Microstructural investigation of the oxide scale on low carbon steel

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Abstract

There has been a long history of studies on the oxidation behaviour of carbon steel at high temperatures. The oxidation behaviour and the scale structure developed are complex. The microstructure and the ratio of the three classical layers of wüstite, magnetite and haematite may be difficult to identified by conventional techniques such as optical, standard Scanning Electron Microscopy (SEM) or X-ray diffraction. An unambiguous characterisation of the scale and the correct identification of the phases within the scale are difficult unless the crystallographic structure for each phase in the scale is considered and a microstructure-texture analysis is carried out. Throughout this work, Electron Backscatter Diffraction (EBSD) has proved to be a powerful technique for identifying the individual phases in the oxide scale accurately in order to obtain a better understanding of the mechanism of the oxide scale growth on steel and how scale microstructures develop. The results have shown how oxidation conditions such as temperature and time of exposure effect the grain size and microstructural development of the oxide phases.

1. INTRODUCTION

Steels subjected to high temperatures in an oxidised environment leads to the formation of oxide layers on their surfaces. This oxide can influence the friction conditions; heat transfer and tool wear during deformation and ultimately influence the surface finish of the final product [a, b]. The microstructures of scales can be highly complex, however, the scales on iron and steel are generally characterized by a three layer model. The innermost layer, closest to the substrate, with the lowest oxygen content is wüstite (FeO); there is an intermediate magnetite (Fe3O4) layer and a final thin oxygen rich haematite (Fe2O3) layer. This classical view of the oxide layers is however, complicated by the heat treatment cycle, oxidation environment, and alloying elements in the steel.

According to most of the published literature, as the oxidation temperature increases the thickness of the scale also increases due to faster diffusion of iron and oxygen ions [c, d, e]. The diffusion of ions is also affected by other factors for example the porosity of the scale, cracks that may develop and the scale adhesion to the substrate. Such factors are particularly important where the steel is subjected to mechanical work. This can cause the opening of cracks and defects allowing increased diffusion of oxygen to the surface of the substrate in localized regions.

The temperature also influences the fraction of the three phases within the scale [f]. At low temperatures (<650°C) the magnetite phase dominates the scale. At higher temperatures the wüstite phase becomes more dominant with the haematite layer remaining low at all temperatures. Work has shown that during cooling the wüstite phase is not stable and can transform to magnetite [c, e]. Magnetite precipitates on the wüstite due to a saturation of oxygen during cooling from the oxidation to room temperature. This precipitation can further complicate the distribution of the phases within the scale.
Recent studies have shown that Electron Backscatter Diffraction (EBSD) can be used to identify the phases within the scale allowing the microstructures to be imaged and analysed [g, h, i]. The aim of the current study is to develop an understanding of oxide scale microstructural development and the processing conditions that affect it by utilising this new technique, which gives more detailed information than conventional methods. The theories and hypotheses related to oxidation from the literature are reviewed throughout this work and compared with the results from this study.

2. EXPERIMENTAL PROCEDURE

Table 1 shows the composition of the low carbon steel used in this study. The steel was supplied as cold drawn tube with an initial grain size of 56 µm.

<table>
<thead>
<tr>
<th>Element</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Al</th>
<th>Cr, Mo, Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>wt%</td>
<td>0.10</td>
<td>0.10</td>
<td>0.34</td>
<td>0.005</td>
<td>0.002</td>
<td>0.028</td>
<td>Trace</td>
</tr>
</tbody>
</table>

