

840. *The Identity of the Cubic Oxide Present in Films on Iron.*

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Some doubt has been felt about the possibility of distinguishing members of the series of cubic iron oxides of which Fe_3O_4 and $\gamma\text{-Fe}_2\text{O}_3$ are end members. New experiments show that the additional lines characteristic of $\gamma\text{-Fe}_2\text{O}_3$ appear when the transformation $\text{Fe}_3\text{O}_4 \rightarrow \gamma\text{-Fe}_2\text{O}_3$ is about 80% complete. Iron, heated in hydrogen (to destroy the original film) and then exposed to oxygen, develops films which are close to $\gamma\text{-Fe}_2\text{O}_3$ if formed at room temperature, but contain more iron if formed at higher temperatures, approaching Fe_3O_4 .

It is still believed in some quarters that it is impossible to distinguish with certainty between the two cubic oxides, magnetite and γ -ferric oxide. In 1945, Verwey¹ stated that the patterns obtained by powder X-ray methods are too similar for a distinction to be made. Later, however, Rooksby² published X-ray photographs, bringing out definite differences between them.

It is indeed often thought that there is no way of knowing whether the invisible film formed on iron exposed to dry air at room temperatures is magnetite or γ -ferric oxide. In regard to films formed at higher temperatures, however, pronouncements have been made, based on slight differences of pattern which are known to exist. Vernon, Calnan, Clews, and Nurse,³ studying oxidation at about 200°, found the film to be duplex, with rhombohedral $\alpha\text{-Fe}_2\text{O}_3$ overlying cubic oxide; they used electron-diffraction examination of the films after stripping them from the metal; those workers who had examined the films on the metal had reported only $\alpha\text{-Fe}_2\text{O}_3$. The two oxides Fe_3O_4 and $\gamma\text{-Fe}_2\text{O}_3$ are the end members of a continuous series of cubic solid solutions, the members having a magnetite structure with an increasing deficiency of iron. Vernon and his colleagues found that the cubic material formed at 225° initially has a composition near to $\gamma\text{-Fe}_2\text{O}_3$ but rather rapidly changes to Fe_3O_4 ; at 180° the change is slow, and even after 453 hours the composition

¹ Verwey, *Z. Krist.*, 1945, **91**, 66.

² Rooksby, Chapter X of Brindley's book "X-Ray Identification and Crystal Structures of Clay Minerals," Fig. X-3, opposite p. 257 (Mineralogical Society), 1951.

³ Vernon, Calnan, Clews, and Nurse, *Proc. Roy. Soc.*, 1952, *A*, **216**, 375.

Fe_3O_4 is not reached. Moreau and Bardolle⁴ state that the oxide present below the $\alpha\text{-Fe}_2\text{O}_3$ is magnetite when formed at about 300° , and $\gamma\text{-Fe}_2\text{O}_3$ when formed at about 250° .

These investigations mainly concern high temperatures, although Vernon and his colleagues, on their schematic diagram, indicate the invisible film formed at room temperature as being "cubic, near to $\gamma\text{-Fe}_2\text{O}_3$." Mayne and Pryor⁵ concluded from electron-diffraction and other experiments that film-free iron when immersed in potassium chromate or chromic acid solution at ordinary temperatures develops a film of $\gamma\text{-Fe}_2\text{O}_3$.

In the course of research on the kinetics of oxidation,⁶ it was found possible to distinguish between the end members of the series by X-rays. The results, which were not included in the original paper, are as follows:

(1) *X-Ray Studies of Powders*.—It seemed important to ascertain the point at which the distinguishing features of $\gamma\text{-Fe}_2\text{O}_3$ appear. Accordingly, X-ray powder photographs of $\gamma\text{-Fe}_2\text{O}_3$ and magnetite were prepared. These showed small but definite differences. The lines corresponding to the spacings, 3.72, 3.40, 2.77, 2.64, 2.32, and 2.24 Å appeared in the $\gamma\text{-Fe}_2\text{O}_3$, but not in the magnetite, photographs. Again, there was a noticeable shift of the lines towards the high-angle end of the $\gamma\text{-Fe}_2\text{O}_3$ pattern, owing to a small difference in lattice parameter.

These results confirm Rooksby's and show that it is possible to distinguish with confidence between the two compounds. The magnetite used for the powder photographs was obtained from two sources, and although the pattern obtained from both samples was identical, the ferrous content was slightly different—neither being exactly the theoretical value. When this magnetite was heated at 400° the ferrous content decreased, and when the transformation to $\gamma\text{-Fe}_2\text{O}_3$ was about 80% complete, the additional lines could be seen.

