Localized Diffusion Processes in the Growth of α-Fe_2O_3 Whiskers and Platelets on Iron

By E. A. Gulbransen, T. P. Copan, and K. F. Andrew
Westinghouse Research Laboratories, Pittsburgh (Pennsylvania) 15235

Dedicated to Professor Walter Feitknecht

Summary

Electron optical studies of the oxidation of iron shows a wide variety of localized oxidation processes occur. Long oxide whiskers, blade shaped and rounded oxide platelets form depending on the environment, metal structure and stress. Selected area electron diffraction was used to determine the structural features of the several α-Fe_2O_3 crystals and their mechanisms of growth.

Introduction

The discovery of oxide nuclei[1, 2] and of oxide whiskers[3, 4] and platelets[5] in the oxidation of metals came as a surprise to many workers. The then-accepted model of

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[1] J. Bardolle and J. Bénard, *Mem. Sci. Rev. Met. 49* (1952) 613.

[2] J. Bénard, *Oxydation des Métaux*, Gauthiers-Villars, Paris 1962.

[3] G. Pfefferkorn, *Naturwiss. 40* (1953) 551; *Z. Metallkde. 46* (1955) 204.

[4] R. Takagi, *J. Physic. Soc. Japan 12* (1957) 1212.

[5] E. A. Gulbransen and T. P. Copan, *Disc. Faraday Soc. 28* (1959) 229.

metal oxidation[6] assumed the presence of a uniform coherent oxide film with reaction occuring by the diffusion of oxygen or metal atoms and ions through lattice defects in the oxide. Dislocation and grain boundary diffusion processes and the influence of stress were not considered in the theory.

The formation of localized oxide growths suggests that the model of metal oxidation is not complete. In addition, the formation of these growths gives a new insight into the mechanisms of formation of oxide films, stress corrosion cracking, and metal fatigue.

The availability of oxide whiskers and platelets for study by electron diffraction and by electron microscopy makes possible an evaluation not only of their structural details but also an evaluation of the various growth mechanisms. Since the growths are single or bi-crystals, they give a unique opportunity for study of transport processes through oxide lattices and through well defined crystal imperfections. Results from these studies may be carried over to the study of the general oxidation mechanisms.

Experimental

a) *Oxide Whiskers*

The formation of long filaments of oxide whiskers during the oxidation of metals was first observed by PFEFFERKORN[3] and TAKAGI.[4] Both workers studied the edges of wires and of fine holes in metal sheets using transmission electron microscopy after oxidation. At this early date, the metals used and the reaction conditions were poorly defined. The oxide whiskers were formed after considerable oxidation of the metal had occurred.

We began a study of oxide whiskers in 1957[5, 7, 8] for the purpose of understanding localized corrosion and oxidation processes on iron and stainless steel. Six factors must be considered in discussing the growth of oxide whiskers and platelets. These are: (1) the crystal structure, (2) the crystal size and morphology, (3) the orientation of the oxide crystal with respect to the underlying interfaces, (4) the nature of the reaction site in the metal or on the oxide, (5) the effect of environment, metal impurities, and stress on the oxide growth, and (6) the mechanism of growth.

GULBRANSEN and COPAN[5, 7] made a careful study of the localized oxide growths formed on high-purity iron under carefully controlled oxidation conditions. In addition to the normal oxide film, fine oxide whiskers were formed on annealed high-purity iron in dry oxygen atmospheres at temperatures of 400° to 500°C. A few small fan-shaped oxide platelets were formed in the early stages of oxidation before the formation of oxide whiskers.

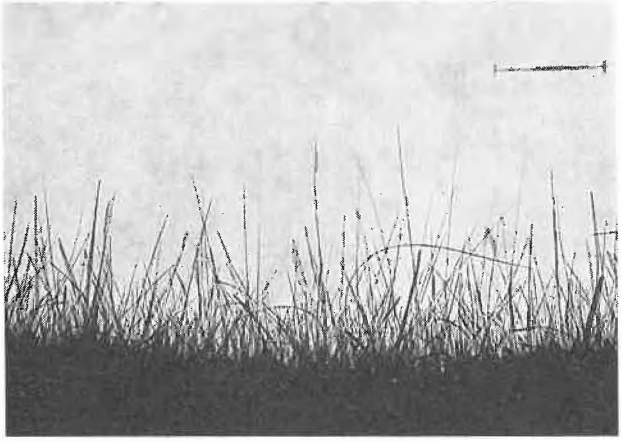

Figure 1. Oxide whiskers formed on Battelle iron at 400°C in dry oxygen for 48 hours. No applied stress. Micron length shown

