EBSD Microstructural Characterisation of Oxide Scale on Low Carbon Steel

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The microstructures of the oxide scale developed at high temperature on steels are very complex and their development depends on many factors including time, temperature, oxidation conditions and alloying elements. The classical model of an oxide scale on steel consisting of wüstite, magnetite and haematite layers, is more complicated in reality and its properties change with the factors that affect their development. An understanding of the oxide scale formation and its properties can only be achieved by careful examination of the scale microstructure. The oxide scale microstructure may be difficult to characterise by conventional techniques such as optical or standard scanning electron microscopy. 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 simultaneous microstructure-microtexture analysis is carried out. In the current study Electron Backscatter Diffraction (EBSD) has been used to investigate the microstructure of iron oxide layers grown on low carbon steels at different times and temperatures. EBSD has proved to be a powerful technique for identifying the individual phases in the oxide scale accurately. The results show that different grain shapes and sizes develop for each phase in the scale depending on time and temperature.

Keywords : oxidation, steel, EBSD, microstructure

1. Introduction

The microstructures of the oxide scales on steels are very complex and their development depends on many factors including time, temperature, oxidation environment and alloying elements. Classically iron and steel scales, are characterised by a three layers: The innermost layer, closest to the steel substrate, with the lowest oxygen content is wüstite (FeO); there is an intermediate magnetite (Fe_3O_4) layer and a final thin oxygen rich haematite (Fe_2O_3) layer.[1] The microstructure characterisation of the oxide scale and verifying its phases helps to obtain a better understanding of the oxidation mechanism. Furthermore, knowledge of the oxide microstructure is critical in understanding how the oxide behaves during the high temperature deformation of steels and more importantly how it can be removed following processing.

The tendency of steel to oxidise at high temperatures is great compared to other engineering materials. However, it is widely used and in high demanding engineering application which create a challenge for researchers and manu-factures to improve steel surface quality. The driving force for iron oxidation is very strong. When the thermodynamic conditions are met for oxidation to occur, the oxidation starts by a nucleation process followed by the growth of the scale. The growth of the oxide scale depends on transport, at the atomic level, of either oxygen or iron through the film. As the oxidation temperature increases, the thickness of the scale also increases due to the faster diffusion of iron ions and oxygen ions.[1-3] 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.[4]

The temperature also influences the distribution of the three phases within the scale.[5] 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 relatively thin at all temperatures. Work has shown however that during cooling the wüstite phase is not stable and can transform

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to magnetite.[1),3)] Magnetite precipitates on wüstite due to a saturation of oxygen during cooling from the oxidation temperature to room temperature. This precipitation of the magnetite on the wüstite can further complicate the distribution of the phases within the scale.[4)]

The complex microstructural development of the oxide scale on low carbon steel makes the analysis of the scale microstructures difficult as the phases cannot be identified easily using standard imaging techniques. In recent years studies have shown that Electron Back-Scatter Diffraction (EBSD) can be used to identify the phases within the scale allowing the microstructures to be imaged and analysed.[6)-8)] Work by Higginson *et al*.[7)] also showed that there may be a complex crystallographic texture relationship between the scale phases themselves and between the scale layers and the substrate. These relationships may be important when considering the mechanical properties of scales particularly when mechanical descaling is used to remove the scale from the finished product.

2. Experimental procedure

Table 1 shows the compositions of the Interstitial Free steel used in this study. The steel was supplied as hot rolled plate of initial grain size of 86 μm. Samples of the plate 0.8×0.8×0.5 cm were cut and the large surface ground to a final finish of 1200 grit.

The samples were oxidised in a standard furnace at temperatures of 650, 750, 900, 1000 and 1100°C for 3600 seconds. 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 to room temperature in laboratory air. The optimum method of sample preparation involves mounting the samples in small aluminium cups in Woods Metal which has a melting temperature of ~80°C.[6)] This method minimized any damage to the scale and gives a completely conductive medium that eliminates any charging problems in the microscope. The sample assemblies were ground on silica carbide paper finishing with 1200 grit followed by polishing using 6 and 1 μm diamond paste. Quantitative optical metallography was carried out on samples after etching in 1% HCl in ethanol following standard sample preparation.[4)] 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 an OIM analysis software package. The sample was tilted to 70° in the SEM sample chamber, the diffraction pattern was averaged and background corrected and then digitised into the computer memory where it was automatically or manually indexed. 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

