Using a plasma FIB system to characterise the porosity through the oxide scale formed on 9Cr-1Mo steel exposed to CO₂

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ABSTRACT

Focused ion beam microscopy and scanning electron microscopy have been used to characterise the porosity of the oxide scale of an experimental 9Cr–1Mo steel sample exposed for 4580 h in a CO₂-rich environment. The magnetite shows a high frequency of spherical pores (∼1 μm³) with no interconnectivity. The Cr-rich spinel layer shows greater interconnectivity, but no single pore spans the total oxide scale. A mechanism for the formation of the different morphologies observed across the scale is proposed, linking porosity changes across the oxide scale to the carburisation and elemental segregation of Cr within the substrate.

GRAPHICAL ABSTRACT

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Introduction

9Cr–1Mo steel is commonly used across the energy industry due to its creep strength and corrosion resistance at medium to high temperatures for extended periods of time without failure. One such use is within advanced gas-cooled reactors which can be exposed to CO2 at high temperatures. To resist corrosion in these aggressive environments, 9Cr–1Mo develops a duplex oxide scale, consisting of an outer Fe-rich magnetite layer and an inner Cr-rich protective Cr-rich spinel layer with both showing very different morphologies. The growth of this oxide takes place through the available space model [1–7], with Fe from the substrate required to diffuse outwards leading to magnetite growth and O2 diffusing inwards to form the Cr-rich spinel oxide layer. During exposure, pores within the oxide are common and develop over exposure time. Typically, these pores are assumed to be a result of reduced Fe diffusion outwards, potentially inhibited by the Cr within the Cr-rich spinel [8]. As the oxide continues to grow, the diffusion distance increases, with the ratio between the two oxide layers progressing from ~ 1:1 magnetite/Cr-rich spinel to 1:>1 ratio [7].

Experimental samples exposed to CO2-rich environments have been shown to form a high volume of substrate carbides due to the reactions taking place between the gas, the metal substrate and the oxide [2, 9, 10]. The driving force for carbon formation is thought to be the Boudouard reaction, detailed in Eqs. 1 and 2.

\[
\begin{align*}
\text{CO}_2 & \rightarrow \text{CO} + \text{O}_2 \\
2\text{CO} & \rightarrow \text{CO}_2 + \text{C}
\end{align*}
\]

Upon exposure, the metal is oxidised by CO2 which is then reduced to CO, increasing the local CO concentration, which then leads to the formation of C (Eq. 2). This C is absorbed by the metal, leading to the carbide formation in the substrate, with the driving force of carbide formation being attributed to reduced O2 concentration at the oxide/metal interface [3, 11–14]. The internally carburised region can penetrate up to three times the depth of the internal oxidation zone and up to five times the total oxide thickness which has potential to span the total sample [15–18]. This increasing carbide presence within the substrate changes both the oxidation and carburisation characteristics of the steel, both through increased carbon concentration and elemental segregation. This elemental segregation across the carburised substrate will lead to uneven elemental distributions within the Cr-rich spinel [17, 19, 20] which are thought to be linked with the morphology of the oxide scale, with previous work proposing that the Cr-rich oxide areas are inhibiting pore migration and coalescence [21].

9Cr–1Mo steels are associated with a phenomenon known as breakaway oxidation. This is typically categorised through rapid mass gain, far greater than observed during earlier exposure. Breakaway oxidation is linked with the loss of the protective nature of the oxide scale and in worst case scenarios component failure [22, 23]. Both carbon and carbide concentrations within the substrate have previously been linked to breakaway oxidation [18], but a single point of initiation has not been fully agreed on [6, 11, 18, 24]. Post breakaway oxidation kinetics show an exponential increase in the oxide growth rate, which is attributed to the loss of protective scale which allows for an increased volume of gas to diffuse through and react with the now exposed substrate.