Figure 1 shows an electron micrograph of an oxidized disk of Battelle grade of iron. The sample was reacted for 48 hours at 400°C in dry oxygen at 620 torr. The oxide whiskers were 150 Å or more in diameter, excluding contamination, and about 15,000 Å in average length. Some grew to lengths of 25,000 Å. A surface density of about 10^8 cm^{-2} was estimated.

Transmission electron diffraction patterns of the oxidized wire gave a pattern of α-Fe_2O_3. A summary of the properties and conditions of formation of oxide whiskers from our studies is given in Table I. The conditions for formation of oxide whiskers are dry oxygen, pure metal, and no stresses. The diameters of the simplest whiskers were uniform along the length of the whisker.

Table I. Summary of Data on Oxide Whiskers

1. Diameter $\sim$150 Å
2. Lengths up to 4×10^5 Å
3. Density up to 10^8/cm^2
4. Weight of 10^5 Å whiskers = 9.25×10^{-15} g
5. Crystal structure – hexagonal α-Fe_2O_3 – single crystal
6. Site area – 1.77×10^{-12} cm^2
7. Percent surface covered for density 10^8/cm^2 = 0.0177%
8. Conditions – dry oxygen, no stress, pure metal, random sites on oxide or metal
9. Elastic strain limit = 5% for 150 Å diameter whisker bent to 1500 Å radius
10. Stress at root = 3.1 ψ for 4×10^5 Å whisker, 150 Å diameter
11. Thickness – nearly independent of time
12. Melting of tip – prevents further growth
13. Effect of H_2 – oxide reduced to metal

b) *Pointed Blade-Shaped Oxide Platelets*

When annealed or cold-worked iron is reacted with water vapor atmospheres containing oxygen, pointed blade-shaped oxide platelets form. Figure 2 shows the genesis of blade-shaped oxide platelets when iron is

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[6] R. PHELPS, E. A. GULBRANSEN, and J. HICKMAN, *Anal. Chem. 18* (1946) 391.

[7] E. A. GULBRANSEN and T. P. COPAN, *Physical Metallurgy of Stress Corrosion Fracture*, ed. by T. RHODIN, Interscience, New York 1959, p. 155.