Traditionally, standard metallographic sample preparation and investigation has been used to characterise the oxide scale by optical or scanning electron microscopy, using etchants containing 0.5-1% hydrochloric acid solutions in ethanol.[4),9),10)] The microstructure of the oxide scale is however not straightforward for example as Fig. 1a. shows; 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 figure, which has the same colour as the magnetite layer. The different colour gradient in wüstite relates to the wüstite composition, as a wüstite cation-deficient structure exists which varies in composition between the iron substrate and magnetite boundaries. This traditional method has been used throughout the last century and still in most research centres today, however, it is not an accurate way of identifying the phase distribution in the scale as it is not correlated to a crystal structure analysis of the phases within the scale. Phase identification by optical microscopy depends on the light reflection from each phase and also from any artefacts generated during sample preparation and etching. Moreover, etching samples does not give any information about the phase grain size, shape, orientation, or grain boundaries.

In contrast to optical microscopy, scanning electron microscopy gives different apparent colour contrast of the oxide phases in the scale. As shown in Fig. 1b, magnetite

Table 1. Composition of the steel used (wt%)

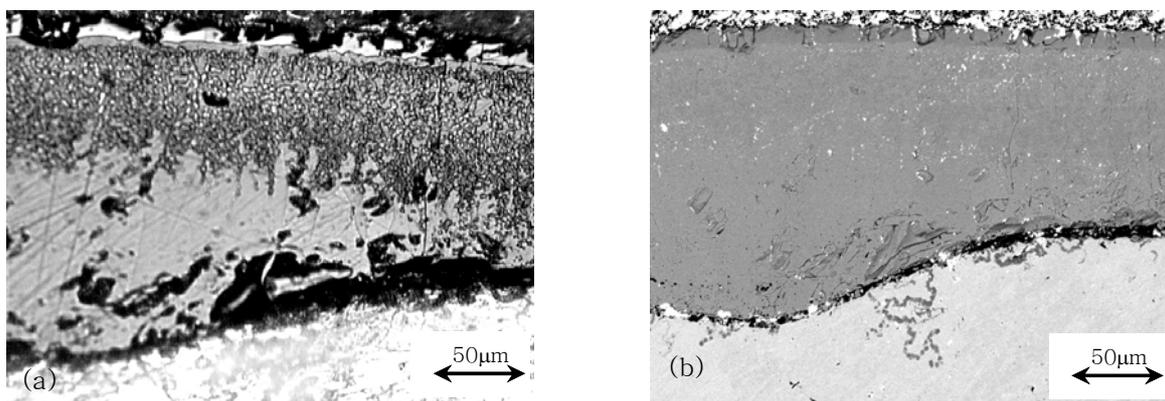| Sample	C	Si	Mn	P	S	Cr	Mo	Ni	Al	Cu	N	C.E
IF Steel	0.0026	0.004	0.004	0.156	0.009	-	-	-	0.05	-	-	-

Fig. 1. Optical micrograph of the scale, formed on IF steel at 1000℃ after 1800 seconds, etched with 1%HCl (a) and SEM-QBSD detector image of the same sample (b)

is appeared darker than wüstite. Standard scanning electron microscopy may give more information about the oxide scale at higher magnification than optical microscopy. However, the limitation of the SEM technique is that, as with optical microscopy, it does not give detailed information on oxide microstructure. As shown in Figs. 1a and b, no indication of grain boundaries in each phase in the scale is evident. The optical, scanning electron microscope, chemical analysis, X-ray diffraction and laser Raman Spectroscopy can give information about the phases present in the oxide scale,[11),12),13)] but they cannot correlate the phase distribution within the scale microstructure.

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 obtained to characterise the scale microstructure. One of the powerful features of the EBSD is the Image Quality (IQ) map, which provides better contrast of the grain boundaries than does conventional secondary electron contrast SEM. This occurs because diffraction patterns taken from the 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.[14)] The image quality map is a grayscale plot where the grayscale level at each point corresponds to the relative intensity of the Kikuchi bands above the background in the EBSD pattern acquired at each point.[15),16)] Therefore, obtaining grain size, shape and detailed microstructure of the phases using EBSD characterisation technique is more reliable than with other techniques. As shown in Fig. 2a, the phases and grain boundaries can be seen clearly in the Image Quality map. Moreover, from the grain boundaries level map, all the grain boundaries in the sample area can be characterized easily whether low (2-15°) or high (15-180°) misorientation grain boundaries, Fig. 2b. Characterizing grain boundary misorientations is important for grain size measurements. Thus, the EBSD user can decided which grain boundaries are to be excluded in grain size measurements. In this study only high angle (15-180°) grain boundaries were included.

