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The Low Temperature Oxidation of Iron

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An electron diffraction study of the oxide films formed on abraded iron specimens by heating in air at temperatures ranging from 80° to 260°C has failed to detect structural effects due to a "critical temperature" in the neighborhood of 200°C. α -Fe₂O₃ was found on specimens which were oxidized at any temperature above about 130°C provided the period of oxidation exceeded a minimum value which depends upon the temperature. Thus 1 hour at 180°, 4 hr. at 165°, 13 hr. at 150° or 1000 hr. at 130° are just sufficient to produce an α -Fe₂O₃ film whose diffraction pattern is well defined. Lower oxidation temperatures or shorter times tend to strengthen the diffraction pattern due to the primary oxide film which is assumed to be γ -Fe₂O₃ (or Fe₃O₄) and is detectable immediately after the initial abrasive treatment. The strengthening of the primary oxide pattern is not accompanied by appreciable

grain growth, however, and traces of iron are present in the pattern after oxidation periods as long as 1700 hr. at 120°C or below. Based on considerations of the presence of these iron rings it is estimated that the primary oxide film cannot be thicker than about 200A over some portions of the abraded surface. At 193°C and above the development of the first order blue interference color is characterized by the appearance of a new α -Fe₂O₃ film which is more coarsely crystalline and has a different type of preferred orientation than the first-formed α -Fe₂O₃ film. It is believed that this secondary film is formed by the outward diffusion of iron through the oxide layer. The axis of preferred orientation of the α -Fe₂O₃ is always symmetrical about the normal to the surface. This orientation cannot be attributed to pseudomorphism of the oxide crystals on the underlying iron as is the case with the primary oxide.

INTRODUCTION

THE nature and thickness of the air-formed oxide film formed on iron at various temperatures has been investigated by a number of workers¹ during the last few years. Many of the results indicate that the film composition or the mechanism of film formation or both depend upon whether the oxidation is effected at temperatures above or below 200°C. Vernon² found that when iron is heated in air at temperatures above 200°C interference colors develop which are characteristic of the oxide film thickness whereas at lower temperatures the color sequence does not appear even under prolonged heating. From gravimetric measurements he concluded that oxide films formed below 200°C were much thicker than indicated by the surface color. In addition he found by gravimetric methods that the oxidation *vs.* time curve is a parabola above 200°C but deviates therefrom at lower temperatures. Miley³ confirmed the absence of interference colors below 200°C. Mehl and McCandless,⁴

however, obtained interference colors on single iron crystals at temperatures as low as 140°C although their color *vs.* time curves at this temperature indicate that the color reaches a constant value which is unchanged on further heating.

Several electron diffraction investigations have shown that oxide formed on iron from room temperature up to some rather poorly defined temperature is cubic with a lattice constant of about 8.4A. Unfortunately both Fe₃O₄ and γ -Fe₂O₃ have a unit cell of this size and they are virtually indistinguishable by diffraction methods. Chemical considerations, however, have led Miley³ and others⁵ to conclude that the cubic oxide is γ -Fe₂O₃.⁶ Preston and Bircumshaw⁷ found the cubic oxide on specimens heated at 135°C and 175°C but rhombohedral α -Fe₂O₃ was present when the oxidation temperature was above 200°C. Their tests were made on small pieces cut from larger sheets which Vernon had used in his gravimetric work and for this reason were not well suited for the purpose.

¹ For recent reviews see: U. R. Evans, *Metallic Corrosion, Passivity and Protection* (London, 1937), Chapters II and III; W. H. J. Vernon, *Chemistry and Industry* **56**, 751 (1937).

² W. H. J. Vernon, *Trans. Faraday Soc.* **31**, 1668 (1935).

³ H. A. Miley, *Carnegie Scholarship Mem.* **25**, 197 (1936).

⁴ R. F. Mehl and E. L. McCandless, *Trans. Am. Inst. Min. Met. Eng., Iron and Steel Div.* **125**, 531 (1937).

⁵ I. Iitaka, S. Miyake and T. Iimori, *Nature* **139**, 156 (1937).