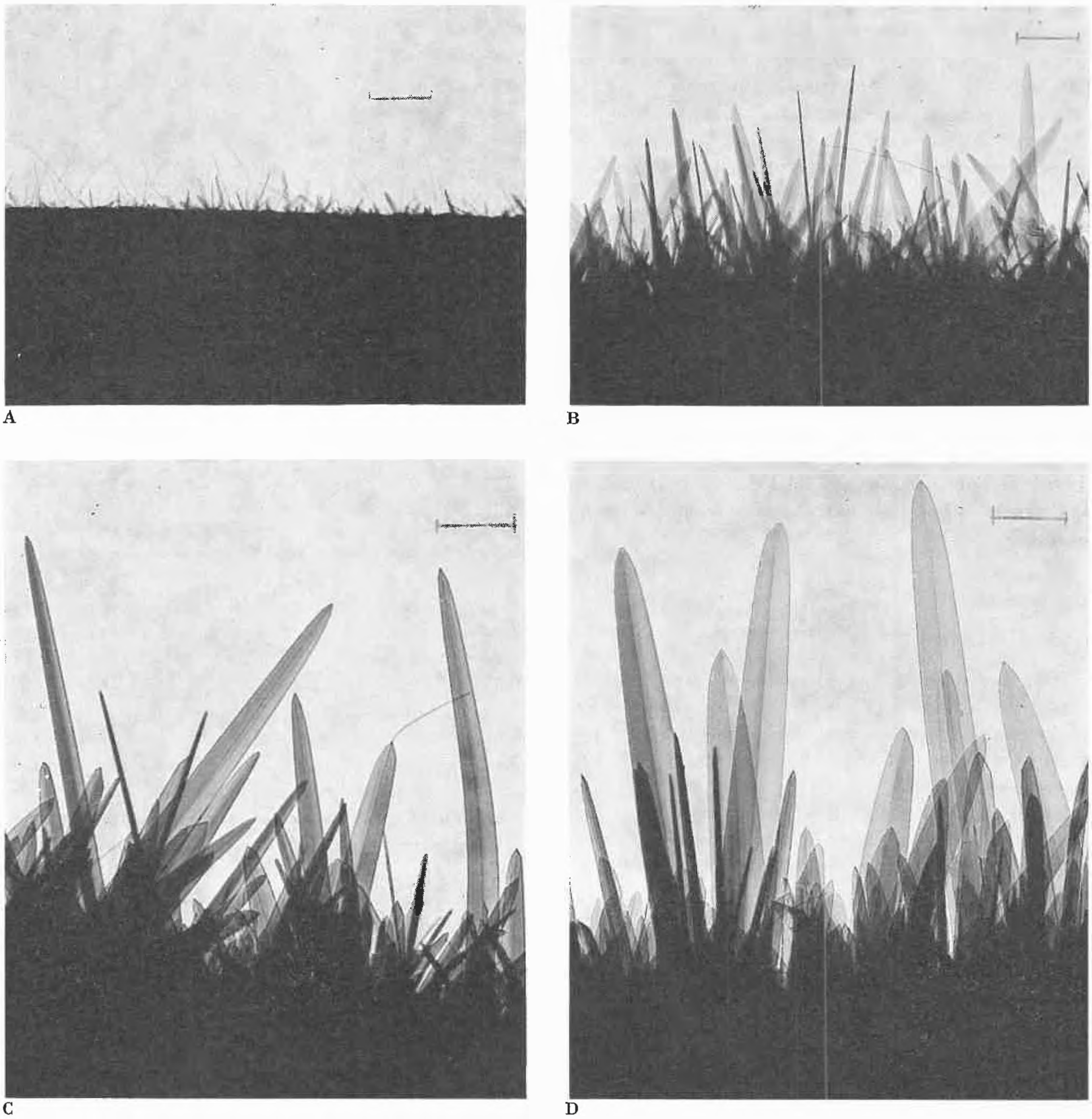

Figure 2. Blade-shaped oxide platelets formed on annealed pure iron in 10% H_2O and 90% argon at 400°C. Micron length shown. (A) 2 hours, (B) 6 hours, (C) 12 hours, (D) 23 hours

reacted with a 10% water vapor and 90% argon mixture. Traces of oxygen were present in the argon gas. Figure 2A shows that both oxide whiskers and blade-shaped platelets were formed after 2 hours of reaction. The whiskers were about 150 Å in diameter and averaged 10,000 Å in length. The oxide platelets were about 150 Å thick, 1000 to 1500 Å wide, and grew to lengths up to 10,000 Å. Figure 2B shows that most of the whiskers have disappeared after 6 hours and only oxide platelets have formed. Figures 2C and 2D show that the size of the oxide platelets increases with time. After 23 hours of reaction, the platelets were 2500 to 6000 Å wide and up to 70,000 Å long, with a surface density of 10^8 cm^{-2}.

Table II shows a summary of the properties and conditions of formation of the blade-shaped oxide platelets of an iron specimen reacted with steam and argon at 400°C for 7 hours. The d_{hkl} values could be correlated exactly with the x-ray diffraction values for hexagonal α-Fe_2O_3.

The shape of the platelets suggests that localized oxidation starts at point sites on the surface. As oxidation continues, the point site grows to a line site to form

