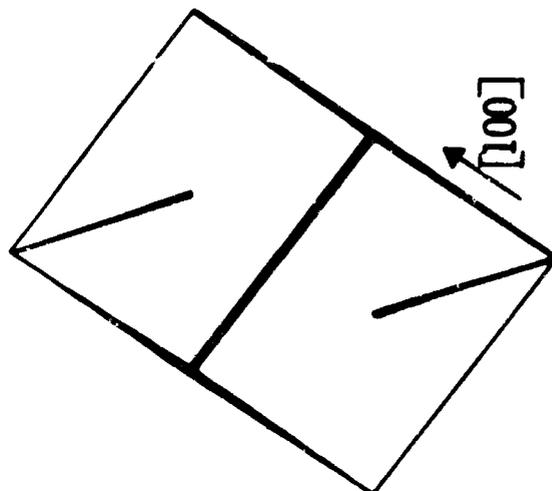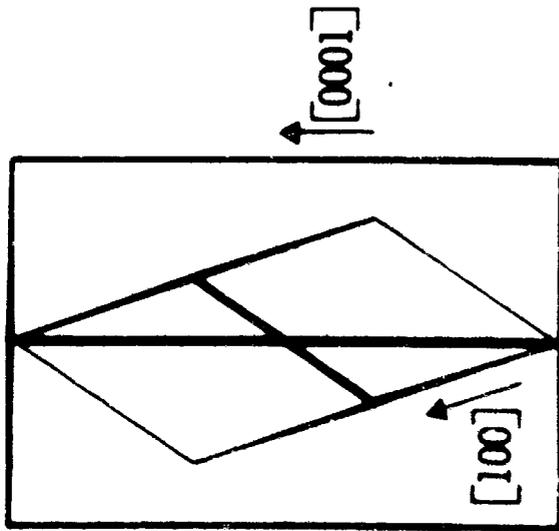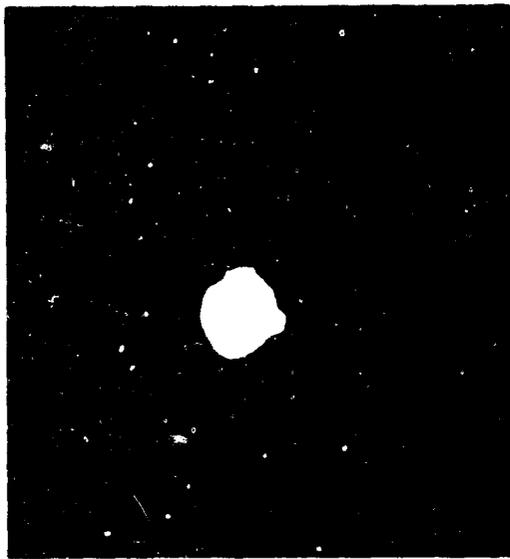
Fig. 2 —Selected area electron diffraction, α-Fe_2O_3 whisker, $1.5\,\mu$ long, 10^{-15} g. Indexed with a face-centered rhombohedron, $\alpha = 85.7°$. Nets normal to $[111]$ and $[110]$ included.

