JOURNAL OF MATERIALS SCIENCE 12 (1977) 2303–2309

# Fracture mechanisms in oxide scale on iron during substrate deformation

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Oxide scales of different thickness and structure were grown on iron. Fracture of scales was studied when the underlying iron substrate was torsionally deformed at room temperature. For thin scales (5 μm) with a porous interface structure, the nucleation and growth of cracks occurred by the successive joining of interface pores. Slowly cooled scales of intermediate thickness (20 μm) failed by crack growth along oxide grain boundaries and from sharp corners of magnetite cuboids within wustite zones. For thick scales (35 μm), cracks nucleated from the base of the outermost magnetite crystallites. Rapidly cooled, thick scales exhibited crack nucleation from the sharp edges of voids at the scale/metal interface. Crack spacing in the oxide scale decreased with increasing substrate strain in a parabolic form.

## 1. Introduction

Stress relaxation in oxide layers growing on metal surfaces may occur by the nucleation and growth of cracks within the bulk scale or close to the scale/metal interface [1]. Prolonged oxidation can cause composition changes in the scale which are often accompanied by a diminished plasticity at elevated temperatures. These features invariably lead to heterogeneous structures and anisotropic properties when scales are cooled to room temperature. If the metal substrate below an adherent scale is then deformed, crack nucleation in the scale will occur at many highly stressed sites which are associated with the growth heterogeneities. The present work was undertaken to study the mechanisms which cause scale detachment.

An analysis of the fracture pattern of a relatively brittle surface coating on a metal surface, when the substrate had undergone plastic deformation, was reported by Grosskreutz and McNeil [2]. At relatively low temperatures and under tensile stress conditions, such a brittle coating cracks normal to the tensile axis. The widening of existing cracks accounts for a decrease in the rate of initiation of new cracks at large strains. The nucleation of cracks in very thin films can be attributed to the interaction of dislocations with an oxide film according to Grosskreutz and Bowles [3]. If the adhesion is strong between a coating and substrate, then fracture will occur as dislocations emerge from the substrate [4].

In the present experimental work, the strength of oxide scale adhesion to the iron substrate has clearly influenced the extent and manner of scale detachment. However, our main objective has been to establish the basic effects of structure, thickness and cooling rate of the scale on the process of detachment through fracture and to examine the relationship between substrate strain and crack spacing in the scale.

## 2. Experimental procedure

### 2.1. Mechanical descaling

Test pieces of high-purity iron in the form of 0.6 cm diameter, 7.6 cm long rods were machined for oxidation and subsequent mechanical descaling by tensile and torsion test. Rods of length 15.2 cm were used for four-point loading bend tests. Each test piece was vacuum annealed at 950° C for 1 h before oxidizing in argon containing traces of oxygen and water vapour at either 800 or 900° C for different periods up to 40 min to give oxide scales of thicknesses in the range 5 μm (thin) as in Fig. 1, to 35 μm (thick) as in Fig. 2. The scaled

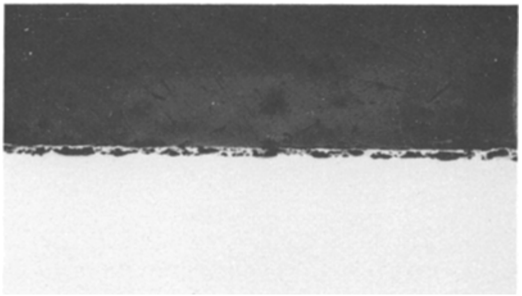

*Figure 1* Slowly cooled, thin oxide scale on iron, etched in 1% HC1 in alcohol (X 300).

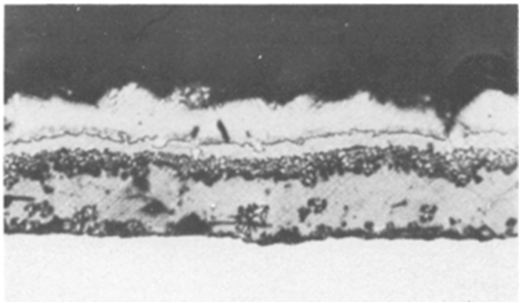

*Figure 2* Slowly cooled, thick oxide scale on iron, etched in 1% HC1 in alcohol (X 480).

specimens were either cooled slowly (in a furnace) or rapidly (in air) to 25° C before commencing the mechanical descaling tests.