Table II. Summary of Data, Pointed Blade-Shaped Oxide Platelets

1. Thickness ~150 Å
2. Widths up to 1.5×10^4 Å
3. Lengths up to 9×10^4 Å
4. Density up to $10^8/\text{cm}^2$
5. Weight = 5.3×10^{-13} g for platelet 9×10^4 Å long, 1.5×10^4 Å wide, and 150 Å thick
6. Crystal structure – hexagonal α-Fe_2O_3 (400°C temperature of formation)
7. Site area – 2.3×10^{-10} cm² for platelet 9×10^4 Å long, 1.5×10^4 Å wide
8. Percent of surface covered for $10^8/\text{cm}^2 = 2.25\%$
9. Conditions – $H_2O + O_2$, stressed or unstressed metal, probably oriented sites, pure metal
10. Reaction site – grows in width with time
11. Thickness – nearly independent of time

a blade-shaped oxide platelet. Hydrogen atoms or ions act on the surface of the oxide or metal to enlarge the reaction area along certain directions. The thicknesses of the platelets are uniform and remain constant over the period of oxidation; they are nearly the same as the uncontaminated oxide core of whiskers formed in dry oxygen atmospheres. The platelet shape suggests that the width of the platelets is a function of time or extent of reaction.

Gulbransen and Copan[8] have shown that blade-shaped oxide platelets are the predominant localized oxide growths for a wide range of O_2–H_2O gas mixtures. To prevent platelet growth, the O_2–H_2O ratio must be greater than 30 : 1. Other studies[9, 10] have shown that traces of oxygen must be present for growth of blade-shaped platelets. A comparison of Figure 1 with Figure 2 shows the oxide present in blade-shaped platelets to be over 250 times the oxide present as oxide whiskers in Figure 1. Water vapor has a unique effect on the corrosion of iron.

Selected area electron diffraction was used by Tallman and Gulbransen[11, 12] in a recent study to determine essential structural features of the α-Fe_2O_3 whiskers. The electron diffraction patterns showed the oxide whiskers to have the axial twist characteristic of an axial screw dislocation. The growth direction was identified as the $[\bar{1}01]$ direction using structural rhombohedral indices.

Selected area electron diffraction and electron microscopy was used by Tallman and Gulbransen to determine the structural features of the pointed blade-shaped oxide platelets. The blade-shaped platelet is a contact mirror twin in which the mirror, composition, and blade-face planes are identical giving a sandwich structure. The blade-face is the rhombohedral face (010) of the primitive structural rhombohedron. The blade-shaped platelets have the same $[\bar{1}01]$ growth direction (structural rhombohedral indices) as the oxide whiskers.

The twinning found in the blade-shaped oxide platelets is not common in natural haematite since we have not found mention of it in textbooks on mineralogy.

c) *Rounded Oxide Platelets*

Thin, rounded oxide platelets formed when cold-worked iron was reacted with dry oxygen. Figure 3 shows an electron micrograph of the crystal habit of the localized oxide growths formed after oxidation of cold-drawn iron wire at 400°C for 48 hours in 760 torr of dry oxygen.

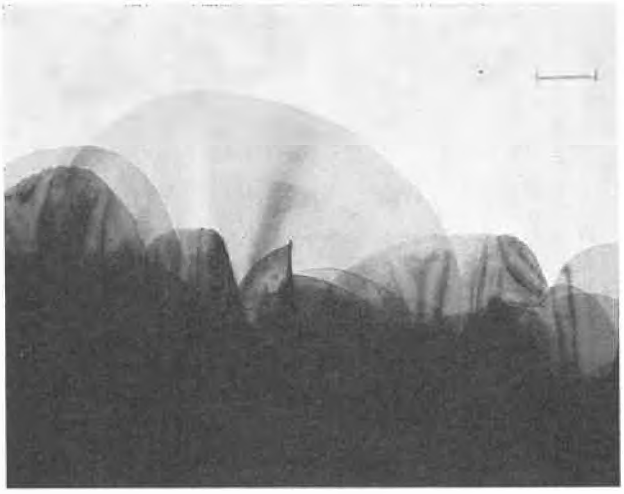

Figure 3. Rounded oxide platelets formed on cold-worked pure iron in 1 atm of dry oxygen at 400°C for 48 hours. Micron length shown

Thin, rounded oxide platelets grow along the axis of the wire to a height of 40,000 Å and to lengths up to 70,000 Å. The thickness of the platelets was estimated to be of the order of 150 Å or the same as that found for the blade-shaped oxide platelets and oxide whiskers. The thickness appears uniform over the platelet and the same for a large number of platelets examined.

Table III shows a summary of the properties and conditions of formation of rounded oxide platelets.