O_2

Tip growth due to internal diffusion in hole

Fe^{+++}

$10^2 < L_z < 10^5 Å$

Fe^{+++}

O_2

$L_x \sim 50 Å$

Lateral growth due to lattice diffusion of iron outward

Growth Site

Fe^{+++}

L_{x_0}

Normal Oxide

Metal
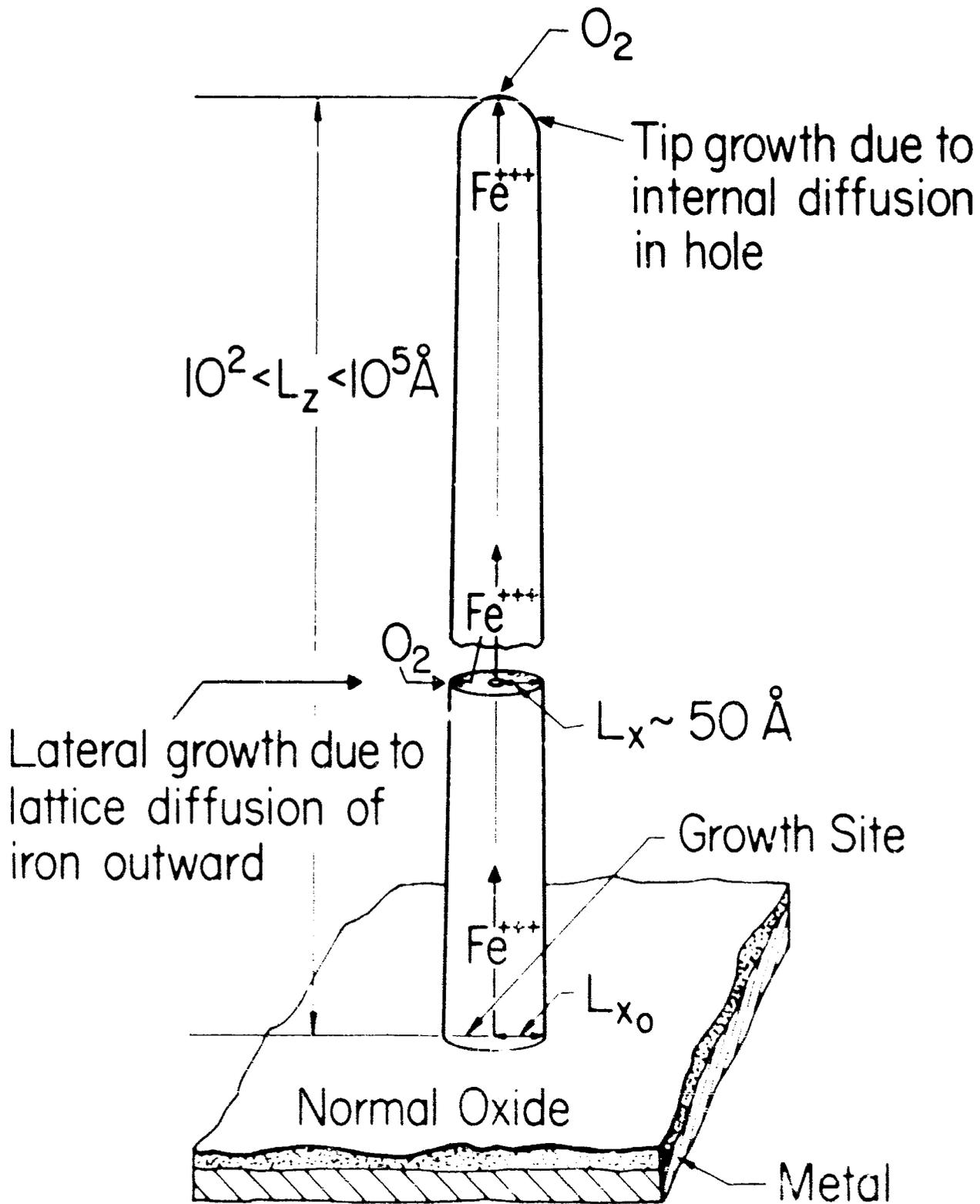
Fig. 3 Model of whiske growth during oxidation of iron 400°C dry O_2

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13 ABSTRACT

Growths on pure iron at 400°C to 500°C in dry oxygen were studied. Selected area electron diffraction patterns of individual whiskers as well as electron diffraction texture patterns of oxidized surfaces showed the whisker axis to be $\{1\bar{1}20\}$. The axial rotation indicated by the pattern is that resulting from an axial twist. The axial twist provides evidence that the most simple oxide whiskers have a single axial screw dislocation with a 5.03 Å Burger's vector. Arguments are presented for the view that growth of the whisker occurs by diffusion of iron atoms or ions through the dislocation and reaction with oxygen at the tip.

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Oxidation						
Crystal growth						
Whiskers						
Corrosion						
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