

MICROTOPOLOGY OF THE SURFACE REACTIONS OF OXYGEN AND WATER VAPOUR WITH METALS

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The effect of dislocations, defects and internal stress on the physical properties of metals and alloys has been studied extensively. The effect of these factors on the chemical reactivity of metals has only recently been recognized.

An electron optical study was made on the localized crystal growths formed when a pure grade of iron was oxidized in pure oxygen or pure water vapour at 400°C. Thin oxide whiskers 100-150 Å in diameter form when pure annealed iron is reacted with dry oxygen. These whiskers may grow to lengths up to 500,000 Å long. Thin blade-shaped platelets 100 Å thick, 300 to 8000 Å wide and 30,000 Å long form when iron is reacted in water vapour at 400°C. Thin, rounded platelets of oxide 100 Å thick, 75,000 Å high and wide form when cold-worked iron is reacted with dry oxygen at 400°C.

Electron optical studies of these localized crystal growths offer a new method for observing the effect of crystal imperfections in the chemical reactivity of metals.

Current theories of oxidation of metals ^{1, 2} assumes the formation of a uniform oxide film separating the reacting gas from the metal. Reaction occurs by diffusion of metal or oxygen atoms or ions through interstitial sites or through cation and anion defects in the oxide film.

Using low-pressure oxidation methods, Bardolle and Bénard,³ and Gulbransen, McMillan and Andrew,⁴ showed that the initial step in the oxidation of iron was the formation of small oxide nuclei rather than a uniform oxide film. In the thick film range of oxidation, Pfefferkorn⁵ and Takagi⁶ have found fine oxide whiskers growing on an iron surface during oxidation. These observations suggest that the chemical reactivity of a metal is not uniform over the surface but depends on structural factors within the metal and oxide film. These factors include grain and sub-grain boundaries, dislocations, inclusions and other defects. Internal and external stress in the metal and the oxide may also play an important role.

This paper will present some recent electron optical observations on the effects of metal structure and chemical environment on the formation of localized oxide growths on pure iron. Electron optical techniques must be used since dislocations and other defects in metals occur on an atomic scale.

To locate the areas of localized chemical reactivity, vapour phase chemical reactions were used. The crystals formed in localized vapour phase reactions remain at the site of the reaction and can be observed directly with the electron microscope.

EXPERIMENTAL

Direct transmission electron microscopy and electron diffraction methods were used. The crystal growths formed on the surface of a fine wire or at the edge of a small hole drilled in a thin metal disc were studied.

Five-mil thick Puron * grade of iron sheet was used for making the $\frac{1}{8}$ -in. diam. specimens. A 5-mil hole was drilled in the centre of the disc. The Puron iron contained 0.005 carbon,

* Puron is a proprietary name for a pure form of iron manufactured by Westinghouse Electric Corporation, Pittsburgh, Pa.

less than 0.0015 other metals and 0.04 oxygen. The oxygen content was reduced by hydrogen annealing. The 7-mil wire iron sample was spectroscopic iron having 0.014 carbon and 0.15 oxygen. The disc specimens after drilling were carefully polished and chemically cleaned. The wire specimens were mechanically polished and degreased.

The Puron disc samples were reacted in the laboratory microbalance system^{7,8} at 0.1 atm of purified oxygen having a dewpoint of -196°C . A second furnace system was used for reaction of specimens under stress and for reactions in water vapour. Water vapour atmospheres were prepared by bubbling welding grade of argon through distilled and de-oxygenated water and passing the gas mixture into the reaction vessel.

Both an EMB 4 and an EMU-3D RCA electron microscope were used. The latter instrument was used at 100 kV and had facilities for taking micrographs at 200,000 magnification. The crystal structures of the oxides were determined in the electron diffraction adapter of the EMU-3D microscope using TiCl as a standard reference.

TYPES OF OXIDE CRYSTAL GROWTHS OBSERVED ON PURE IRON

Three types of localized oxide crystal growths are found when iron is oxidized in oxygen or water vapour. These are: (i) thin whiskers, (ii) blade-shaped platelets, and (iii) fan-shaped platelets.

