

OXIDATION OF IRON IN THE RANGE 100–400° C.

FOR many years, investigations into the films formed during the oxidation of iron have been proceeding in two corrosion laboratories, situated respectively in the Chemical Research Laboratory at Teddington and the Department of Metallurgy, University of Cambridge. Recently two pieces of work, undertaken quite independently but almost concurrently, have had a similar objective, namely, the elucidation of certain phenomena in the oxidation of iron around 200° C. Although the methods employed have been different, the two sets of results are essentially complementary. The Teddington work on this occasion has been collaborative, conclusions based on electron diffraction technique having been contributed from the Metallurgy Division of the National Physical Laboratory. Since the Cambridge and Teddington results present pictures of the same subject as viewed from different angles, it has been thought convenient to print in juxtaposition the preliminary accounts of the two investigations which follow.

Investigations at Cambridge

Early film-stripping experiments by J. Stockdale at Cambridge¹ suggested that the oxide formed on abraded iron at low temperatures was greatly interlocked with the metal, whereas at higher temperatures the oxide film and metal were separated by a relatively smooth surface. Vernon's early researches at Teddington² indicated that oxidation of abraded surfaces below 200° C. showed two differences from that above 200°, since (1) obedience to the parabolic law ceased and (2) no interference colours appeared even after ample oxygen-uptake. Colours were, however, obtained below 200° on single crystals by Mehl and McCandless³ and on polished surfaces by Winterbottom⁴. Two equations have been put forward to express the oxidation of various metals at low temperature where the parabolic law fails, but, despite much discussion⁵⁻⁷, there is no general agreement regarding their theoretical basis. The present note endeavours to reconcile these diverse facts, especially explaining why Vernon's two phenomena occur at the same temperature, and to provide basis for the asymptotic growth law; the logarithmic law has been discussed elsewhere⁶.

The line of thought was started by a microscopic study of films transferred at Cambridge by a combination of earlier methods^{8,9}. The iron sheet, kindly provided by the British Iron and Steel Research

Association, contained 0.02 per cent carbon, with 0.04 per cent oxygen as a magnetite network. In the main experiments, the metal was used in the as-rolled condition, degreased in xylene and or acetone; but a number of experiments were carried out on specimens from which the original surface layers had been removed either by abrasion, anodic etching (in sodium-chloride/zinc-sulphate solution) or preferably by heating to produce a first-order interference tint, the oxide film being then destroyed by reductive dissolution with zinc and hydrochloric acid; in the latter method, the liquid was removed with de-watering oil, which was itself removed with xylene.

About two hundred and fifty specimens were heated to produce superficial oxidation, and the films were transferred to 'Vaseline' glass. A veil of magnetite was always found clinging to the oxide film, but in some cases it was easily removed by a water jet. Thus iron tinted pale blue by heating 4.5 min. at 370° C. yielded on washing a clean, uniform ferric oxide film, recalling gold leaf; areas of the specimen which had been freed from oxide with zinc and hydrochloric acid just before transfer were represented after transfer by bare glass.

This easy removal of the veil is characteristic of the first-order films, but the 'invisible' film formed at low temperatures shows a strong adhesion to the veil particles. Gentle washing leaves the veil clinging to the film, while a powerful water-jet removes them both together. The adhesion suggests that the pre-existing magnetite serves as nuclei for the invisible film, but not for the colour-films. The higher temperature and longer time involved in producing colour-films will provide for the nucleation energy, whereas at low temperatures the transformation of iron containing oxygen in solid solution into oxide will occur readily only where oxide particles already exist, or where the atoms are in such disarray that the energy needed to form nuclei is exceptionally low.

The veil, if left in position, develops shrinkage phenomena, gathering into aggregates; this indicates that the internal magnetite network must have been *in tension*, probably as a result of rolling. On the thinner films, the change produces cracks in the ferric oxide layer; apparently the veil, as it shrinks, drags with it the firmly attached film. Fig. 1 shows the film taken from a specimen exposed to a temperature gradient (hot region at the top). The right-hand side was freed from veil before the shrinkage had occurred,

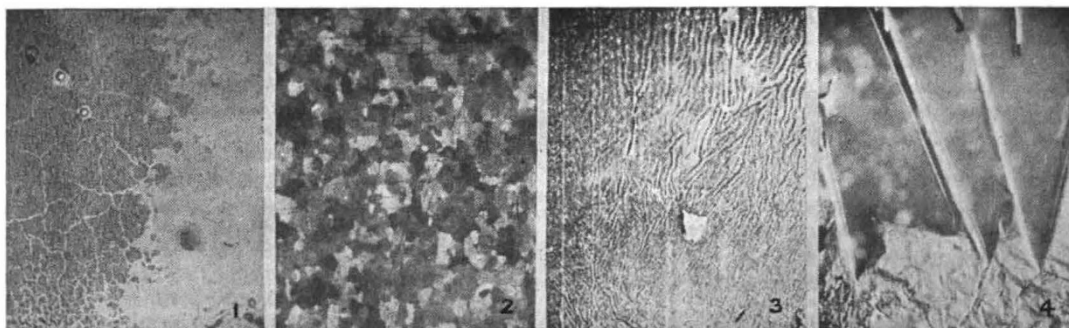


Fig. 1. Transmitted light, $\times 20$ Fig. 2. Transmitted light, $\times 75$ Fig. 3. Reflected light, $\times 4$ Fig. 4. Reflected light, $\times 4$

so that the transparent film remains uncracked. On the left, the veil was not removed, and a network of cracks has developed, penetrating the film; the 'mesh' of the network becomes smaller as the lower (thin-film) end is approached.