⁶ The conclusion of others that this primary oxide is γ -Fe₂O₃ has been accepted here for purposes of designating diffraction patterns but it must be emphasized that the experiments described herein do not distinguish between Fe₃O₄ and γ -Fe₂O₃.

⁷ Reported by Vernon, *Trans. Faraday Soc.* **31**, 1677 (1935).

Since these investigations indicate a critical temperature in the neighborhood of 200°C it seemed desirable to find out what electron diffraction methods could determine about films formed in air at temperatures above and below 200°C. In some earlier work⁸ it was demonstrated that the cubic crystals of the room-temperature air-formed film bear a definite orientation relationship with the underlying iron but no attempt was made to study films formed at higher temperatures.

EXPERIMENTAL

The specimens were small ($\frac{1}{2}'' \times \frac{1}{2}'' \times \frac{1}{4}''$) rectangular blocks cut from ingot iron (Armco) of the following analysis:

Carbon	0.02 percent
Manganese	0.03
Phosphorus	0.019
Sulphur	0.026
Copper	0.05

The initial surface treatment consisted of grinding all six surfaces on successively finer grades of emery paper ending with a very light abrasion on dry 4/0 paper. The resulting surface is in a finely abraded condition and gives a faint diffraction pattern due to $\gamma\text{-Fe}_2\text{O}_3$ overlying the stronger $\alpha\text{-Fe}$ pattern.⁹

The samples were heated in cylindrical electric furnaces equipped with automatic controls which maintained the temperature constant to within $\pm 1^\circ\text{C}$. The ends of the furnaces were closed with loose fitting refractory plugs which permitted free access of air. Ordinary air without purification was used for oxidation. Some of the samples were placed in the furnace in small alundum boats; others were supported by the thermocouple wires used to measure the temperature of the sample.

The oxidation temperature was determined by means of a thermocouple the elements of which

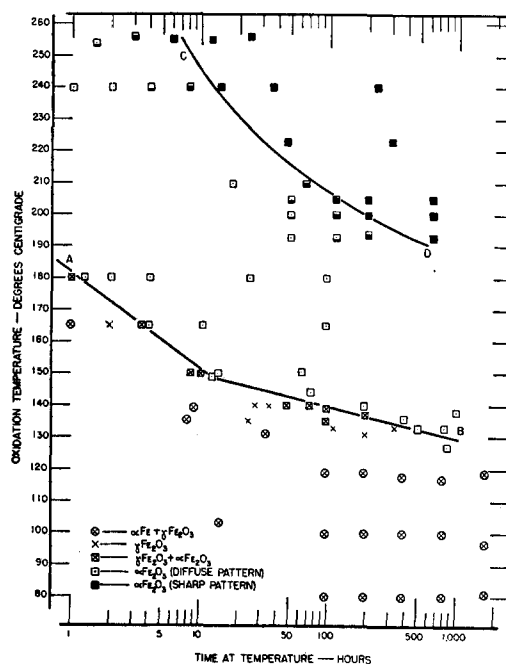


FIG. 1. Graphical representation of the results of heating iron specimens for various times at various temperatures.

were wedged or peened into two small holes drilled in the sides of the specimen. Air temperatures near the test surface were sometimes measured by a second thermocouple or a mercury-in-glass thermometer placed close to but not touching the specimen. The temperature close to the sample as measured by this method was not appreciably different from that of the sample itself as determined by the attached couple.

The diffraction camera is similar to that described by Thomson and Fraser¹⁰ with a hot cathode source of electrons. Constant accelerating potentials of 30 to 40 kv are provided by a transformer, rectifier and filter system. The grazing incidence or "reflection" method was used with a sample-to-plate distance of 40 cm.

RESULTS

The results on abraded iron surfaces are summarized graphically in Fig. 1. Each point represents a single experiment in which a specimen was heated continuously at the indicated temperature for the time given on the

⁸ H. R. Nelson, J. Chem. Phys. 5, 252 (1937).

