A Study of Passivity of Iron Using Electron Diffraction.

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Introduction. Since the discovery of passivity of iron in the eighteenth century, various explanations have been suggested. Lately, through careful experiments and studies, such as the electrolytic isolation of a transparent film by U. R. Evans⁽¹⁾ or the optical observations of L. Tronstad,⁽²⁾ it has been shown that the phenomenon is definitely associated with a thin protective film on the surface of iron. However, the electron diffration method has not yet given a sufficiently satisfactory result in this study. G. P. Thomson's⁽³⁾ examination of passive iron in nitric acid does not enable us to determine the composition of the film and the work of E. Rupp⁽⁴⁾ merely suggests that the film might be α-Fe_2O_3.

The present author examined iron rendered passive in nitric acid or in a chromate solution by reflective diffraction of electrons from the surface film and also by transmissional diffraction, by first isolating the film. A part of this work has already been reported last year in a paper⁽⁵⁾ from the Iitaka Laboratory and the present paper gives further details and also reports on the results of advanced experiments.

The Invisible Film. (a) *Isolation of an invisible film.* The isolation of an invisible film was carried out using the electrolytic method of U. R. Evans. A strip of electrolytic iron (0.15 mm. thick and 1 cm. wide) was cleaned by gentle polishing with emery papers of increasing fineness and then rendered passive by immersing it in a 0.1 N solution of potassium chromate. The passive strip was gently rinsed with water and the end, to be immersed into a 6% solution of sodium chloride contained in an electrolytic cell, was trimmed cross-wise after which it was immersed in the electrolytic bath to the depth of one centimeter. The cell was divided into an anodic and a cathodic section by means of a porous porcelain cylinder. With the passive strip as the anode electrolysis was immediately started, care being taken to maintain the current density constant at 6–7

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(1) U. R. Evans, *J. Chem. Soc.*, **127** (1927), 1020.

(2) L. Tronstad, *Nature*, **127** (1931), 127.

(3) G. P. Thomson, *Proc. Roy. Soc.* (London), A, **128** (1930), 657.

(4) E. Rupp, *Kolloid-Z.*, **69** (1934), 375.

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

milliamperes per square centimeter throughout the process. And also throughout the electrolysis, fresh sodium chloride solution was continually fed into the cell drop by drop while the excess was overflowed through a siphon. After continuing the electrolysis for some eighteen hours, two transparent, colorless but lustrous films were isolated, one from each side of the strip. The films were carefully scooped up with a piece of fine brass netting and transferred with the netting into water containing a small amount of alcohol and then thoroughly and carefully washed.

(b) *Transmissional electron diffraction by the film.* A piece of the film free from any stain whatsoever was selected, scooped up on a netting and then dipped first into a 50% solution of alcohol and next into a 95% alcohol. After the film was completely dried on a small piece of netting, it was placed with the net into an electron diffraction camera.

The electron beam used was accelerated with about 50 KV. potential (corresponding to about 0.05 Å in wavelength); the exact wavelength was determined from the diffraction pattern of zinc oxide used as a reference, the oxide being placed in the camera always ready for use immediately after each exposure.

In many cases, the films gave diffraction patterns composed up of only two or three vague rings attributable only to nearly amorphous substances; however, as shown in Table 1, in a few cases several rings were distinguished.

Table 1. Diffraction patterns of thin films.

Intensity	Spacing of rings (Å)				Indices of planes	Side of unit cube (Å)
	Exp. 1	Exp. 2	Exp. 3	Exp. 4		
m or *w*			4.5	4.6	(111)	8.0
w				2.96	(200)	8.37
s	2.5	2.53	2.54	2.53	(311)	8.43
s or *m*		2.07	2.09	2.08	(400)	8.32
w				1.63	(333), (511)	8.48
s	1.5	1.48	1.49	1.48	(440)	8.35
w				1.39?	(135)	8.45
					Mean	8.40 Å
				X-ray data(6)	8.380 Å for Fe_3O_4 8.322 Å for γ-Fe_2O_3	

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(6) G. Hägg, *Z. physik. Chem.*, B, **29** (1935), 102.

The above table clearly indicates that the thin film is composed of either γ-Fe_2O_3 or Fe_3O_4 and not of α-Fe_2O_3. Many previous investigators, on the contrary, assumed the film to be α-Fe_2O_3. The magnetic property of the film, which is ferromagnetic, confirms without doubt the results as in above and proves that the film is either γ-Fe_2O_3 or Fe_3O_4 and also shows that the previous assumption is erroneous.