A. OXIDE WHISKERS

Thin oxide whiskers are the most common localized crystal growths to form on iron.^{5,6} Whiskers are found alone or in combination with platelets of oxide. We have observed that whiskers are formed when annealed pure iron is reacted with dry oxygen. A few small fan-shaped oxide platelets also form in the early stages of oxidation.

Fig. 1 shows an electron micrograph of an oxidized disc sample of Puron iron. The specimen was reacted for 48 h at 500°C in an atmosphere of dry oxygen at 0.1 atm having a dewpoint of -196°C .

Fig. 1 shows the whiskers to be 300-600 Å in diameter and 15,000 Å in average length. Some of the whiskers grew to lengths up to 75,000 Å. A surface density of 5×10^7 to 10^8 whiskers per cm^2 was estimated. Studies on specimens oxidized for 220 h at 500°C in wet oxygen atmospheres showed whiskers having lengths up to 500,000 Å.

Studies on oxide whiskers at high magnification show that great care must be used in using the electron microscope if contamination is to be avoided. Fig. 2 shows an electron micrograph of a small iron oxide whisker at high magnification. The micrograph shows a heavy sheath of contamination around the oxide core. The central core was 100 to 150 Å in diameter. This value is in agreement with the minimum whisker thickness observed by Takagi.⁶

The identification of the outer sheath as contaminant was proved by two experiments. First, continued electron bombardment of the whisker caused the outer sheath to grow in diameter at a rate of 1 to 7 Å per sec. Secondly, photographs of whiskers taken quickly at low beam-intensities show very little contamination. The oxide whiskers formed at 400°C were 100 to 150 Å in diameter.

Electron diffraction analyses showed the whiskers to be hexagonal $\alpha\text{-Fe}_2\text{O}_3$ with the d_{hkl} values agreeing to 0.1 % of the X-ray diffraction values. No evidence was noted for exotic crystal habits observed by other workers.^{5,6} Some of these exotic crystal habits may be introduced by electron bombardment and by contamination.

Intense electron bombardment of the whiskers melts the oxide at the tip or at other points along the whisker. These whiskers when re-oxidized do not grow at the tip although some growth may occur in their thickness. Growth may stop due to destruction of the growth step at the tip. Heating the oxide whiskers in pure hydrogen at 500°C reduced the oxide whiskers to metal.

The existence of oxide whiskers having lengths to diameter ratios of 5000 suggests a calculation of the maximum stress at the root of the whisker. Using the flexure formula $S = MC/I$, we have calculated the maximum stress S for a whisker 500,000 Å long and 100 Å in diameter. Here M is the maximum bending moment and I/C is the section modulus. A stress of 510 g/cm^2 was calculated. This is a very low stress considering the length to diameter ratio.

B. THIN BLADE-SHAPED PLATELETS

If annealed or cold-worked iron wire is reacted with water vapour, thin blade-shaped platelets of oxide are formed in addition to oxide whiskers. The genesis of the

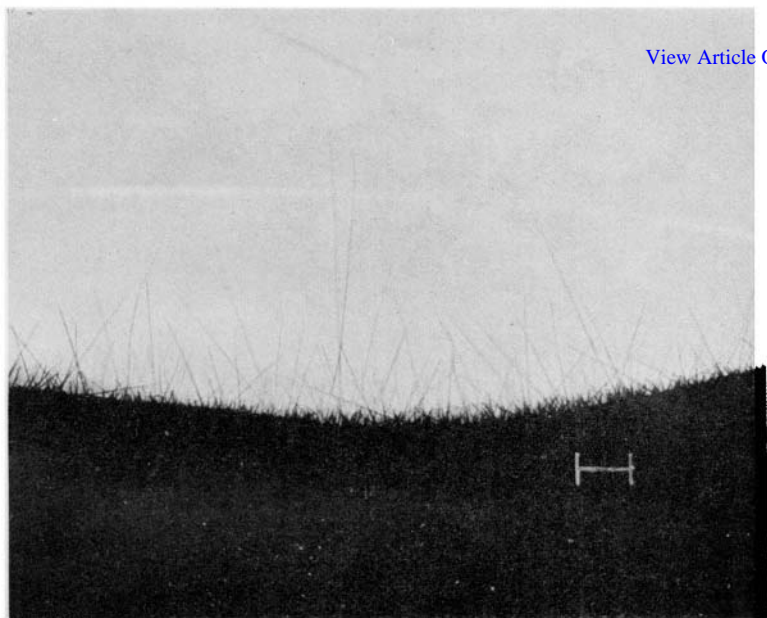


FIG. 1.—Fine oxide whiskers formed on Puron at 500°C in dry oxygen for 48 h; no applied stress; mag. 8000 \times .