The presence of pores within the scale has the potential to alter the gas transport mechanisms taking place through reducing the diffusion distance of gas within the oxide scale, allowing for increased volume of gas to penetrate through the oxide. These pores are also providing an increased surface area within the oxide scale. This increased surface area may provide additional area for catalysis of the Boudouard reaction to take place, leading to increased carbon presence within the scale [25] with continued exposure due to the ever increasing surface area within the oxide scale. Should an interconnected network of pores span the total distance through the oxide scale this will lead to a dramatic increase in the inwards gas diffusion resulting in rapid oxide growth and potentially breakaway oxidation. Better understanding the development of oxide morphology development with exposure time will allow for better estimates of breakaway oxidation should a network of interconnected pores develop.

Work previously investigating porosity variations between 9Cr–1Mo steels exposed to a steam atmosphere found that porosity across both magnetite and Cr-rich spinel layers increases with exposure time.
The total volume fraction and pore size increase across the scale [21] with the maximum porosity fraction being found near the magnetite/Cr-rich spinel interface. The distribution across the oxide of the pores was also observed to be different across the oxide scale, with the Cr-rich spinel pores showing greater interconnectivity at longer exposure times relative to shorter exposed samples. This increased connectivity is of importance because if an interconnected network of pores were to develop it would allow for increased rate of gas transport through the scale, increasing the rate of oxidation and potentially initiating breakaway oxidation.

Banding of pores within the oxide formed on 9Cr–1Mo steel has been observed on 9Cr–1Mo steels exposed to CO₂ [2, 7, 26] and steam [8, 27], with porosity bands forming parallel to the substrate/oxide interface, thought to be linked with the prior substrate microstructure [20]. This banding has been previously attributed to elemental segregation of Cr and Fe in the Cr-rich spinel oxide, with the pores forming in Cr deficient regions unable to migrate through Cr-rich regions [21].

Porosity changes within the oxide of 9Cr–1Mo steel exposed to CO₂ have been previously investigated using SEM imaging techniques [28], but SEM micrographs only give a 2D snapshot into the oxidation processes and porosity development taking place within the oxide scale. In comparison with traditional SEM imaging, focused ion beam microscopy allows for the removal of material, either as a large section or very thin layers (< 100 nm).

Selective removal of small volumes of material, followed by an image being taken, allows for a series of micrographs spanning the total area of interest. These images can then be analysed, and the distribution of features can be reconstructed. This is known as a slice and view. Data can then be extracted from these images allowing for 3D reconstruction of features across the area of interest. This reconstruction allows for better understanding of any features in 3D in comparison with SEM where the features can only be observed in 2D and may not be fully representative of the oxidation processes taking place through the total oxide scale.

The aim of this research was to characterise the oxide structure through the oxide scale formed on 9Cr–1Mo steel when exposed to a CO₂-rich atmosphere within a relatively large volume of material relative to previous work. The use of a plasma focused ion beam (PFIB) microscope allows for the milling of larger sample volumes. This allows for far greater volumes to be characterised in a shorter period of time in comparison to a traditional Ga FIB system. This will give us far more information relating to the porosity through the oxide scale due to the increased volume of material which has been analysed.

**Experimental**

Experimental 9Cr–1Mo steel samples have been exposed to a CO₂-rich atmosphere for varying lengths of time on behalf of EDF energy with the aim of better understanding the corrosion of 9Cr–1Mo steel. The elemental composition of the virgin material prior to exposure is given in Table 1.

Within this study, samples exposed up to 15,068 h to a CO₂-rich environment were compared, and the details are given in Table 2. The samples were aged in autoclaves with an inner volume of 22.5 l at a pressure of 4.24 MPa (600 psig) and a gas composition consisting of 0.01% H₂, 0.03% CH₄, 0.07% H₂O and 1% CO by volume with the remainder being CO₂. The gas was continuously flowed through at a rate of 20 cc/min (at standard temperature and pressure). Samples HRA-8547-2538 and HRA-8547-4580 show no signs of breakaway oxidation, whereas sample HRA-8537-15068 has suffered breakaway oxidation.