⁹ Abraded surfaces were used partly because they most nearly represent a type of mechanically worked surface often met in practice. More important, however, is the fact that freshly abraded iron surfaces give an easily reproducible and interpretable pattern in which changes can readily be followed. Polished surfaces, on the other hand, give a poor pattern which, irrespective of its interpretation, is certainly not characteristic of metallic iron. With etched surfaces difficulty was experienced in removing the last traces of etching products which, it is reasonable to suppose, might profoundly affect the oxidation process.

¹⁰ G. P. Thomson and C. G. Fraser, Proc. Roy. Soc. A128, 641 (1930).

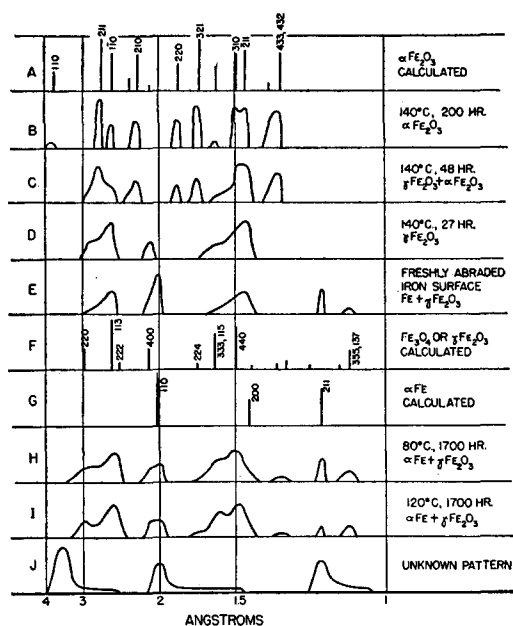


FIG. 2. Observed and calculated diffraction patterns. Heights of the curves represent estimated relative intensities.

logarithmic time scale after which the surface was examined in the diffraction camera. The character of the resulting diffraction pattern is indicated by the type of plotted point. A circle means that rings due to iron were present in the pattern. Crosses indicate the presence of the primary oxide $\gamma\text{-Fe}_2\text{O}_3$, while squares represent $\alpha\text{-Fe}_2\text{O}_3$. The lines *AB* and *CD* are drawn simply to separate the time-at-temperature area into fields within which the indicated type of diffraction pattern was observed.

A freshly abraded iron sample gives a diffraction pattern consisting of broad diffuse rings and a few fairly sharp rings. As has been shown previously⁸ this pattern is due to iron and the primary oxide. The latter is present in exceedingly small crystals as evidenced by the lack of resolution of the diffraction rings (cf. Fig. 2 *E*, *F*, and *G*). The iron rings are fairly sharp unless they happen to lie so close to oxide maxima as not to be resolved therefrom.

When such an abraded surface is heated in air at temperatures of 120°C or lower there is very little change in the pattern after heating periods as long as 1700 hours. (See Fig. 2, *H* and *I*.) In general the oxide pattern becomes slightly stronger with a slight tendency for the diffuse

maxima to be resolved into their component rings. The resolution is never good even with the longest oxidation periods used and there was little difference in the patterns obtained from specimens heated at 80°C and 120°C for 1700 hr.

The presence or absence of iron was determined by the presence or absence of the strong (110), (211) and (321) reflections of iron in the pattern. The (110) ring was never completely resolved from the (400) ring of the oxide but the other two could be checked easily since they do not fall near oxide maxima. As can be seen in plots *H* and *I* of Fig. 2 iron was present after heating 1700 hr. at 120°C or below.

When an abraded iron specimen is heated at temperatures above about 130°C the observed patterns follow the sequence shown in plots *E*, *D*, *C*, *B* of Fig. 2. Rings due to iron disappear fairly rapidly in heating times which depend upon the temperature. The disappearance of the iron is accompanied by a strengthening of the primary oxide pattern but there is no appreciable sharpening of the diffuse rings before they begin to be replaced by new rings due to rhombohedral $\alpha\text{-Fe}_2\text{O}_3$. After still longer heating periods the primary oxide is entirely replaced by $\alpha\text{-Fe}_2\text{O}_3$, Figs. 3 and 2*B*. This sequence of patterns has been observed at temperatures as low as 133°C and as high as 210°C. At the higher temperatures these changes take place before the specimen has reached temperature equilibrium, consequently the time required for the various changes could not be determined accurately. These results show conclusively that abraded iron surfaces develop a film of $\alpha\text{-Fe}_2\text{O}_3$ on heating in air at temperatures above about 130°C. The slope of the right-hand end of the line *AB* suggests that this oxide can be produced at even lower temperatures if sufficiently long oxidation periods are used. One specimen heated for 850 hr. at 127°C gave a well-developed $\alpha\text{-Fe}_2\text{O}_3$ pattern. It is not known why this result falls so far out of line.