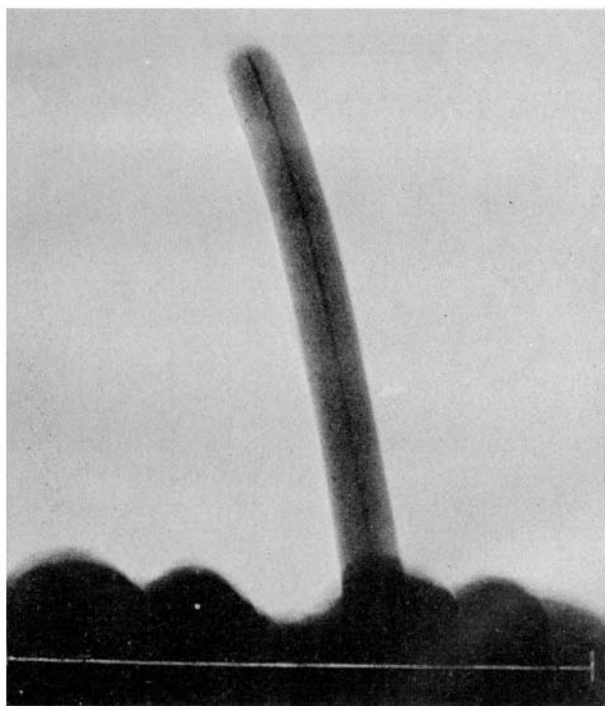


FIG. 2.—Contamination on oxide whisker formed on Armco iron; mag. 90,000 \times .

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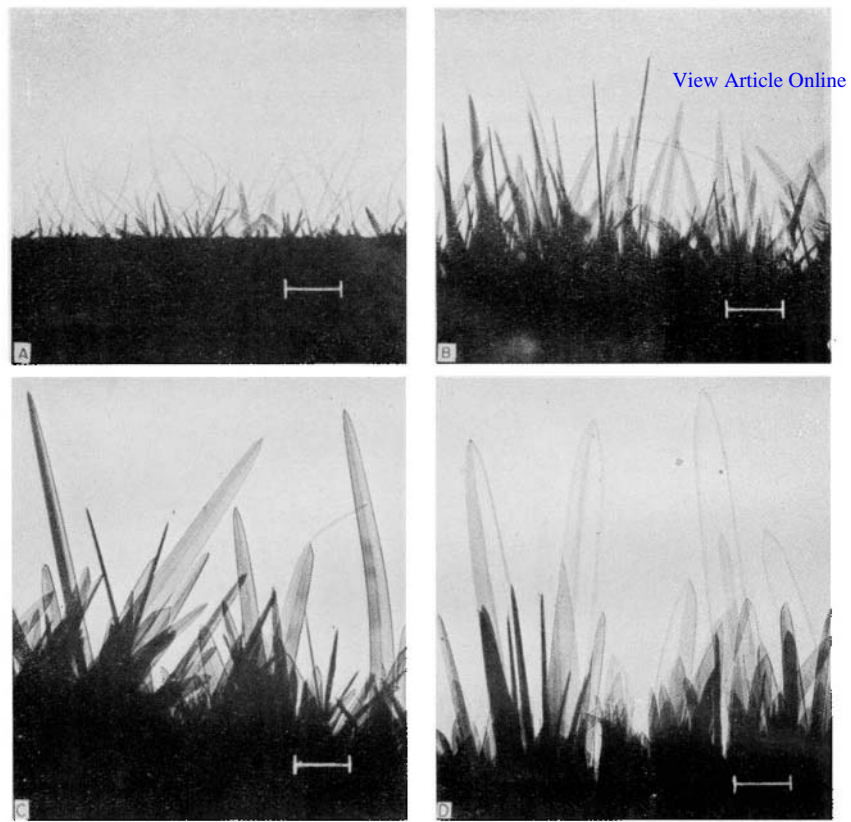


FIG. 3.—Blade-shaped oxide platelets formed on annealed iron in 10 % H_2O and 90 % O_2 at 400°C . (a) 2 h; (b) 6 h; (c) 12 h; (d) 23 h.