(c) *Invisible film on polished iron (not passive).* U. R. Evans(1) first ascertained through experiments that an invisible film similar to the one on passive iron also exists on iron polished in air but in this case. the cracks and pores present in the film in countless numbers make it vulnerable to reagents. A piece of non-passive electrolytic iron exposed for several hours to dry air after being polished, also yielded thin films by electrolysis; but in this case, unlike in the passive iron, the film always broke into fragments and were stained badly with rust. It was extremely difficult to select a sufficiently good film for a proper examination of its composition. Diffraction patterns obtained in a few cases were identical with that of Table 1, Exp. 2 or Exp. 1 and show that its composition is the same as that of passive iron.

Reflectional Election Diffraction with Passive Iron. (a) *Iron made passive in concentrated nitric acid.* Examination of iron made passive in concentrated nitric acid gave a result no more revealing than that obtained by G. P. Thomson(3) or E. Rupp.(4) The ring corresponding to 2.6 Å usually showed itself besides the iron pattern and merely indicates the existence of a thin oxide layer of a structure of the type similar to Fe_3O_4. Probably, the oxide layer cannot become any thicker in nitric acid so as to be detectable, because concentrated nitric acid has two properties, that of a strong oxidizer and that of a strong acid. It was observed, as a matter of fact, that iron made passive in a chromate solution after being highly polished, lost its luster and appeared as if etched when left in concentrated nitric acid overnight.

(b) *Iron made passive in potassium chromate solution.* In order to obtain a sufficiently thick protective film for study, potassium chromate solution was selected as the oxidizing reagent which also has the advantage of not dissolving the film. When a polished iron specimen was used, the diffraction pattern indicated no difference from that of non-passive iron; the pattern was identical with that of the invisible film, Table 1, Exps. 1 and 2. On the other hand, when iron etched with concentrated hydrochloric or nitric acid was used, at first a diffraction pattern similar to the one made passive in nitric acid was obtained; but a prolonged immersion in the chromate solution gradually made the iron pattern fainter, finally turning it into the "Fe_3O_4 pattern". This change took place without any manifestation in the outward appearance of the specimen. (Fig. 2–5).

These results obtained by transmissional and reflectional diffraction of electrons by the protective film clearly indicate that the film on passive iron may be isolated without undergoing any change during the process and that its composition is either γ-Fe_2O_3 or Fe_3O_4.

Supplementary Experiments and Discussion. From examinations made thus far, it can be readily seen that the protective film on passive iron is composed of either γ-Fe_2O_3 or Fe_3O_4 and because the diffraction patterns are similar, it is impossible to make a distinction and consequently some other method must be resorted to in order to make the identification. Hence, the following experiments were carried out:

(a) *Passivity of* Fe_3O_4. When iron coated with Fe_3O_4 by heating in water vapor at 400°C. was immersed in a dilute nitric acid, the oxide coating rapidly dissolved away. On the other hand, when the iron coated with Fe_3O_4 was immersed in concentrated nitric acid, the oxide did not dissolve at all; subsequent immersion in a dilute nitric acid had no effect upon the oxide so treated. Further, treatment of the Fe_3O_4 coating with a chromate solution gave precisely the same result as above. It can therefore be seen that Fe_3O_4 can be rendered passive by treating it with an oxidizing agent. From the diffraction pattern and also from the outward appearance of the oxide film, it is seen that in the above treatment, passivity takes place without visible changes. It naturally follows that the passive state is produced by an oxide having the same diffraction as the superficial layer of Fe_3O_4 previously formed. With due regard of these phenomena, it is conceivable that the protective surface film of passive iron is probably also γ-Fe_2O_3.

(b) *The "unknown primary oxide"*. A passive iron giving a good γ-Fe_2O_3 reflection pattern was heated in high vacuum at 600°C. in order to determine whether the oxide will actually transform into α-Fe_2O_3. Instead of this transformation, a very interesting phenomenon took place which is worthy of detailed description here. The heated specimen gave a pattern heretofore unknown among those given by various oxides of iron and in this paper the substance producing the pattern will be referred to as the "unknown primary oxide". This oxide was also obtained in the author's previous work(7) and it was found that its formation took place at a temperature between 200–300°C. or at 500°C. and at a very low pres-

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(7) T. Iimori, *Nature,* **140** (1937), 278; *Sci. Papers Inst. Phys. Chem. Research* (Tokyo), **34** (1937), 60.

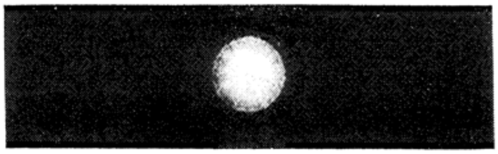

Fig. 1. The best photograph obtained from a protective film of passive iron.

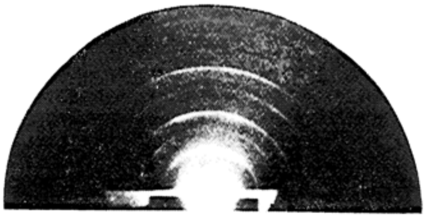

Fig. 2. Iron.