The mechanical tests were selected to explore the effects of different modes of metal substrate plastic deformation on the extent of scale detachment in general, and the response of the relatively brittle scales to the tensile, compressive and shear stresses of each specific test in particular. Surface crack nucleation and growth in the scales was followed photographically by direct observation during each test. A highly sensitive strain gauge was used in the torsion test to detect crack initiation in the bulk scale.

Our present observations refer mainly to the torsion test results, i.e. the response of the scales to shear stresses, because it was clear from the initial experiments that this mode of stressing proved to be the most effective means of detaching the oxide scale from the metal substrate.

## 2.2. Fractography

The external evidence of fracture in the oxide scales was observed by taking a series of photographs during a torsion test. Crack nucleation began at several highly stressed surface sites from which rapid growth occurred to give cleavage fracture characteristics.

To establish the micromechanisms of cracking within the scale, specimens were twisted through an angle of $\sim 9^\circ$ at slow strain rates of $9 \times 10^{-5}$ sec$^{-1}$, sectioned and examined metallographically.

Finally, scanning electron micrographs of the oxide surface and bulk fractures were obtained.

To characterize the fracture behaviour of a uniform brittle surface coating on a deformable substrate, a comparative study was undertaken using the resinous material known as 'stresscoat' ST-70. The primary crack paths due to the tensile component of the applied shear stress for torsionally tested specimens of resin-coated iron are shown to be inclined at 45° to the specimen axis as shown in Fig. 3. The behaviour of oxide scales as indicated in Fig. 4, shows some similarities in the general fracture pattern to that of the brittle resin.

The results showing the relationship between

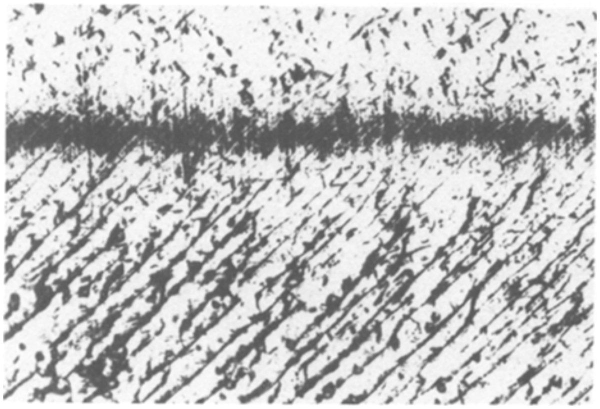

*Figure 3* Fracture pattern in stresscoat on iron due to torsional shear stress. Cracks aligned at 45° to axis of specimen (X 8).

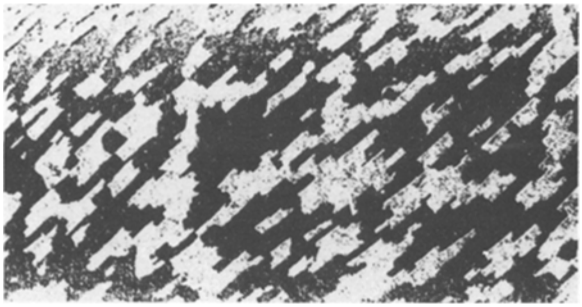

*Figure 4* Fracture pattern in oxide scale on iron after 12% torsional strain in substrate. Cracks aligned at 45° to axis of specimen (× 6).

substrate strain and crack spacing for oxide scales and 'stresscoat' resin will be discussed in the following section.

## 3. Results and discussion

### 3.1. Thin scales

The microstructure of the thin, slowly cooled, oxide scale (5 $\mu$m), shown in Fig. 1, exhibits a highly porous interface zone arising mainly from vacancy condensation during oxidation. The authors are aware that metallographic preparation artefacts can be mistaken for porosity, but mounting, sectioning and polishing techniques specially developed for friable scales have ensured that the incidence of misleading mechanical damage has been kept to a minimum. The continuation of oxidation during the slow cooling period is believed to have contributed to the greater porosity of the interface when compared to that of the rapidly cooled thin scale. One consequence of the early development of such a porous interface is that the flux of iron cations entering the growing scale would diminish. This would lead to the gradual conversion of initially adherent wustite (FeO) to pro-eutectoid magnetite ($Fe_3O_4$) as was observed. When these structures were strained in torsion, the shear stress acting in the scale/metal interface zone caused the initiation and growth of cracks by the joining of interface pores, which readily detached the thin scale layer from the metal surface.