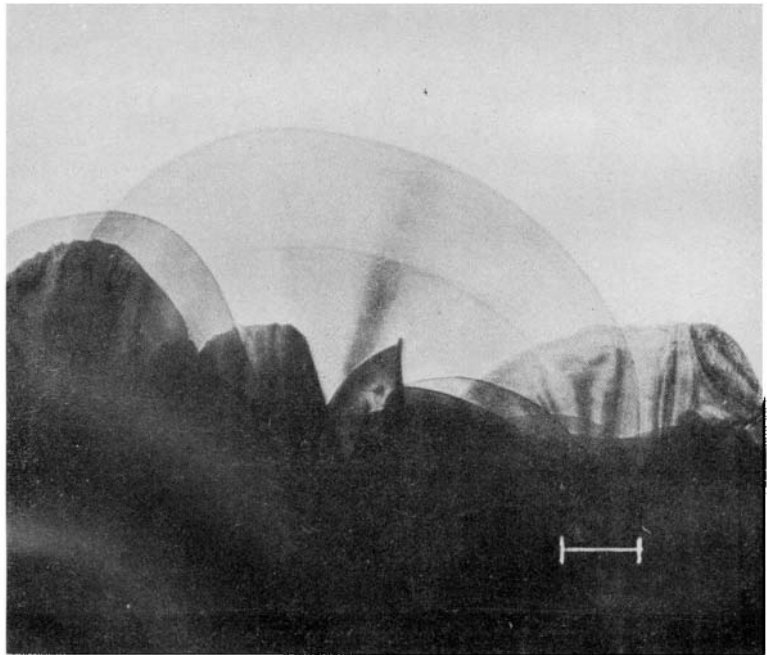


FIG. 4.—Rounded oxide platelets formed on cold-worked iron in 1 atm of dry oxygen at 400°C for 48 h; mag. 11,250 \times .

blade-shaped oxide platelet is shown in fig. 3 for a reaction temperature of 1400°C and a 10 % water vapour + 90 % argon atmosphere. The results are also shown in table 1. During the first 2 h of reaction, both whiskers and platelets were formed on the wire. The whiskers were 100 to 150 Å in diameter and average 10,000 Å in length. The platelets were very thin, 1000 to 1500 Å wide and grew to lengths up to 10,000 Å long. We estimated the thickness of the oxide platelets to be 100 Å or less. After 6 h of reaction, most of the whiskers have disappeared and platelets were observed. As the time of reaction increases, the size of the platelets increases. After 23 h of reaction the platelets were 2500 to 6000 Å wide and up to 70,000 Å long. The surface density was of the order of 10^8 per cm^2 . The platelets grew in a parallel arrangement along the axis of the wire. About 0.06 % of the surface area was involved in the reaction to form platelets.