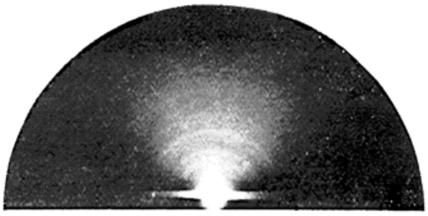

Fig. 5. Passive iron (immersed in a chromate solution 30 days).

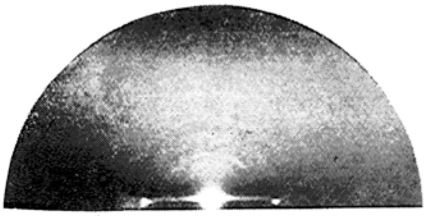

Fig. 3. Passive iron (immersed in a chromate solution 2 hours).

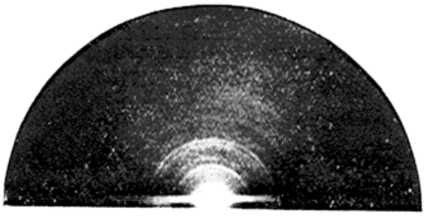

Fig. 6. γ-Fe_2O_3 (formed on etched iron in air at 300°C. and 10 mm.).

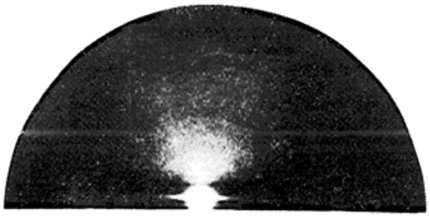

Fig. 4. Passive iron (immersed in a chromate solution 45 hours).

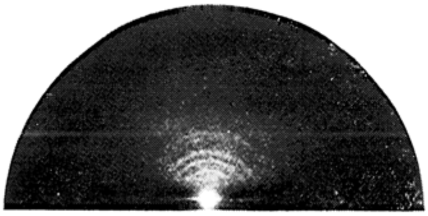

Fig. 7. The "unknown oxide" pattern formed by heating a passive iron at 600°C. in vacuum).

sure. Apparently, the formation of this unknown primary oxide takes place before that of either γ-Fe_2O_3 or Fe_3O_4. In the previous work, the rings obtained were quite vague but in the present case, the pattern was somewhat clearer and the rings identified are shown in Table 2.

Table 2. "Unknown primary oxide."

Spacing of rings (Å)	3.38	2.96	2.53	2.05	1.62	1.48	1.18
Intensity	*s*	*w*	*s*	*s*	*w*	*s*	*m*

Whether the oxide is simple or mixed is yet unknown, moreover, the exact condition favorable to its formation being still quite hazy further consideration cannot be made here. It is supposed, however, that the oxide is formed by the reduction of the protective film by migrating iron atoms.

(c) *Consideration with other experiments.* In the previous paper⁽⁷⁾ by the present author, it was reported that the oxide formed on iron at lower temperatures is γ-Fe_2O_3 and the favorable pressure for the formation of Fe_3O_4 approaches that of vacuum as the temperature becomes low. Since the protective film on passive iron is the same as that formed on polished iron by mere exposure to dry air at room temperature, it is obvious that the surface film on passive iron is γ-Fe_2O_3 or, to say the least, some modification of ferric oxide.

Recently, on the basis of electrolytic experiments, U. R. Evans and H. A. Miley⁽⁸⁾ are in the opinion that the oxide formed below 200°C. is γ-Fe_2O_3 because although being ferric it seems to be different from α-Fe_2O_3.

W. D. Bancroft and J. D. Porter⁽⁹⁾ assumed the protective film on passive iron to be an adsorbed layer of FeO_3 and considered that the transformation from the unstable FeO_3 to the stable Fe_2O_3 occurs during the isolation of the film. But, in view of the fact that diffraction patterns obtained with the isolated film and with the unisolated one are identical, it might follow that the assumption of the existence of a protective film of FeO_3 is superfluous.

In conclusion, the experimental results described above and also their consideration infer that the protective film on passive iron is a layer of γ-Fe_2O_3 forming a perfectly compact covering.

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(8) U. R. Evans and H. A. Miley, *J. Chem. Soc.*, **1937**, 1295.

(9) W. D. Bancroft and J. D. Porter, *J. Phys. Chem.*, **40** (1936), 37.

Summary.

The transmissional electron diffraction pattern of the isolated film from passive iron and the reflectional one obtained from iron rendered passive in a chromate solution are in both cases either γ-Fe_2O_3 or Fe_3O_4. Collaborating with the author's previous work and consideration of the passivity of Fe_3O_4, the protective oxide film is believed to be γ-Fe_2O_3.

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