In contrast, a rapidly cooled, thin scale of 11 $\mu$m thickness showed a less porous interface structure with a thin outer layer of pro-eutectoid magnetite (Fig. 5.). Crack nucleation in this structure as a result of substrate deformation was observed above the junction of two slip lines in the substrate as shown in Fig. 6. If the height of the slip step so formed is large, then the associated high stress concentration will enhance the scale detachment process if it reaches or exceeds the fracture strength near the interface. This mode of fracture is in agreement with the model proposed by Evans and Schwarzenberger [4] in which they demonstrated how a fracture could occur within a strongly adherent thin film when the substrate undergoes a heavy plastic deformation.

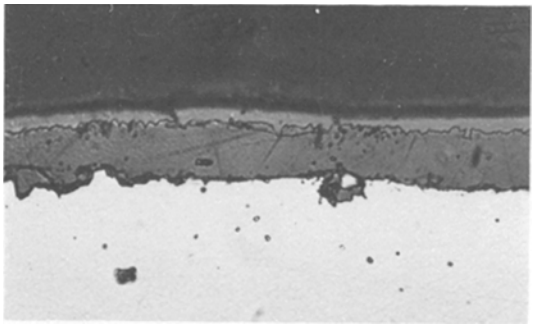

*Figure 5* Rapidly cooled, thin oxide scale; etched in 1% HC1 in alcohol (× 900).

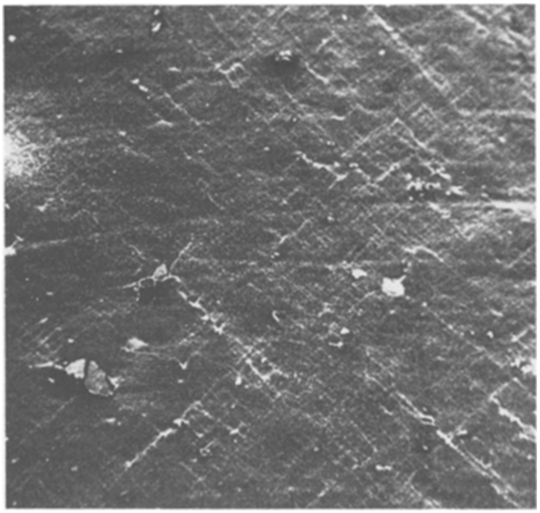

*Figure 6* Crack nucleation in thin oxide scale at junction of slip lines in substrate deformed by 3% (× 88).

## 3.2. Intermediate and thick scales

The nucleation of cracks within slowly cooled, intermediate ($20\,\mu m$) and thick ($35\,\mu m$) scales was totally dependent on the morphology of the scales. An examination of the surface topography of such scales revealed an outer zone of pro-eutectoid magnetite grains (Fig. 7). Below this layer, the remaining bulk scale comprised wustite within which cuboids of eutectoid magnetite were precipitated. Preferential precipitation of the magnetite cuboids during the slow cooling had occurred adjacent to the columnar grain boundaries of the wustite. Crack nucleation in these scales had evidently arisen from the sharp notches provided by the magnetite crystallites (Fig. 8.) intruding into the bulk wustite such that crack growth was in the direction of the scale/metal interface.

*Figure 7* Scanning electron micrograph of slowly cooled, oxide scale on iron indicating top surface layer of magnetite crystallites (× 2100).