TABLE 1.—CRYSTAL STRUCTURE AND HABIT OF LOCALIZED GROWTHS FORMED ON IRON WIRE AT 400° AT 0.1 atm H_2O + 0.9 atm ARGON

time	crystal structure	effect of time	
		crystal habit	
		whiskers	platelets
2	$\alpha\text{-Fe}_2\text{O}_3$	many, 100-150 Å diam., 10,000 Å long on average up to 30,000 Å long; density $\approx 3.0 \times 10^7/\text{cm}^2$	many, 100 Å thick, 1000 to 1500 Å wide; up to 10,000 Å long; density $\approx 2.0 \times 10^7/\text{cm}^2$
6	$\alpha\text{-Fe}_2\text{O}_3$	few whiskers, 100-150 Å diam., 30,000 Å long	many, 100 Å thick; 2000 to 3000 Å wide; up to 30,000 Å long; density $\approx 10^8/\text{cm}^2$
12	$\alpha\text{-Fe}_2\text{O}_3$	none	many, 100 Å thick; 2000 to 4000 Å wide; up to 60,000 Å long, density $\approx 10^8/\text{cm}^2$
23	$\alpha\text{-Fe}_2\text{O}_3$	none	many, 100 Å thick, 2500 to 6000 Å wide; up to 70,000 Å long; density $\approx 10^8/\text{cm}^2$

Table 1 shows the results of an electron diffraction analysis of the thin blade-shaped platelets. The d_{hkl} values could be correlated exactly with the X-ray diffraction values for $\alpha\text{-Fe}_2\text{O}_3$. The shape of the platelets suggest that the reaction of water vapour with annealed pure iron starts at a point. As reaction proceeds, certain nucleating centres broaden to form an array of blade-shaped platelets. Fig. 3c shows a whisker growing at the tip of a platelet. It appears that platelet growth has taken over after the whisker was formed. Such being the case, one might then postulate that the transition from whisker to platelet occurs very rapidly once the transition conditions prevail. One explanation for the transition of whiskers to platelets is that hydrogen dissolves in the lattice of the oxide or metal and enlarges the reaction area along certain crystallographic directions.

C. ROUNDED PLATELETS

Thin rounded platelets of oxide are formed when cold-worked iron is reacted with dry oxygen. Fig. 4 shows an electron micrograph of the crystal habit of the oxide film formed during the oxidation of cold drawn iron wire at 400°C for 48 h in 1.0 atm pressure of dry oxygen.

Thin oxide platelets grow perpendicularly 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 100 Å or the same as that found for the blade-shaped platelets. Internal and external stress was probably important in the growth of oxide platelets. The thickness of the platelets appears to be uniform over the platelet and appears to be the same for a large number of platelets examined irrespective of oxidation time. Electron diffraction analyses show the oxide platelets to be hexagonal $\alpha\text{-Fe}_2\text{O}_3$. Stress calculations at the root of the platelets show values similar to those calculated for the oxide whiskers.

DISCUSSION

Two interpretations may be given for the origin of localized oxide growths. They may arise from nucleation sites within the oxide layer or they may arise from nucleation sites in the metal. Let us consider the two interpretations.

α -Fe₂O₃ and Fe₃O₄ are formed on iron when oxidized below 570°C.⁹ Electron diffraction studies have shown that Fe₃O₄ is formed adjacent to the metal and α -Fe₂O₃ in the outer layer in contact with oxygen. Since the localized growths are α -Fe₂O₃, it is probable that the α -Fe₂O₃ crystals are nucleated on the Fe₃O₄ interface at certain defects in the oxide structure. These sites could be areas of local stress in the oxide film, crystal boundaries, etc.

On the other hand, Bardolle and Bénard,³ and Gulbransen, McMillan and Andrew,⁴ have shown that oxidation is a discontinuous process. Oxide nuclei are observed at a very early stage of the oxidation process. These experiments

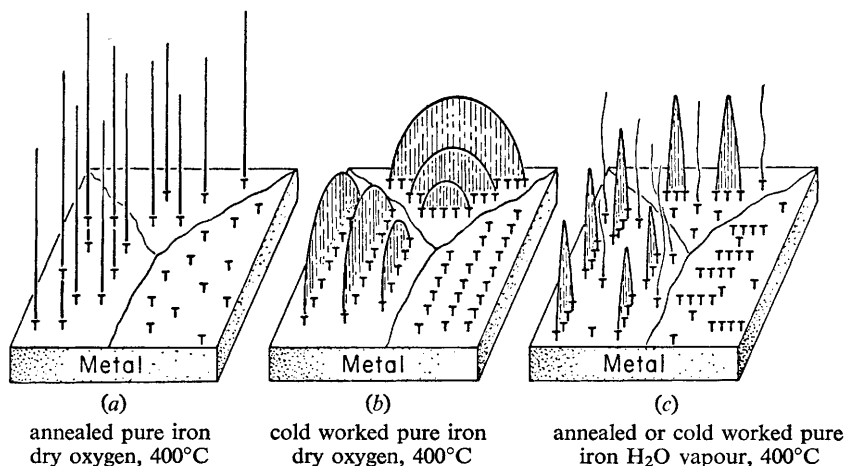


FIG. 5.—Localized oxide growth habits in the oxidation of iron (a, b) oxygen reaction, (c) water vapour reaction.