Samples were mounted in Bakelite® and polished to a 1-μm finish to ensure high-quality SEM micrographs. The samples described here are all finned samples, and an example is shown in Fig. 1a, b. All experimental work, unless indicated otherwise, was conducted across the top of the fin tips, due to the fin tips showing increased oxidation rates relative to the body and being more susceptible to breakaway oxidation [29]. The elemental composition of virgin material prior to exposure is given in Table 1.

Scanning electron microscopy was performed using either a JOEL 7800F or 7100F field emission gun SEM (FEGSEM), both equipped with Oxford Instruments X-max 80 silicon drift energy-dispersive X-ray spectroscopy (EDS) detectors. Typically, the backscatter electron detector was chosen for SEM imaging with an accelerating voltage of 10 kV and a probe current of 12 nA with a working distance of 10 mm. For EDS analysis, typically 20 kV
accelerating voltage was used with a probe current of between 14 and 16 nA with a working distance of 10 mm.

For 2D analysis of porosity, a series of micrographs were taken through the oxide scale starting at the outer magnetite edge. These micrographs were then combined using ImageJ to create a montage which then was thresholded removing all but the pores present. The pore volume fraction across the oxide was then measured using ImageJ, where the pore volume could be measured per horizontal line of the montage.

For 3D analysis, a FEI Helios G4 PFIB CXe PFIB was used to perform both the lift-out and slice and view experiment. The large section was prepared at the fin tips of the sample with a target volume of 10μmx10μmx120μm (Fig. 1b). A Pt layer of 20μmx5μmx120μm was deposited to cover the total area of interest and account for material loss during milling. For the initial large lift-out, 2.5 μA and 30 kV were used. This allowed for rapid removal of material, and the high current helped to ensure that no redeposition occurred. The lift-out was mounted on a Si holder, which is shown in Fig. 1d.

Sample HRA-8547-4580 was selected for 3D analysis due to the longer exposure time (in comparison with HRA-8547-2580) and because it has not suffered from breakaway oxidation. The centre of a fin was selected as the area of interest. The location of this is indicated in Fig. 1. Material surrounding this region was selectively milled away leaving the bridge and the large section remaining (Fig. 1c). The large section was removed from the fin tips using the EZ lift-out system where it was moved to a pre-tilted Si holder (Fig. 1d) after which the slice and view settings could be configured.

For the slice and view, milling of the sample was performed using 15 nA at 30 kV, slices of 60 nm thickness were chosen, and a 5° rocking mill was used to decrease curtaining. Milling was performed at 15 nA at 30 kV with micrographs collected after each slice. This milling current was chosen as a compromise between milling speed and to reduce ion beam damage to the region of interest. For imaging,

| Table 1 | Elemental composition of the as-received 9Cr–1Mo steel prior to exposure (wt%) |
|---------|----------------------------------|---|---|---|---|---|---|---|---|---|---|
| Element | C  | Cr  | Mo  | Mn  | P  | Ni  | Co  | Cu  | Nb  | Ti  | V  | W  | Si  |
| As-received | 0.093 | 9.2 | 1.04 | 0.47 | 0.011 | 0.21 | 0.02 | 0.16 | < 0.02 | < 0.02 | < 0.05 | < 0.05 | 0.67 |

| Table 2 | Sample ID and exposure conditions of samples exposed |
|---------|----------------------------------------------------|
| Sample reference | Exposure time (h) | Exposure temperature (°C) | Breakaway oxidation? |
| Virgin | n/a | n/a | N |
| HRA-8547 | 2538 | 600 °C | N |
| HRA-8547 | 4580 | 600 °C | N |
| HRA-8537 | 15,068 | 600 °C | Y |

![Figure 1](a, b showing the location the chunk lift-out was prepared from c the chunk lift-out whilst still connected via bridge and d top-down view showing the lift-out connected to the Si holder.)
BSE and SE micrographs were taken at a current of 6.4 nA at 10 kV. The total distance through the oxide milled was 114.72 μm with a total of 1912 slices spanning the total oxide scale.