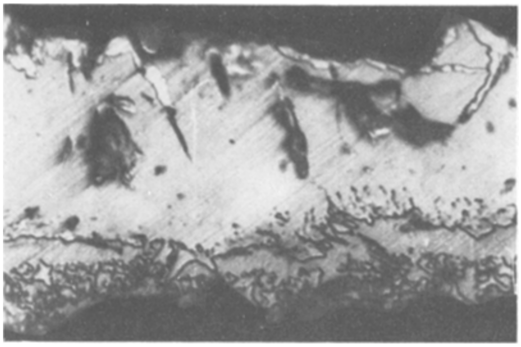

*Figure 8* Slowly cooled, thick oxide scale on iron showing crack nucleation from base of outer magnetite crystallites; etched in 1% HC1 in alcohol (× 1020).

Furthermore crack nucleation was also observed along the wustite grain boundaries with secondary cracking from the sharp corners of the eutectoid magnetite cuboids. A model portraying these features is shown in Fig. 9. The usual appearance of magnetite cuboids in partially transformed wustite is shown in Fig. 10.

Rapidly cooled, thick scales were found to detach more readily from the underlying deformed substrate. The rapid generation of thermal stresses, as a result of the differential thermal contraction of the substrate and oxide layer, has led to a more extensive crack growth mechanism. This has been enhanced for thick scales by the presence of potential flaws like interface pores and fine cracks within the scale coupled with zones of weak adhesion along the interface (Fig. 11). The figure clearly illustrates the development of cracks from the sharp tips of interface pores which appear to have been preferential sites for crack nucleation. As mentioned earlier, the extent of damage to scales during metallographic preparation has been minimized but where gross voids from oxide fall out are produced they are readily recognisable.

Slowly cooled, thick scales did not show internal ruptures from thermal stresses. In the unaffected adherent interface zones crack nucleation and growth during substrate deformation was less evident.

## 3.3. Crack spacing

The scatter in crack spacing measurements was ± $0.5\,\mu m$ and the plotted data are based on the average of 50 measurements per cm length of each of three test specimens showing a uniform crack pattern.

From the experimental data, the relationship between the inverse of crack spacing, $D$, in the oxide scale and substrate strain $\epsilon_0$ showed a parabolic form as indicated in Fig. 12, which can be expressed as

$$1/D = k\epsilon_0^{1/2}$$

where $k$ is a constant which is dependent upon the applied stress system and the oxide scale thickness. The relationship is generally in agreement with the earlier work of Durelli and Okubo [5] and Edeleanu and Law [6], both of whom showed that substrate deformation generated surface coating cracks for which a logarithmic relationship existed between the inverse of crack spacing and substrate strain.