At higher temperatures the surface film of $\alpha\text{-Fe}_2\text{O}_3$ undergoes a change characterized by a gradual replacement of the diffuse diffraction maxima by new, sharply defined rings due to the same oxide (see Figs. 4 and 5). There is also a change in the type of preferred orientation which is discussed later. The transition from the diffuse to the sharp $\alpha\text{-Fe}_2\text{O}_3$ pattern is coincident with

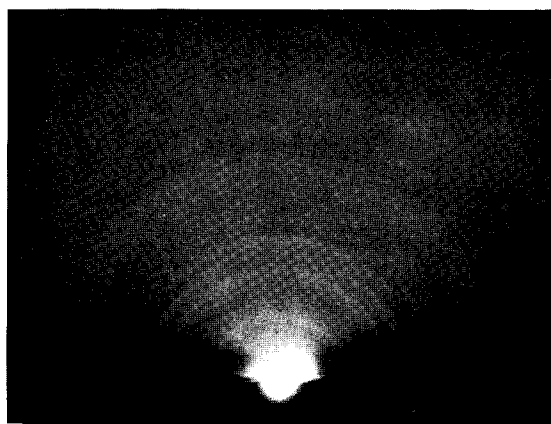


FIG. 3. α -Fe₂O₃ (diffuse pattern) from iron heated in air at 133°C for 800 hr.

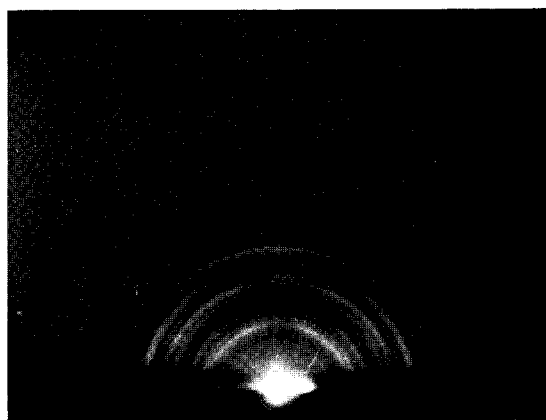


FIG. 4. α -Fe₂O₃ (diffuse pattern) from iron heated in air at 240°C for 4 hr.

the development of the first order blue interference color. Sharp diffraction rings begin to appear on the diffuse pattern when the surface reaches the purple stage. The diffuse maxima are entirely gone when the surface has become deep blue.

Above and to the right of *CD* in Fig. 1 only the sharp α -Fe₂O₃ pattern is obtained; below and to the left is a region in which the pattern due to this oxide is at least partly diffuse. It will be apparent from Fig. 1 that the data do not determine the shape of the curve *CD*. A straight line could be drawn to separate the fields nearly as well as the curve. The fact that at 193° this curve has not deviated sharply to the right indicates that the sharp α -Fe₂O₃ pattern characteristic of higher temperatures might be obtained from samples oxidized sufficiently long at temperatures well below 200°. Experimental data in the range 170° to 180° and 1000 to 10,000 hr. are necessary to test this point.