Samples of the plate 8×8×5 mm were cut and the large surface ground on to a final finish of 1200grit. The samples were oxidised at temperatures of 650, 750, 900, 1000 and 1100°C for 600, 1200, 1800 and 3600 seconds in free flowing air. After removal from the furnace a piece of aluminium sheet was adhered to the surface using a conducting medium to retain the oxide in position on the substrate surface. The samples were then cooled down to room temperature in air. The optimum method of sample preparation involves mounting the samples in small aluminium cups in Woods metal which has a melting temperatures of ~80°C [g]. This method minimized any damage to the scale and gives a completely conductive medium that eliminates any charging problems. The sample assemblies were ground on silica carbide paper finishing with 1200grit followed by polishing using 6 and 1µm diamond paste. Quantitative optical metallography was carried out on samples that were etched in 1% HCl in ethanol following standard sample preparation [j]. Prior to examination in the SEM final polishing was carried out using colloidal silica for a minimum of 15 minutes just prior to insertion into the microscope. The samples were characterized using a LEO 1530VP Scanning Electron Microscopy (SEM) fitted with a field emission gun. The microscope is fitted with a TSL-EBSD system, which allows simultaneous chemical EDS analysis to be carried out during the EBSD scan. The data was obtained and analysed using OIM analysis package. The operating voltage used was 20 kV to obtain optimum quality of diffraction patterns. Working distances were varied from 15 to 18 mm.

3. RESULTS AND DISCUSSION

3.1 Oxidation Rate

Fig. 1 shows a plot of oxide thicknesses versus time. As expected, there is an increase in the oxide scale thickness with increasing time of exposure and oxidizing temperature. At ~1800 seconds of exposure, the oxide thickening reaches a maximum rate at all temperatures except 650°C. After this point the oxidation rate slows and the thickness of the scales remains approximately constant or grows very slowly. This is as would be expected when considering the diffusion of the iron and oxygen ions across the scale layer, which becomes more difficult as the scale thickness increases [e]. At 650 and 750°C, the oxidation rate is less clear. In fact, at 650°C the oxidation rate is very controversial in the literature whether it is linear or
parabolic [c, d, e, j]. The current data, however, trends to be more parabolic than linear. At 900, 1000, 1100°C temperatures, the oxidation rates are parabolic.

![Figure 1](image1.png)

**Figure 1**: Oxide thickness vs. time on low carbon steel at different temperatures.

An Arrhenius plot of the parabolic rate constant from this study is shown in Fig. 2. From the data the activation energy was calculated to be 214 kJ/mole. The parabolic kinetics can be fully suitable of fitting data in the absence of volatile compound and growth of continues coherent surface films [c]. However, the oxide scale developed on the steel in this study was not adherent to the substrate and not uniform at these temperatures and so may not obey parabolic law fully.

![Figure 2](image2.png)

**Figure 2**: Arrhenius plot of parabolic rate constant for oxide scale grown on low carbon steel.

The difficulties in fitting the data to the rate equation and comparing the results are related to the fact that the reaction rates and corresponding rate equation for the oxidation of any metal are functional of a number of factors such as temperature, oxygen pressure, elapsed time of
reaction, surface preparation, composition of the steel and pre-treatment of the metal [c]. Thus, the comparison between the results obtained from this study and the literature is difficult.

3.2 Oxide Microstructure

The study of the oxide microstructure is of great importance in the understanding of the nucleation, growth, kinetics, oxide mechanical properties and descaling properties of the scale. At each oxidation temperature the oxide develops different grain shapes, sizes and orientations, making the oxide scale available with a wide range of mechanical properties that leads to a consideration of microstructural engineering to improve the descaling processes. In addition to the factors that affect oxide scale microstructure, as mentioned previously, it is believed that even the substrate texture has an affect on oxide development and thus oxide microstructure [g, h, i].

Traditionally, standard metallographic sample preparations have been used to characterise the oxide scale by optical or scanning electron microscopy (using etchants containing 0.5-1% hydrochloric acid solutions in ethanol) [j, k, l]. The microstructure of the oxide scale is however not straightforward. For example, as shown in Fig. 3, wüstite appears dark relative to the magnetite, and haematite is the lightest of the etched oxide layers. The magnetite precipitation on wüstite can be seen in the same micrograph. This traditional method has been used throughout the last century and in most research centres today. However, this is not an accurate way of identifying a phase’s distribution in the scale as is not correlated to crystal structure analysis of the phases within the scale. The phase identification by optical microscopy depends on the light reflection from each phases and most probably artefacts generated during sample preparations and etching methodology. The current results from EBSD shows that the traditional methods are probably misleading. Moreover, etching samples does not give any information about the phases grain size, shapes, orientation, or grain boundaries.