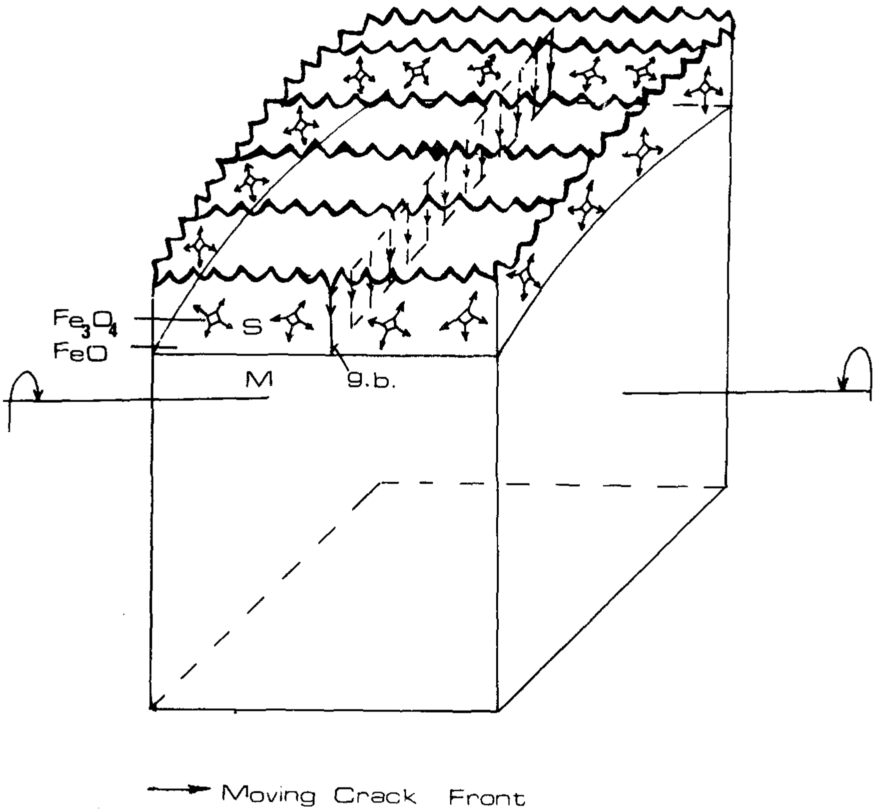

*Figure 9* Model of crack growth along grain boundaries (g.b.) and from corners of magnetite ($Fe_3O_4$)·cuboids in wustite (FeO).

Furthermore, in the present study it was found that when the crack spacing in the scale reached about 4 to 5 $\mu$m then the effect of subsequent strain for further crack nucleation became practically zero. This can be explained in terms of the greater stress relaxation achieved through the widening of existing cracks by substrate deformation thereby increasing the area of oxide-free metal surface between isolated adherent oxide blocks. Therefore, only at exceptionally high strains would it be possible to widen existing cracks and to generate further cracks simultaneously within the remaining adherent scale.

Grosskreutz [7] presented a model for the multiplication of cracks in adhering oxide films

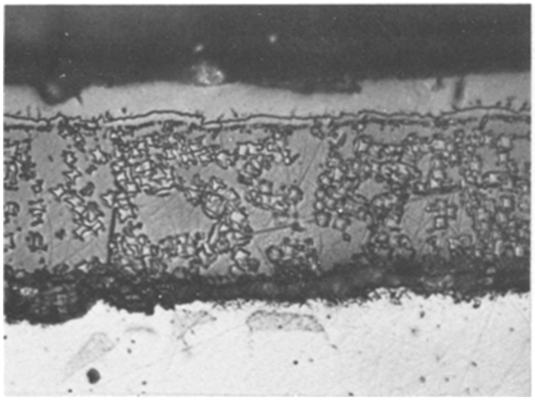

*Figure 10* Magnetite cuboids in partially transformed wustite in a thick scale, etched in 1% HCl in alcohol (× 900).

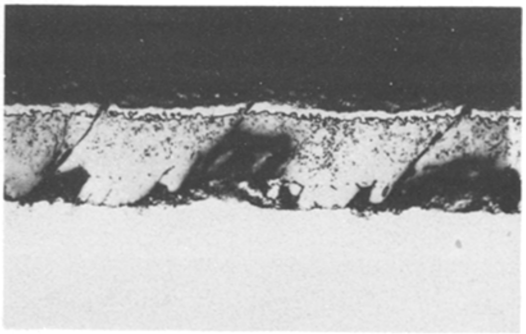

*Figure 11* Crack nucleation from sharp corners of pores along a scale/metal interface, etched in 1% HCl in alcohol (× 408).