On completion of the slice and view, the micrographs were cropped across with the “V” dip included to maximise area characterised. This was performed in ImageJ and resulted in an area of 18.3 μm × 23.5 μm per slice. After accounting for the corners, an area of 312.0 μm² of material was analysed per slice. An FFT filter was applied to all micrographs in ImageJ to remove curtaining. After this, the data set was thresholded and imported into Avizo version 9.2.0 for reconstruction and analysis. Manual thresholding was completed using ImageJ prior to importing into Avizo allowed for more accurate identification of the pores within the substrate. The data set was split up and thresholded in smaller data sets so as to minimise any merging of the pores due to the thresholding. The effect of this would be greater with smaller pores closer together in comparison with fewer, less frequent larger pores.

Transmission electron microscope (TEM) sample preparation was performed using a focused ion beam (FIB) microscope (FEI Nova 600 Nanolab Dualbeam FEGSEM system). A standard lift-out procedure was used with the lamella samples attached to a Cu grid for transfer into the TEM system [30].

Results and discussion

SEM analysis

Prior to 3D analysis, the area of interest was characterised using SEM imaging and EDS analysis. EDS maps taken at the fin tip of sample HRA-8547-4580 are shown in Fig. 2. The Cr-rich spinel and magnetite interface can be seen labelled in the Cr map, with the interface between the two assumed to be the location of the original metal surface. Cr-rich carbides can be seen scattered throughout the substrate. Bands of various sizes of pores can be seen across the Cr-rich spinel running parallel to the substrate oxide interface. This micrograph is taken top down, a typical SEM view of the finned sample cross section.

A micrograph of the total oxide scale of sample HRA-8547-4580 is shown in Fig. 3. There are multiple regions showing different morphologies through the scale, and five different areas have been labelled.

These areas of porosity observed through SEM imaging (top down) can be described as:

Region 1 Circular pores ~1 μm² which appear to show no interconnectivity in the magnetite. These pores are found throughout the magnetite oxide layer in random distribution.

Region 2 Pores larger than those highlighted in region 1, up to ~5 μm in size, found closer to the magnetite/Cr-rich spinel interface.

Region 3 Very fine banded porosity with individual pores smaller than type 1, alternating with bands of no porosity. High total area fraction of porosity is seen in this region. The banding of pores is finer closer to the magnetite interface and increases in size into the Cr-rich spinel layer.

Region 4 Pores with similar morphology to those found in region 3 but larger in size. Banding is not as clear or uniform as region 3 but is still present. The pores in this area increase in size through the Cr-rich spinel oxide layer and then decrease at the internal oxidation zone. Non-porous regions in this area are more clearly defined in comparison with region 3 due to the size of both porous and non-porous areas.

Region 5 Internal oxidation zone forming at the oxide substrate interface, pores have begun to form in this area so therefore are thought to form as oxidation of the substrate is taking place.

EDS was performed on a region showing large pores within the magnetite of sample HRA-8547-4580 (region 2), and this is shown in Fig. 4. There are no elemental differences surrounding these regions, so it is therefore thought that these pores form due to a growth defect or grain pull-out rather than porosity development during exposure. The O concentration shows variation within the pores (both higher and lower), and this is thought to be due to edge effects from the morphology of the pores (angled and sunken below the surface).

The banded micro-porosity (region 3 from the previous figure) can be seen across the areas close to the magnetite with the pores within the banding increasing size further from the magnetite. An area
has been highlighted which shows this banding and the size changes with distance into the Cr-rich spinel. Higher-magnification micrographs of regions 3, 4 and 5 are shown in Fig. 5 with the various types of morphology seen in the SEM micrographs.

**Porosity area fraction measurements (SEM micrographs)**

The area fraction of porosity across the oxide scale was measured using an SEM, and the results are shown in Fig. 6. The increase in porosity at ~ 50% through the oxide scale is representative of the magnetite/Cr-rich spinel interface. Within the Cr-rich spinel the recorded porosity shows a trend to increase with the max porosity reaching approximately 35% area fraction at ~ 50% through the Cr-rich spinel and again at ~ 75% through the Cr-rich spinel, but with undulation across all the total scan, which was observed from micrographs in Fig. 3.