EBSD is a technique that can provide identification of unknown crystalline phases while exploiting the excellent imaging capabilities of the SEM. EBSD patterns contain a large amount of information about the crystal structure of the phase such as the lattice plane spacing, lattice parameter and crystal plane. It is possible to use this information to determine the space group of the phase from the symmetry elements contained in the pattern. The combination of EBSD and a crystallographic database is becoming a standard technique for the identification of unknown crystalline phases.[14)] To distinguish between phases, the selected crystals must either have different structures or have a unit cell parameter difference greater than 10%. When these conditions are met, a mapping program can distinguish between the phases (phase discrimination).[15)]

Fig. 2c shows the phase distribution in the oxide scale layer grown on the steel at 1000°C for 1800 seconds. As can be seen from the figure, the two existing phases within the scale can be clearly identified and the magnetite precipitates distribution within wüstite grains can be observed. During this work analysis of the misorientation between individual grains was carried out using the EBSD data. The results showed that the magnetite grains are separated by either low or high grain boundaries depending on their

location within the scale. Whilst magnetite precipitates and wüstite grains are separated by very low grain boundaries and even appear as one grain in the image quality map, as they have the same orientation. This leads to the conclusion that the transformation from wüstite to magnetite during cooling does not cause a change in orientation. Therefore the magnetite is separated from the surrounding wüstite grain by very low angle phase boundaries. This is in agreement with Goldschmidt,[17] who claimed that there is a close connection between the three phase structures (iron, wüstite and magnetite), which are all cubic. While the transition Fe → FeO is considered as true oxidation, the change FeO → Fe_3O_4 is not, because the number of oxygen ions per crystal volume remains constant, only the number of iron ions being different. Moreover, there is a strong crystallographic relationship between wüstite and magnetite. The current authors believe that segregation of crystallites of Fe_3O_4 from primary FeO may well take place without causing a physical disruption. Supporting

this assumption is that the orientation of wüstite and magnetite precipitations were the same or very similar. Fig. 2d shows the EBSD-EDS oxygen map for the same scanning area in 2a. As expected, the magnetite phase contains higher oxygen concentration than wüstite. Furthermore, the EDS map is used as a double check for indexing parameters in the phase map. The contrast EBSD and EDS maps, Fig 2c and d, are very similar, indicating that the diffraction patterns from each oxide phase in the scale were accurately indexed. The two-layered oxide scale is clearly seen in Fig. 2. This microstructure can be explained on the basis of iron oxidation growth theory,[18-20] where wüstite, being close to the substrate, is richest in iron, while haematite, the outer scale, is richest in oxygen. The large gap seen between the substrate and the oxide does not appear to disturb the three-layer structure of the scale. It should be noted that haematite was not observed.