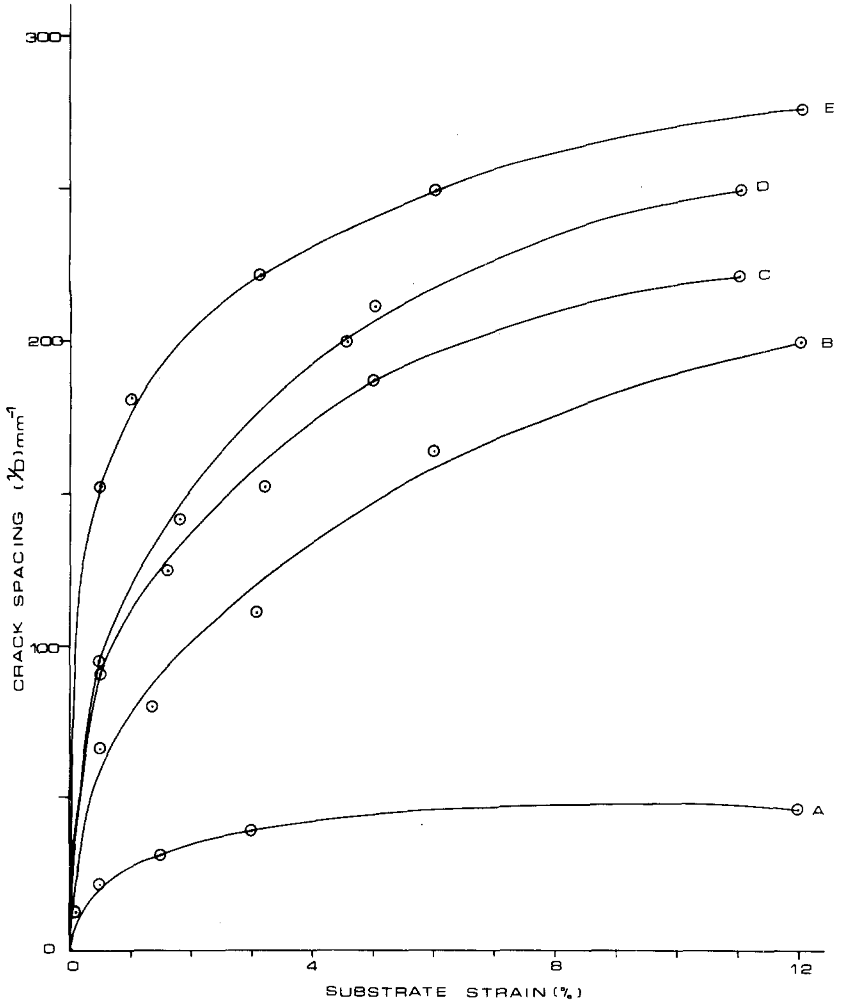

*Figure 12* Reciprocal of crack spacing, $1/D$, versus substrate strain; A stresscoat tested in tension, B rapidly cooled, thick oxide scale (35 $\mu$m) tested in torsion, C rapidly cooled, thick oxide scale (35 $\mu$m) tested in tension, D rapidly cooled, thin oxide scale (5 $\mu$m) tested in tension, E rapidly cooled, thin oxide scale (5 $\mu$m) tested in torsion.

from which he showed that

$$\ln \epsilon/\epsilon_0 = (4g/d)[1 - d/d_0]$$

where $\epsilon$ is the subsequent strain in the oxide, $\epsilon_0$ the strain in the substrate, $d_0$ the oxide fracture spacing, $d$ the spacing predicted after subsequent strain $\epsilon$, and $g$ is half the crack width which is regarded as a constant dependent upon film thickness.

He observed further that a consequence of the model of regular fracture was that when the predicted crack spacing was of the order of the crack width, further cracking should not occur, and thus the saturation crack spacing should be larger, the thicker the oxide film.

The present work is in agreement with the predictions of Grosskreutz's model, since it was found that the thicker scales (35 $\mu$m) showed a larger crack spacing than the thinner scales (5 $\mu$m) for the same substrate strains. However, even though the differences in thickness, morphology and adhesion exhibited by the iron oxide scales may not justify a close comparison with the adherent anodic thin films of $Al_2O_3$ studied by other workers [2, 7], the general fracture patterns show many similar characteristics.

## 4. Conclusions

(i) Slowly cooled, thin oxide scales (5 $\mu$m) became detached from the torsionally strained iron substrate by fracture along the scale/metal interface through the successive joining of pores.

(ii) Crack nucleation in strongly adherent, thin scales occurred at the junction of slip lines in the substrate.

(iii) Crack nucleation in slowly cooled scales of intermediate thickness ($20\,\mu m$) was found to be along grain boundaries of the bulk wustite scale and from the corners of magnetite cuboids in the bulk scale.

(iv) For the slowly cooled, thickest scales ($35\,\mu m$) crack nucleation took place from the sharp boundaries between pro-eutectoid magnetite grains in the outer scale region.

(v) For the rapidly cooled, thick scales, crack nucleation was observed to be mainly from the sharp edges of pores along the scale/metal interface.

(vi) Crack spacing in the oxide scale decreased with increasing substrate strain in a parabolic form.

## Acknowledgements

The authors are grateful to Professor K. M. Entwistle for the provision of research facilities and to the British Independent Steel Producers Association for their encouragement and material support for the work.

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Received 30 November 1976 and accepted 1 April 1977.