(2) *Electron-diffraction Studies of High-temperature Films*.—The iron used contained C, 0.034; Si, 0.010; Mn, 0.145; S, 0.015; P, 0.032; Ni, 0.030; Cr, 0.007; and Mo, 0.005%. It was first heated in hydrogen to destroy the invisible film, and then in oxygen. The visible films thus obtained were stripped by the alcoholic iodine method and examined by (i) X-rays, (ii) electron diffraction (transmission method, applied to the stripped film). In addition, electron-diffraction reflection studies were made of the film on the metal, except in the case of films formed at 175° , where the rings were too diffuse. The patterns showed that the films formed at 175° and 225° consisted of $\alpha\text{-Fe}_2\text{O}_3$ alone, and those formed at 300° contained $\alpha\text{-Fe}_2\text{O}_3$ along with cubic oxide (this was also true of films formed at 175° on abraded, as opposed to hydrogen-treated, iron). At 250° the films were $\alpha\text{-Fe}_2\text{O}_3$ alone after 2 hr., but $\alpha\text{-Fe}_2\text{O}_3$ with cubic oxide after 10 hr. No lines of metallic iron were found in any case. The cubic oxide may have been magnetite or any phase between magnetite and 80% Fe_2O_3 .

The results were confirmed by gravimetric and electrometric measurements, and by chemical examination of the films. The fact that the inner layer of the duplex film was not $\gamma\text{-Fe}_2\text{O}_3$ but a cubic oxide containing ferrous iron was shown by destroying the $\alpha\text{-Fe}_2\text{O}_3$ by reductive dissolution⁷ and stripping the remaining film in alcoholic iodine. It was found to be magnetic, and chemical tests showed it to contain ferrous iron as well as ferric.

(3) *Electron-diffraction Studies of Low-temperature Films*.—Electron-diffraction was applied to a specimen heated in hydrogen, cooled, and then exposed to oxygen at room temperature, but the reflection pattern was *diffuse*. A transmission photograph of the film stripped from such a specimen was still too diffuse, but after vacuum annealing at 360° for 1 hr. the pattern became *sharp* and contained the extra rings first observed in the X-ray pattern of $\gamma\text{-Fe}_2\text{O}_3$. To ascertain whether the ferric oxide might have been formed by oxidation of Fe_3O_4 owing to traces of oxygen, experiments were carried out by heating films in air. This, however, produced the rings of $\alpha\text{-Fe}_2\text{O}_3$ (the form stable at the annealing temperature). It is concluded that the air-formed film is either $\gamma\text{-Fe}_2\text{O}_3$ or a cubic oxide, the composition of which lies between 80% Fe_2O_3 and $\gamma\text{-Fe}_2\text{O}_3$.

Dr. J. E. O. Mayne has kindly made the following observation: "The conclusion

⁴ Moreau and Bardolle, *Compt. rend.*, 1955, **240**, 520.

⁵ Mayne and Pryor, *J.*, 1949, 1831.

⁶ Davies, Evans, and Agar, *Proc. Roy. Soc.*, 1954, *A*, **225**, 443.

⁷ Pryor and Evans, *J.*, 1950, 1259—1276.

regarding the composition of the air-formed film is based on the assumption that the fragments of stripped film did not change in composition when they recrystallized during vacuum annealing at 360°.

“ Either, or both, of the following changes could have occurred : (i) *Oxidation*. It has recently been found, by Hancock,⁸ that the air-formed film thickened by 10% when heated in a vacuum at 70° for 6 hr. This may have been due to residual oxygen, or to adsorbed air evolved from the heated glass walls. (ii) *Reduction*. Evans,⁹ who first isolated the air-formed film, noted that it frequently contained small particles of metallic iron. This has been confirmed by the observation that portions of films stripped from passivated specimens frequently developed rusty spots after storage for some months in methanol. These particles of iron might have taken part in the recrystallization during annealing.”

The authors appreciate these possibilities, but the effect of oxygen or iron traces had not been overlooked. Oxygen was found to convert magnetite into α -ferric oxide, the stable form, as stated above; the existence of γ -ferric oxide in the film cannot, therefore, be explained in that way.

The presence or absence of metallic iron in films from abraded iron was found in early work¹⁰ to depend on the level at which films are undermined. It is less likely to occur in films from unabraded specimens, and appears to be absent from the films studied, since no iron lines could be seen. Had it been present, it might have reduced ferric oxide to magnetite; it could hardly have changed magnetite to ferric oxide.

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⁸ Hancock, unpublished work.

⁹ Evans, J., 1927, 1020.

¹⁰ Evans and Stockdale, J., 1929, 2651.