A diffraction pattern due to some unknown film was obtained in a number of experiments. (See Figs. 2*J* and 6.) The pattern is characterized by three strong diffuse rings which are rather sharply defined on the inside but poorly defined on the outside. The innermost ring which corresponds to a spacing of about 3.5Å, is much stronger than the others. This pattern was always obtained when samples were heated at temperatures of 125°C or below in one of the several furnaces used for these tests. It could not be reproduced in any of five other furnaces which

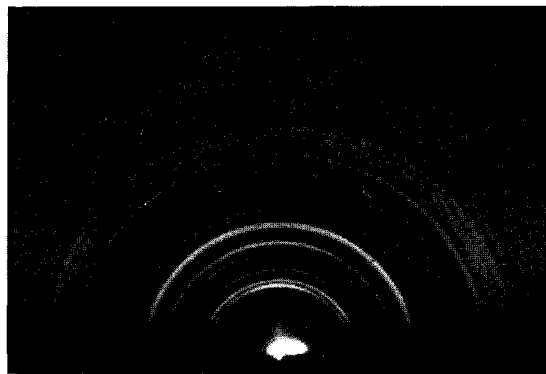


FIG. 5. α -Fe₂O₃ (sharp pattern) from iron heated in air at 240°C for 14 hr.

were used. Above 130°C this particular furnace gave results entirely consistent with those obtained in the other furnaces. The possibility that some unknown material from the walls of the furnace condensed on the surface and produced this pattern was tested by heating the test sample simultaneously with copper and nickel specimens placed beside it in the furnace. In every case the iron gave the diffuse ring pattern while the control surfaces did not. Moreover, the unknown pattern was obtained on a wide variety of iron surfaces, e.g. on electrodeposited iron films, on mirrors formed by vacuum evaporation and condensation of iron, and on etched and polished as well as abraded surfaces.

Attempts to analyze and explain this pattern have failed and at present it must be considered an anomalous result. It has not been included in

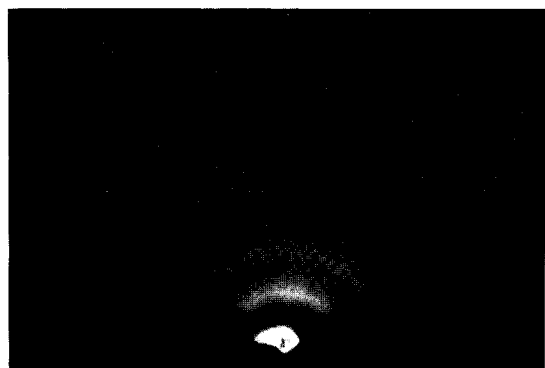


FIG. 6. Unknown diffuse ring pattern from iron heated in air at 122°C for 1850 hr.

the experimental results plotted in Fig. 1. The effect has been mentioned here, however, because it suggests the possibility that an amorphous oxide may be formed when iron is heated at temperatures below 125°C under certain special conditions which this experiment has failed to define.

A few experiments were performed on highly polished surfaces and various etched surfaces were tried. Although the results were similar to those obtained on abraded specimens there was evidence that the initial films left by such methods of preparation were too variable to give reproducible results (see footnote⁹).

In a previous paper⁸ it was shown that the primary oxide crystals stand in a definite orientation relationship with the iron crystals on which they form. It follows, therefore, that on abraded iron surfaces in which the iron crystals are randomly oriented the primary oxide should also be randomly oriented. Such in fact was observed on all abraded surfaces irrespective of the temperature at which the specimens were heated. By similar reasoning we conclude that α -Fe₂O₃ crystals should be randomly oriented if they bear a definite orientation relationship to the primary oxide or to the underlying iron. Actually, however, the α -Fe₂O₃ patterns always show a low degree of preferred orientation. In the initial α -Fe₂O₃ (open squares in Fig. 1) the [111] directions of the rhombohedral crystals tend to be perpendicular to the surface. Referred to hexagonal axes this means that basal planes tend to lie parallel to the surface of the specimen.

The appearance of the sharp α -Fe₂O₃ pattern is

accompanied by the development of a new type of preferred orientation characterized by a slight tendency for (211) rhombohedral planes to lie parallel to the surface. As can be seen in Fig. 5 this is a very low degree of orientation.

In order to determine the possible effect of orientation in the original iron surface the oxidation of electrodeposited surfaces was studied. The crystals formed when iron is plated onto polished or abraded iron tend to stand with [111] directions approximately perpendicular to the surface. The primary oxide film forms with an equally high degree of orientation because of the definite spacial relationship between it and the underlying iron. The preferred orientation exhibited by α -Fe₂O₃ films grown on such surfaces, however, was found to be exactly the same as was observed on abraded surfaces.