The 2D porosity measurements give insight into the total volume of porosity present across the oxide but provide no insight into the interconnectivity. The relatively small region investigated using SEM micrographs may also not be representative of the porosity across the sample with the total area measured being 120 µm × 30 µm, not accounting for uneven oxide thickness across the scan, whereas with the PFIB slice and view the volume investigated is ~ 120 µm × ~ 20 µm × 20 µm.

**3D FIB reconstruction analysis**

The porosity was reconstructed from the micrographs taken, and the reconstruction is shown in Fig. 7. In comparison with the SEM micrographs, the porosity appears to be more varied with eight separate regions labelled, and these micrographs are taken following the FIB lift-out plane. These different porosity regions observed can be summarised as follows:

Region (a) Smaller more circular pore type form throughout the outer magnetite, no interconnectivity between pores. This type of porosity has also been previously identified from the SEM micrographs (Fig. 3, region 1).

Region (b) Large pores present near the magnetite/Cr-rich spinel interface; these have also been observed in the 2D SEM micrographs (Fig. 3, region 2). This type of
Porosity is thought to occur due to growth defects at the Cr-rich spinel/magnetite interface during oxide growth. This type of porosity has been previously observed in long-term aged 9Cr–1Mo samples exposed to a steam atmosphere [21]. In the regions surrounding this type of pore, the frequency of region (a) pores is decreased.

Region (c) Increased pore area fraction relative to the magnetite layer. A high frequency of micro-porosity has also been observed from 2D SEM in this region (Fig. 3, region 3). Some of these Cr-rich spinel pores show interconnectivity and begin to increase in size.

Region (d) Similar to region (c) but the size of these pores is increased, and interconnectivity between pores is more common; the trend between (c) and (d) from the 3D reconstruction is similar to the increase in pore size observed from SEM (Fig. 4).

Region (e) Pores continue to increase in size from the magnetite interface and also show increased volume and interconnectivity. There are also high volumes of smaller pores dispersed throughout the larger interconnected pores. Some of the larger pores in this region span the entire extracted lift-out meaning that the pores may be larger than measured here.

Region (f) Main Cr-rich spinel bulk shows largest pores spanning the greatest distance through the oxide in both Z through the oxide and in the X, Y. Some of the pores in this region may be connected outside the measured slice and view zone, but due to the limitations of the slice and view this is not clear.

Region (g) Continuation of large interconnected pores through Cr-rich spinel but closer to the substrate; there is evidence of prior carbides, showing similar contrast to that of the substrate, which has been previously observed within the outer Cr-rich spinel oxide layer [19].

Region (h) Internal oxidation zone. Regions of oxide can be seen penetrating ahead of the main oxide front following both grain boundaries and a criss-cross pattern inside the grains. The penetrating oxide is formed of Cr-rich oxides [31]. Pores can be seen throughout this region showing that the porosity of the scale begins to develop upon oxide formation.

**Porosity area fraction measurements (3D FIB micrographs)**

The area fraction from each slice used for the 3D reconstruction was measured, and this was plotted as a function of distance through the oxide scale. The results of this are shown in Fig. 8. The magnetite shows less than ~ 5% porosity area fraction throughout. At the Cr-rich spinel region, the porosity area fraction increases and then undulates between ~ 20 and 30% across the Cr-rich spinel.

The 3D slice and view values obtained for pore area fraction show similar values to the values obtained by 2D SEM, with similar total area fractions and undulation/profiles across the oxide scale. Additional data could be extracted from each individual slice, such as average pore size and pore frequency. These were measured, and a comparison between average pore size and pore area frequency is shown in Fig. 9, with Fig. 10 showing the Cr-rich spinel region in more detail. A moving average of 10
(600 nm) was applied to the average pore size, and the Cr-rich spinel/magnetite interface can be seen indicated with a red line spanning the region of crossover.

