

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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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

sheet heated for various times at 180° and 225°. The crystal structure, as observed by electron diffraction (work carried out in the Metallurgy Division, National Physical Laboratory), has been compared with the composition of the film as determined by chemical analysis, the relative thickness being assessed from the total iron content of the film.

The films have been stripped by the alcoholic iodine method², using specimens previously dipped in 'Formvar' (polyvinyl formal) resin. The oxide film is removed together with the thin resin backing and the reinforced film transferred to a wire grid for examination in the electron diffraction camera. For chemical analysis the films are dissolved in acid and the solution examined for ferrous and ferric iron.

The electron diffraction work was carried out on a Finch camera with the usual type of cold-cathode electron source and saturated diode stabilization. The films were examined both *in situ* on the metal surface by the reflexion method and by the transmission technique after stripping. At least two separate areas of each specimen were examined.

Confirming earlier work, there was no progression of interference colours at 180°, but at 225° the usual sequence of bright colours was observed.

Electron diffraction (reflexion and transmission) patterns showed that the films, both at 180° and 225°, consist of an outer layer of rhombohedral α -Fe₂O₃ overlying cubic oxide of composition between γ -Fe₂O₃ and Fe₃O₄. It follows, therefore, that the phenomenon in question cannot be associated with any major crystalline change in the film at the critical temperature. On the other hand, preliminary chemical analyses have yielded the remarkable result that, for films produced at 180°, the values of ferric and total iron are approximately constant over the range 20–453 hours of heating. It follows that over this range there is virtually no increase in the thickness of the film removed by stripping. On the reasonable assumption (for which previous work² provides evidence) that it is on this film that the development of interference colours depends, a simple explanation is forthcoming why such colours do not, in fact, develop. It remains, however, to explain why thickening of the film is suspended, notwithstanding that oxygen uptake continues, with progressive increase in the weight of the specimen.

At 225°, for all periods of heating, uptake of oxygen contributes directly to the thickening of the film, as shown by its total oxygen content. At the lower temperature, oxygen uptake in excess of that required to produce the strippable film must add to the content of iron oxide *beneath* the film, that is, in the immediately underlying 'mixed zone' ('iron oxide incorporated sporadically in a matrix of iron'³) or "zone of interlocking"³. Clearly, however, this can occur only by the diffusion of oxygen inwards through the surface film (in accordance with the views of Valensi⁴), in contradistinction to the accepted Wagner mechanism at the higher temperatures in which metal ions diffuse outwards through a defective lattice of the oxide.

The mode and rate of growth of the film must depend upon the relative rates of diffusion of (i) oxygen (whether as ions, atoms or molecules) through the outer rhombohedral zone, and of (ii) iron ions through the inner cubic zone. It is unlikely that the temperature coefficient will be the same for each of these processes. The evidence suggests that the curve for (ii) is steeper than that for (i) and that the two curves intersect at c. 200°. Thus, below 200° oxidation is

propagated mainly by diffusion of oxygen inwards, above 200° by diffusion of iron outwards; on this view, the difference in the slopes of the respective (diffusion) temperature-coefficient curves accounts for the inflexion in the (oxidation-rate) temperature-coefficient curve that is experimentally observed at 200°. It is inherent in this argument that the relative diffusion rates will depend very appreciably upon the initial surface condition of the metal. Thus, the value of c. 200° is characteristic of polycrystalline surfaces prepared by careful abrasion (not 'polishing'). As mentioned in Dr. Evans's contribution, lower critical values have been reported for single crystals and for surfaces produced by polishing.

Furthermore, the diffusion of iron ions outwards through the lattice of the oxide film (> 200°) must produce new oxide on the outer interface; there is no reason to suppose that this could result in anything but a simple thickening of the film. The position is quite different with the reverse process (< 200°), since oxygen atoms arriving at the metal/film interface encounter a mixed assembly of metal matrix and (magnetic) oxide nuclei. It can readily be understood that oxidation will now proceed by the growth of pre-existing nuclei rather than by simple film-thickening. This conclusion is in substantial agreement with that reached, as the result of an entirely different mode of approach, by Dr. Evans in his accompanying contribution.

It remains to add that the 'veil' of magnetite described by Dr. Evans as clinging to his separated film is, in the Teddington film-stripping technique, left as a residue on the metal substrate when the film is removed. The distinction arises necessarily from the different experimental characteristics of the two methods. In each case, however, the material must incorporate the magnetic oxide 'nuclei' referred to in the two communications.

The foregoing is a preliminary account of work still in progress, the results from which will be published in greater detail elsewhere. We wish to express our indebtedness to Dr. F. Wormwell for helpful discussion.

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SCIENTIFIC RESEARCH IN THE RHODESIAS AND NYASALAND

A REPORT to the Central African Council on the Regional Organisation of Research in the Rhodesias and Nyasaland*, by Dr. J. E. Keyston, who is relinquishing his present position as research secretary under the Council towards the end of the year, has been considered by the Central African Council and by the three Governments. Although Dr. Keyston's main recommendation that a joint research council should be established has not been adopted, a Standing Advisory Committee for Research

* Central African Council. A Report on Regional Organisation of Research in the Rhodesias and Nyasaland. By Dr. J. E. Keyston. Pp. iv+91. (Salisbury: Central African Council, 1949.) 5s.