The selected area electron diffraction patterns and dark field images of the broad rounded platelets show sandwich structures in which the individual platelet crystals have faces parallel to the basal plane.[13, 14] In

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[8] E. A. Gulbransen and T. P. Copan, *Proceedings of the European Regional Conference on Electron Microscopy, 1960, Delft, 1* (1961) 225.

[9] E. A. Gulbransen, *Mem. Sci. Rev. Met. 62* (1965) 253.

[10] E. A. Gulbransen, T. P. Copan, and W. M. Hickam, *Proceedings of the 5th International Congress on Electron Microscopy, Philadelphia, 1* (1962) 1.

[11] R. L. Tallman and E. A. Gulbransen, *J. Electrochem. Soc. 114* (1967) 1227.

[12] E. A. Gulbransen and R. L. Tallman, *Chemical Physics of Surface Reactions of Metals*, AD-653723, Clearinghouse, Springfield (Virginia) 1967.

[13] R. L. Tallman and E. A. Gulbransen, to be published.

[14] R. L. Tallman and E. A. Gulbransen, *Nature 218* (1968) 1946–7.

Table III. Summary of Data on Rounded Oxide Platelets

1. Thickness ~150 Å
2. Widths up to 2 × 10^5 Å
3. Lengths up to 1.5 × 10^5 Å
4. Density – $10^6/cm^2$
5. Weigth = 3.1 × 10^{-12} g for platelet 2 × 10^5 Å long, and 1.5 × 10^5 Å wide
6. Crystal structure – hexagonal α-Fe_2O_3
7. Site area – 3 × 10^{-9} cm^2 for platelet 2 × 10^5 Å wide and 1.5 × 10^5 Å long
8. Percent of surface covered for $10^6/cm^2$ = 0.3%
9. Conditions – O_2, metal in stressed conditions, impurities in metal
10. Reaction site – line site on metal, grows with time
11. Thickness – nearly independent of time

these unusual twins, the composition plane is a twist grain boundary. So far, four twist angles have been identified in the patterns: the twist angle $13.174° = 2$ arc cosec $\sqrt{76}$ is common. One example with the twist angle $21.787° = 2$ arc cosec $\sqrt{28}$ has been identified. These two angles have a special geometrical significance in that they rotate lattice rows in the basal plane into coincidence. One example each of 26.66 ± 0.2° and 35.22 ± 0.2° has been identified. Because no definite geometrical significance has been attached to these angles, the measured values are given with estimated error limits. It is of interest to note that $13.174° + 13.174° = 26.348°$ and $13.174° + 21.787° = 34.961°$.

It is possible that the twist angle varies slightly over the face of an individual platelet. Also, two apparently arbitrary angles were found which suggests that the set of all twist angles which may occur may include one or more broad continuous ranges of angles.

Growth Mechanisms and Conclusions

Takagi has shown that whiskers and blade-like platelets grow from the tip.[4] All the growths appear too perfect to have been extruded. In the temperature regions in which the growths have been observed, the lattice diffusion coefficients of iron and oxygen[15] are so small that only negligible lattice transport could add to the growth. Surface diffusion rates are limited by sintering measurements[16] to values several orders too small to provide the iron diffusion necessary for the observed growth rates of up to 10–100 Å s^{-1}. This and other arguments[11, 12] favor internal diffusion mechanisms in which the iron is transported along the screw dislocation core of a whisker and along the mirror twin and twist twin composition planes of the two types of platelets.

Rapid diffusion along the blade length and slow diffusion across the blade width are consistent with the crystallographic symmetry of the blade, and can explain the growth shape. Similarly, the surface diffusion coefficient for a twist grain boundary on the basal plane should be isotropic. It is likely, however, that the unknown structures at the bases of all these growths determine their breadths. Thicknesses are probably determined by the growth mechanisms at the growth sites, which are at the growing tips and edges.

Short-circuit diffusion in gas-metal and solid state reactions in general must be all-important at temperatures where lattice diffusion rates are small. The α-Fe_2O_3 growths illustrate dramatically the unexpected extremes to be expected where short-circuit diffusion paths are involved.

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[15] W. C. Hagel, *Trans. Met. Soc. A.I.M.E. 236* (1966) 179.

[16] R. L. Coble, *J. Amer. Ceram. Soc. 41* (1958) 55.