Within the Cr-rich spinel region close to the magnetite boundary (Fig. 7c), the high area frequency of pores with a low average size shows pores here are smaller relative to deeper into the Cr-rich spinel, where the average pore size is larger but pore count is lower. This pattern repeats through the Cr-rich spinel oxide with increases in average size associated with a decrease in pore area frequency. This is visible from SEM; an example is shown in Fig. 3, region 3. This banding of pores is thought to be linked with the Fe and Cr concentrations within the oxide [21].

From the 3D porosity reconstruction data, the volume of the individual pores can be extracted, with the location, size and volume able to be compared. The plotting of these data allows for the porosity to be analysed in three dimensions through the scale.

The centre (average coordinate) of the pores in the Z- and Y-axis was plotted with the relative volume of pores for the 250 largest pores in the oxide shown in Fig. 11. The largest pores span through the Cr-rich spinel with the frequency of larger pores increasing between ~70 and 100 μm through the oxide from the outer magnetite edge.

Within the Cr-rich spinel, the increase in the total volume of porosity can be seen relative to the magnetite with larger pores surrounding the smaller pores showing the total volume of porosity. The Cr-rich spinel side of magnetite/Cr-rich spinel interface shows a large increase in smaller pores with little overlap relative to the porosity deeper into the Cr-rich spinel.

Figure 4  BSE micrograph and corresponding Cr, O, Fe and Mo EDS maps showing large pores within the magnetite thought to be due to growth defects occurring during oxidation. Examples of large pores are highlighted with a box.

Figure 5  Micrographs showing regions 3, 4 and 5 from Fig. 4 at higher magnification.
The pores within the magnetite can be seen dispersed throughout, with the larger ones present between ~40 and 50% through the total oxide scale. In the area surrounding these pores, there is no other porosity observed, and similar results were found in previous work looking at the steam oxidation of 9Cr–1Mo steel for long periods of time [21]. One limitation with this method is the pores within the oxide are not perfect circles and may span a far greater distance in both the Z and Y directions through the oxide, therefore showing increased overlap in porosity volume at some areas which may influence the gas transport mechanisms through the oxide scale.

All pores smaller than 10 \( \mu \text{m} \) were removed from the data set, and the pores were reconstructed into a 3D model; this is shown in Fig. 12a where the morphology of the larger pores can be more clearly seen with the smaller ones removed. Figure 12b shows the measured volume of the pores plotted in their respective Z-axis location through the oxide scale, and the interface between the magnetite and Cr-rich spinel can be seen highlighted with a red bar. It is worth noting that most of the pores are in contact with the edge of the area investigated and can potentially be interconnected outside the reconstructed area. This means that the total interconnectivity may be greater than this data set suggests. This large volume of pores within the Cr-rich spinel has the potential to increase the rate of gas diffusion through the scale and increase the rate of oxidation. The large volume present also will provide a greater surface area for the Boudouard reaction to take place, which may lead to an increased local concentration of O.

Figure 12b highlights the bunching of the larger pores towards the middle Cr-rich spinel region. When the smaller pores are also taken into consideration (Fig. 11), the diffusion distances between any voids are greatly reduced which will allow for increased gas diffusion through the scale, and at a certain level may trigger the rapid oxidation kinetics associated with breakaway oxidation.

Through comparing the volume of pores present within the Cr-rich spinel, it can be seen that the pores towards the middle Cr-rich spinel increase in volume and size and will have a large influence on the gas transport mechanisms taking place during oxidation due to this increase in volume and at the very least offer a reduced diffusion distance for the gas to take to diffuse to the substrate below.

### Porosity discussion

It has been shown that there is no complete porosity network spanning the total Cr-rich spinel oxide with the total volume of porosity increasing through the Cr-rich spinel oxide layer and decreasing towards the IOZ/substrate. The porosity of the Cr-rich spinel consists of interconnected bands of pores which span large distances through and across the oxide scale, with smaller less interconnected pores dispersed throughout. The pores closer to the substrate show increased interconnectivity relative to those near the magnetite interface, but one limitation is that these pores may be interconnected outside of the area investigated, which may mean the total interconnectivity is far greater than has been reported here.
Area fraction of porosity across the oxide scale was measured using both 3D FIB and 2D SEM imaging techniques, and the results are compared in Fig. 13, with both methods showing good agreement with similar undulation through the oxide, and differences being attributed to oxide variation.