Fig. 3 shows a graph of the grain size of the oxide scale phases versus temperature; the exposure time of oxi-
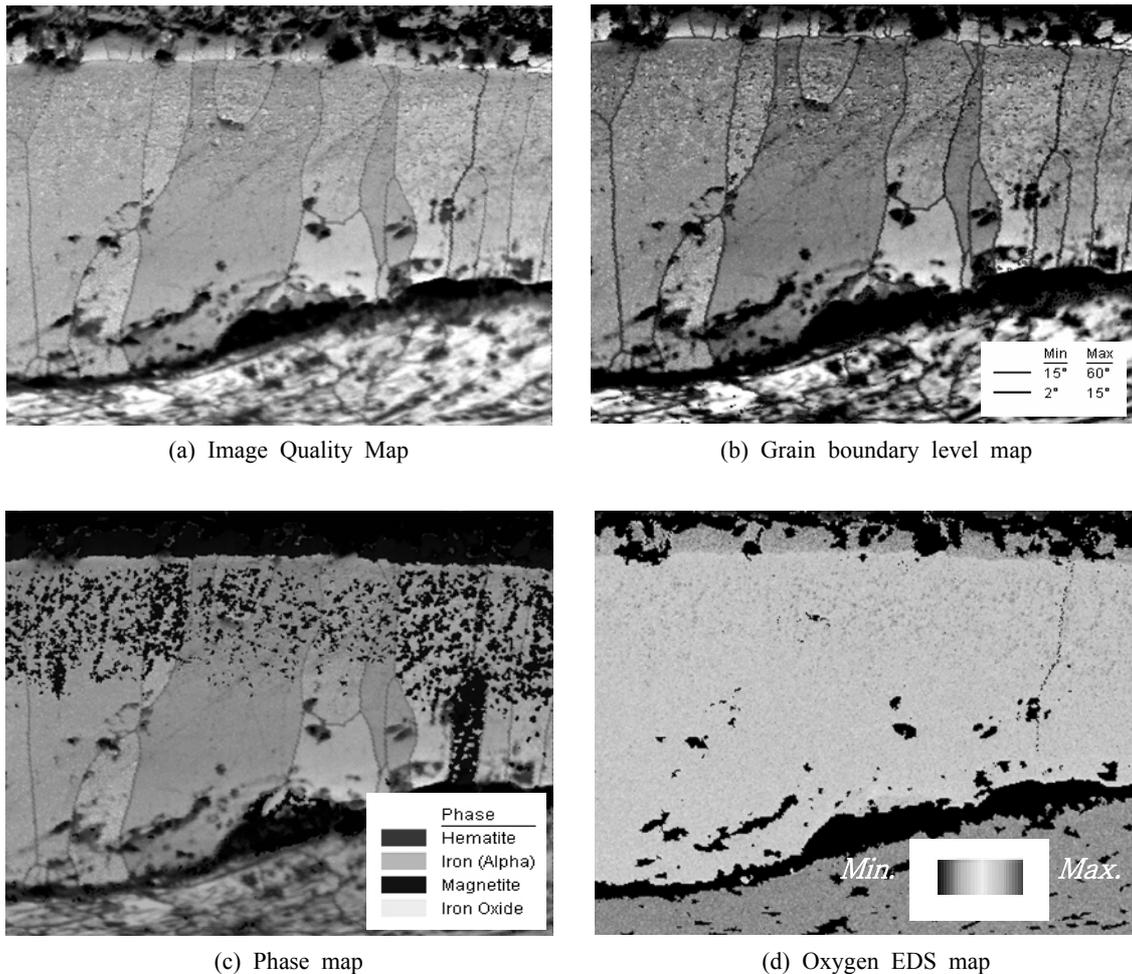

(a) Image Quality Map

(b) Grain boundary level map

(c) Phase map

(d) Oxygen EDS map

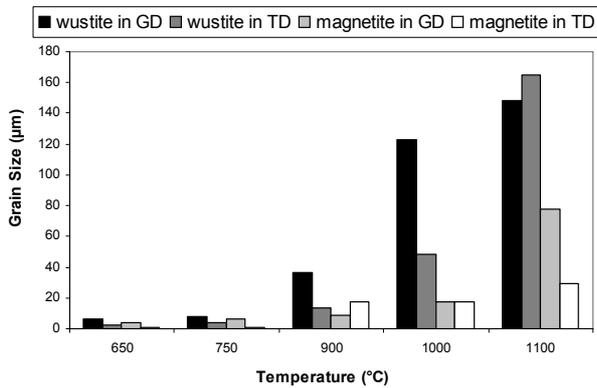**Fig. 2.** EBSD maps of oxide scale formed on IF steel at 1000 ℃ after 1800 seconds

Fig. 3. Oxide phase grain size v. temperature in both Growth (GD) and Transverse (TD) directions of IF steel oxidised for 1800 seconds.

dation was 1800 seconds. As can be seen from the figure, the wüstite and magnetite grain sizes increase with increasing temperatures in both the growth and transverse directions. Only at 1000℃, the aspect ratio of the magnetite grain size was close to 1. At the rest of the oxidation temperatures the grains were columnar.

From this study, the limitation of optical and scanning electron microscopy have been shown as they can reveal the phase boundaries but not the grain boundaries of the oxide scale on steel. EBSD image quality maps 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 the 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 allows better models 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.

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 scale. Furthermore, EBSD is shown to be a valuable tool in the study of the oxide scale. The results show that the microstructure of the scale can be easily imaged and the phases clearly identified. Different grain shapes can exist for each phase in the scale depending on time and temperature of oxidation. Moreover, the wüstite grain size increases with increasing temperature, causing the numbers of grain boundary to decrease with increasing temperature; this is believed to affect the descaling process.

Acknowledgements

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