**Figure 3**: Optical micrograph of oxide scale developed on low carbon steel at 1100°C-1200 seconds, etched with 1%HCl and ethanol.

**Figure 4**: SEM image of oxide scale developed on low carbon steel at 900°C-1800 seconds, etched with 1%HCl and ethanol.
Notwithstanding, standard scanning electron microscopy may give more information about the oxide scale at higher magnification than optical microscopy. The limitation of the SEM technique is that, as with optical microscopy, it does not give detailed information of oxide microstructure. As shown in Fig. 4, no indication of grain boundaries in each phase in the scale is evident. In the current study, EBSD was used to eliminate the ambiguity of existing phases in the oxide scale and correlate microstructures. The ambiguities can be eliminated only if the grain and crystallographic structure for each phase in the scale is considered and its microstructure-texture analysis used to characterise the scale microstructure.

One of the most powerful features of EBSD is that the Image Quality (IQ) map provides better contrast of the grain boundaries than conventional secondary electron SEM images. This occurs because diffraction patterns taken from grain boundary regions result in a poor pattern quality index, since the EBSD patterns obtained from these regions are generated from both grains. Thus, the pattern quality map is an excellent method of highlighting grain boundaries while still observing the microstructural features [m]. Figs. 5-8 show Image quality maps, which are a greyscale, plot, where the greyscale level at each point corresponds to the relative intensity of the Kikuchi bands above the background in the EBSD pattern acquired at each point [n]. Obtaining the grain size, shape and detail of the microstructure of the phases using EBSD characterisation technique is therefore more reliable than other techniques. Carpenter et al. [o] investigated the oxide scale microstructure using optical and scanning electron microscopy. They came to the conclusion, after experiments on low carbon steel, that haematite has an equiaxed type grain structure, magnetite is columnar and wüstite due to magnetite precipitation is not clear but looked to be of a columnar grain type. Throughout this study, however, different ideas about grain shape of the phases have been obtained by using EBSD. As shown in Figs 5, 6, 7 and 8, different grain shapes can exist for each phase in the scale depending on time and temperature.

![Figure 5: EBSD Image quality of low carbon steel oxidised at 750°C-1800](image)

![Figure 6: EBSD Image quality of low carbon steel oxidised at 900°C-1800](image)

The grain shape and sizes with increasing temperature after oxidation for 1800 seconds are shown quantitatively in Tables 2 and 3. The wüstite grain size increases with increasing
temperature. The magnetite grain size also increases but less dramatically than wüstite grain size, which may be why descaling at higher temperatures is more difficult, as less grain boundaries exist in the scale. It is believed that grain boundaries act as a diffusion path and in some cases due to internal stress change to vertical or lateral cracks that help in the mechanical and chemical descaling processes [c, e, f].

Kofstad [c] reported that the columnar grain shape of oxide scale developed as a result of competition between grains during the oxidation process. Furthermore, the authors of this study believe that cracks and porosity also affect the grain shape. Any assumption of the effect of cracks and pores on the grain shape should consider whether the cracks and pores are formed during the oxidation processes or cooling period. Currently, the microstructure images formed by EBSD can only reveal the final stage of the oxidation and after cooling is completed. Thus, it is very difficult to determine when the cracks and pores are formed. Moreover, how they affected the microstructure development of the oxide scale.