The film from iron showing a first-order colour consists essentially of ferric oxide with occasional clinging magnetite particles; the removal of these particles seems most difficult at the two ends of the first-order range. In the second-order range, a continuous magnetite layer appears below the outer ferric oxide layer, as found on other materials⁸; it is thin and transparent, and the duplex films viewed by transmitted light reproduce the grain structure of the metal (Fig. 2). The films show wrinkling (Fig. 3), indicating that the ferric oxide must have been in compression when on the metal. In the third-order region, the magnetite is thicker, and the duplex films curl into tight rolls (Fig. 4)—a phenomenon not noticed on other samples of iron. Apparently the oxide has grown inwards and incorporated part of the pre-existing magnetite network; the existence of two layers, respectively in tension and compression, must cause curling in the direction actually observed.

The observations suggest that oxidation extends inwards—which accords with the view long held by Valensi¹⁰—and that the oxide envelops inclusions which retain their internal stresses; the inheritance of internal stress by an oxide film was shown in earlier work on nickel⁹.

Rhines¹¹, when studying copper-manganese alloys, showed that at low temperatures particles of manganese oxide appeared preferentially at grain boundaries, whereas at higher temperatures they appeared within the grains; doubtless the energy necessary for the transformation of oxygen-solid solution to oxide is least at the grain boundaries, which are places of disarray. Presumably on Vernon's iron, the spontaneous formation of fresh nuclei at the external surface was a frequent phenomenon above 200° C., leading to a film sufficiently uniform to produce interference colours and thicken by the parabolic law. Below 200°, there was probably insufficient energy for the formation of nuclei at typical points on the surface, so that oxidation started either at points where oxide nuclei existed already, or at places of atomic disarray, where the formation of nuclei would require comparatively little energy. Such local or internal oxidation would be unfavourable for interference colours and inconsistent with parabolic growth.

We see, therefore, why Vernon's two phenomena set in at the same temperature. On materials containing no internal point of disarray, nuclei would in time be formed at the surface, so that slow colouring would be expected even at low temperatures—as on Winterbottom's mirrors and Mehl's single crystals.

The interlocking of oxide and metal at low temperatures¹ shows that rapid oxidation only occurs at favoured points. Probably the paths along which oxidation penetrates represent lines of atomic disarray. The degree of disarray needed for penetration will increase as temperature drops, so that at low temperatures the number of paths will diminish as they extend (at higher temperatures bifurcation of some paths will compensate for the termination of others). If the chance of a path terminating in length-element dl is defined as kdl , the chance of the total length falling between l and $l + dl$ will be $\exp(-kl) \cdot kdl$, so that the limiting weight-increase will be

$$N_0 \int_0^{\infty} \omega l \exp(-kl) \cdot kdl,$$

where N_0 is the initial number of paths and ω the weight-increase associated with unit path-length. The integral possesses a finite value ($N_0\omega/k$), so that, in absence of any other factor, there is a weight-increase which can never be surpassed, however long the experiment is continued. This may explain the asymptotic character of certain oxidation curves, and meets the main requirements of Lustman⁷, who has questioned the tunnel-effect theory³ on the grounds that "it predicts no temperature dependence of the constants". The existence of asymptotic growth laws is becoming increasingly recognized, notably by Champion¹².

The empirical equations supposed to hold in circumstances where the parabolic law fails are the non-asymptotic $W = k_1 \ln(k_2 t + 1)$, and the asymptotic $W = k_1 \{1 - \exp(-k_2 t)\}$. Provided that $k_2 t < 1$, the two equations, when expanded, only diverge at the third term,

$$W = k_1 [k_2 t - \frac{1}{2} k_2^2 t^2 + \frac{1}{3} k_2^3 t^3 - \frac{1}{4} k_2^4 t^4 \dots]$$

$$W = k_1 [k_2 t - \frac{1}{2} k_2^2 t^2 + \frac{1}{6} k_2^3 t^3 - \frac{1}{24} k_2^4 t^4 \dots],$$

so that sometimes a short-time experiment might give results consistent with either equation.

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⁸ Evans, U. R., Fifth Report of the Iron and Steel Institute Corrosion Committee, 1938, p. 225.

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Investigations at Teddington (Oxidation of Iron around 200° C.)

An earlier investigation¹ on the oxidation of abraded mild steel sheet in air at atmospheric pressure revealed the existence of a 'critical temperature' at c. 200°. Thus (i) interference colours, the characteristic sequence of which is a function of film thickness above 200°, do not appear below 200°, although the corresponding oxygen uptake may be appreciably exceeded; (ii) oxidation-time curves, characteristically parabolas above 200°, show marked non-conformity below 200°; (iii) the temperature-coefficient curve shows an inflexion at c. 200°. Recent advances in film-stripping technique at the Chemical Research Laboratory having facilitated the study of films removed from the substrate, the opportunity has been taken to investigate the phenomenon more closely. Films have been removed from mild steel