No careful attempts were made to determine the interference color of the specimens as a function of time and temperature. As has already been mentioned, however, the curve *CD* in Fig. 1 very nearly coincides with the appearance of the first order blue. The lowest temperature at which blue was obtained was 193°C. 1000 hr. at 138° gave a faint yellow similar to that observed after about 4 hr. at 180°. Specimens heated at 120° became perceptibly darker as the oxidation was prolonged. At 80° there was only a barely detectable darkening after 1700 hr.

DISCUSSION

During the course of this work Iimori¹¹ reported electron diffraction experiments in which he studied oxide films formed on etched iron surfaces heated in air at various pressures and temperatures. Below 340°C he found only the cubic oxide which he believes is γ -Fe₂O₃. At first sight this seems difficult to reconcile with the present results. However, Iimori reports only four experiments performed at atmospheric pressure and of these only two fall in the temperature range covered in Fig. 1. He finds γ -Fe₂O₃ after 1 hr. at 250°C or 24 hr. at 150°C. Both of these points fall within the region of diffuse α -Fe₂O₃ patterns obtained on abraded surfaces. The discrepancy is undoubtedly due to the different surface treat-

¹¹ T. Iimori, Sci. Papers, Inst. Phys. Chem. Research, Tokyo **34**, 60 (1937).

ment used in the two investigations and one is forced to the important conclusion that results on one type of surface cannot be applied to another. In fact Iimori states that on polished surfaces he obtained sharp $\alpha\text{-Fe}_2\text{O}_3$ patterns as low as 250°C.

The real purpose of this investigation, *viz.*, to study the nature of a critical temperature near 200°C, has not been achieved. The results give no evidence of a critical temperature in this region. Long oxidation periods in the neighborhood of 180° might establish a lower temperature limit for the formation of the sharp $\alpha\text{-Fe}_2\text{O}_3$ diffraction pattern. On the other hand comparatively short oxidation periods were sufficient for Vernon to show the existence of a critical temperature. It is apparent, therefore, that the difference between the oxidation mechanism above and below 200°C does not manifest itself in structural differences in the topmost layer of the oxide film.

The preferred orientations observed in the $\alpha\text{-Fe}_2\text{O}_3$ films cannot be due to pseudomorphism on underlying crystals as is the case with the primary films. Since the axis of orientation is always normal to the surface with complete randomness in other directions it seems likely that the crystalline orientation is in some way associated with the diffusion of oxygen through the oxide film or, more probably, the diffusion of iron outward to form new layers of oxide at the outer surface of the film. Pfeil¹² has shown that iron diffuses outwards through thick layers of oxide when ferrous materials are heated at high temperatures. This suggests a possible reason for

the appearance of the sharp $\alpha\text{-Fe}_2\text{O}_3$ pattern with its new orientation at the higher temperatures. The sharp diffraction rings mean that the new oxide crystals are much larger than those which gave the diffuse pattern. Careful examination of plates showing the transition from the diffuse to the sharp pattern leads to the conclusion that this transition is not due to crystal growth or to a process resembling recrystallization. Instead it appears that new crystals with the new orientation grow on top of the old film. If this interpretation is correct, iron must diffuse through the oxide film to the surface. The curve *CD* in Fig. 1 may, therefore, be some sort of measure of the rate of diffusion of iron through the oxide layer and the curve's lower temperature limit, if there is such a limit, would determine the temperature at which the diffusion rate becomes negligible.

The presence of diffraction rings due to metallic iron after oxidation periods of 1700 hr. at 120°C and less is surprising. In the "reflection" method the electrons pass through jagged ridges and projections left by the abrasion process. In passing through such a projection an electron would pass first through an oxide film, then through the unoxidized core and finally emerge through the oxide film. In such a path the electron might be scattered in either the iron or the oxide. Since, however, electrons cannot penetrate more than several hundreds of angstroms of solid material without suffering multiple scattering or absorption, the presence of iron rings in the diffraction pattern fixes an upper limit of about 200Å for the thickness of the oxide film.

¹² L. B. Pfeil, J. Iron and Steel Inst. **119**, 501 (1929).