Given that it is not currently possible to monitor the oxide development during the oxidation process. The following observations have been made on consideration of the final structure. As shown in Fig. 7, grains near the cracks are more columnar than equiaxed in shape. This could be explained by accumulating gas in the crack which promote further oxidation of the area beside the crack, and that makes grains grow alongside the crack direction. This assumption is only valid if the crack is considered to form during the oxidation period. However, porosity has different affect on the grains shape. It has been noted that the grains surrounded by pores, are more equiaxed than columnar. In some areas within the scale pores are distributed all around some grains, unlike a crack that goes alongside grain only in one side of the grain. Moreover, accumulating reactant gas all around the grain causes equal growth of the grain in each direction Figs. 5 and 6.
Table 2: Steel oxide scale phases grain size (µm-diameter) in Growth Direction (GD)

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Time (s)</th>
<th>Wüstite</th>
<th>Magnetite</th>
<th>Haematite</th>
</tr>
</thead>
<tbody>
<tr>
<td>1100</td>
<td>1800</td>
<td>185.95 ± 10.32</td>
<td>131.74 ± 29.36</td>
<td>52.11 ± 1.23</td>
</tr>
<tr>
<td>1000</td>
<td>1800</td>
<td>111.56 ± 25.69</td>
<td>24.21 ± 0.63</td>
<td>Not observed</td>
</tr>
<tr>
<td>900</td>
<td>1800</td>
<td>22.89 ± 5.36</td>
<td>7.31 ± 0.68</td>
<td>Not observed</td>
</tr>
<tr>
<td>750</td>
<td>1800</td>
<td>8.73 ± 9.84</td>
<td>3.91 ± 0.85</td>
<td>Not observed</td>
</tr>
</tbody>
</table>

Table 3: Steel oxide scale phases grain size (µm-diameter) in Transverse Direction (TD)

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Time (s)</th>
<th>Wüstite</th>
<th>Magnetite</th>
<th>Haematite</th>
</tr>
</thead>
<tbody>
<tr>
<td>1100</td>
<td>1800</td>
<td>216.35 ± 9.60</td>
<td>196.63 ± 36.42</td>
<td>41.36 ± 2.69</td>
</tr>
<tr>
<td>1000</td>
<td>1800</td>
<td>72.63 ± 12.36</td>
<td>26.84 ± 0.79</td>
<td>Not observed</td>
</tr>
<tr>
<td>900</td>
<td>1800</td>
<td>10.73 ± 2.41</td>
<td>6.92 ± 0.96</td>
<td>Not observed</td>
</tr>
<tr>
<td>750</td>
<td>1800</td>
<td>1.46 ± 6.35</td>
<td>1.99 ± 2.37</td>
<td>Not observed</td>
</tr>
</tbody>
</table>

The limitation of optical and scanning electron microscopy is that it only reveals phase boundaries not the grain boundaries of the most etched oxide scale on steel. Whilst EBSD image quality map can reveal the grain boundaries clearly. The number and type of grain boundaries is important for studying oxide microstructure as they act as a diffusion path during oxidation process. This technique has been shown to be a valuable tool in the study of oxide scale development. It gives considerable information on the microstructure and allow better model of oxide growth to be developed. This will lead to a better understanding of scales and how their properties can be controlled to give optimum performance during both processing and descaling operations [p, q].

4. CONCLUSIONS

The oxidation process of low carbon steel has been reviewed in the light of previous studies and comparing oxidation theories with the results obtained by EBSD as a new and powerful technique for studying oxide scales.

The oxidation rate of low carbon steel at 650, 750, 900, 1000, and 1100°C has been studied. At all of temperatures the oxide reaches a plateau level after relatively short oxidation times with higher temperatures leading to greater oxide thicknesses. The oxidation rate was found to be parabolic at all temperatures and activation energy of 214 kJ/mole was calculated.

EBSD is shown to be a valuable tool in the study of oxide scale. The results show that the microstructure of the scale can be easily imaged. Different grain shapes can exist for each phase in the scale depending on time and temperature.

The wüstite grain size increases with increasing temperature, causing grain and grain boundaries number to decrease with increasing temperature. Cracks and porosity may have a considerable effect on oxide grain shapes.
5. REFERENCES


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k) CAPLAN, D., etc. The effect of FeO grain size and cavities on the oxidation of Fe. Corrosion science, 1981, volume 21, no 9, page 689.