suggest that oxide whisker growth may be a continuation of chemical reactivity at the same nucleation sites brought out by low-pressure oxidation. Gulbransen and Andrew¹⁰ have recently shown that the pattern of the nucleation sites can be changed by annealing in hydrogen. Annealing in hydrogen leads to a linear type of nucleation pattern.

These observations together with the experimental work of this paper lead us to suggest a reaction mechanism in which the metal structure itself determines the localized crystal growths. The mechanism is supported by experimental observations that chemical composition of the metal, chemical environment and stress have major influence on the chemical reactivity of metals.

Fig. 5 shows our interpretation of the formation of localized oxide growths in oxygen and in water vapour. Fig. 5A shows a nearly random pattern of nucleation sites. We postulate that a metal having this pattern of nucleation sites reacts with oxygen to form fine long whiskers of oxide in addition to the normal oxide film.

Fig. 5B shows our interpretation of the nucleation pattern of a cold-worked specimen of iron. An ordered arrangement of nucleation sites is formed in the metal by the metallurgical treatment. Platelets of oxide are formed when a metal having this metallurgical structure is reacted with oxygen. Line growth of oxide is formed. The minimum distance between sites has not been determined but probably is of the order of a few 100 Å to a micron.

FIG. 5c shows the nucleation pattern after water vapour has reacted with iron. After reaction, pointed and blade-shaped oxide platelets are formed. This fact suggests that water vapour during reaction acts to enlarge the reaction site possibly along certain crystallographic directions. We postulate that hydrogen ions from the water vapour reaction diffuse into the metal at 400°C and modify the impurity distribution or the nucleation sites. The water vapour generates new reaction sites as reaction occurs. However, the growth of the reaction site appears limited to a width of about 8000 Å.

Earlier work has suggested that reaction occurs by surface diffusion of metal ions to the growth step at the tip of the whisker or platelet where reaction with oxygen occurs. This mechanism is supported by the fact that localized melting of the whisker tip stops growth of the whisker. We have confirmed this observation of Takagi.⁶ We have also noted that vacuum annealing does not affect the length of the oxide whiskers. In the absence of oxygen no growth occurs.

It is of interest to speculate on the condition of the metal at the root of the whiskers and platelets. If the metal atoms originate at or near the base of the whisker or platelet, a small pit, or a narrow trench may form even if the oxide is nucleated at the Fe₃O₄/oxygen interface.

The formation of thin oxide platelets of the order of 100 Å was unexpected. The thickness of the oxide platelet is roughly constant for the several types of platelets or several metals and for the several chemical environments. This leads us to suggest a new structure factor in metals which may play an important role in metal behaviour.

¹ Wagner, *Atom Movements* (Amer. Soc. for Metals, Cleveland, 1951).

² Mott, *Trans. Faraday Soc.*, 1940, **36**, 472.

³ Bardolle and Bénard, *Rev. Metall.*, 1952, **49**, 613.

⁴ Gulbransen, McMillan and Andrew, *Amer. Inst. Min. Eng. Trans.*, 1954, **200**, 1027.

⁵ Pfefferkorn, *Naturwiss.*, 1953, **40**, 551.

⁶ Takagi, *J. Physic. Soc. Japan*, 1957, **12**, 1212.

⁷ Gulbransen and Andrew, *Ind. Eng. Chem.*, 1949, **41**, 2762.

⁸ Gulbransen, *Advances in Catalysis* (Academic Press Inc., New York, 1953), vol. V, p. 119.

⁹ Hickman and Gulbransen, *Amer. Inst. Min. Eng. Trans.*, 1947, **171**, 306.