Both methods identify large individual pores near the magnetite/Cr-rich spinel interface (magnetite side) which are thought to be due to growth defects. Both techniques show the increase in porosity area fraction at the magnetite interface and the undulation through the oxide scale. The 3D FIB data show a smoother profile, which can be attributed to the

Figure 7 A summary schematic showing the various morphologies of pores within the oxide of sample HRA-8547-4580, with the magnetite layer shown at the top and the substrate at the bottom. Various regions of porosity are labelled (a) through (h). Scale for all is shown in (a).
increased volume/area investigated (336,512 μm² vs 3600 μm² for the SEM technique), meaning that one feature will not either greatly increase or decrease the measured area fraction.

From this comparison, it can be concluded that in terms of area fraction of porosity and the distribution of porosity across the oxide scale, SEM is a viable alternative to 3D slice and view. This will reduce the time to complete the experimental measurements from ~3 days for the large slice and view performed down to minutes. This method, however, will not offer insight into the interconnectivity of the pores which only 3D analysis can and may not be fully representative of the total oxide scale due to the small volume investigated. This is in contrast to previous work where it was thought that the only way to accurately analyse the porosity though the oxide was by using a FIB [32]. The 2D porosity area fraction has previously been investigated by the authors where various samples are compared, and this showed the development of porosity with exposure, with the area fraction and oxide thickness increasing with exposure time and with the characteristic banding of the Cr-rich spinel clearly visible [28].

Porosity discussion and mechanism

From the experimental work performed, a mechanism for the porosity variations observed through the oxide scale can be proposed, linking carburisation of the substrate with the 3D structures observed in the 3D reconstruction.

During exposure to a carburising atmosphere, the volume of substrate carbides increases with exposure time, resulting in increased mass gain of the samples and elemental segregation within the substrate [7, 17, 19, 33]. Over exposure time, these carbides increase in volume and size with increasing volume of Cr being segregated to the grain boundaries within the substrate. The carbide elemental composition also changes with exposure time, with M23C6 being predicted to consist of higher volumes of Fe at later stages of oxidation [19, 33]. A visual example showing the substrate Cr distribution between four 9Cr–1Mo samples exposed for up to ~15,000 h at 600 °C is shown in Fig. 14. This series shows that with exposure time Cr segregates in increasing volumes towards grain boundaries and also larger more frequent intergranular carbides. At early exposure times, the Cr is dispersed relatively uniform throughout, with less grain boundary segregation, whereas the opposite is true for the sample exposed for 15,068 h. These changes in the elemental distributions will affect the oxidation characteristics of the steel, with the uneven elemental distributions remaining in the Cr-rich spinel [34].

The micrographs taken through the oxide scale (in the slice and view) show a snapshot into the various stages of the oxide morphology development. The micrographs from the region closest to the interface show the oxide morphology during the very early
stages of oxidation due to the available space model [1–7]. Deeper into the oxide, from the outer magnetite layer, the oxide will have formed after longer periods of exposure with the newest forming new oxide being formed at the internal oxidation zone. Previous work has shown the carbide volume fraction and carbide size increases with exposure time [17, 21, 34]. The increasing carbide size and frequency in the

Figure 9  Pore counts through the oxide scale, and average pore size relative to oxide location. Percentage through oxide indicates 0 at the outermost region of magnetite and 100% at the 9Cr substrate below where the slice and view were stopped.

Figure 10  Pore area fraction in combination with average pore size across the Cr-rich spinel layer. Percentage through oxide indicates 0 at the outermost region of magnetite and 100% at the 9Cr substrate below where the slice and view were stopped.
substrate will affect its oxidation characteristics and will lead to differences in the oxide morphology due to the difference in elemental segregation. This has been previously discussed by the authors [34]. These oxide differences will affect the pore size, with the larger carbides leading to larger pores within the substrate.

During exposure, it is known that coalescence of the pores will take place, increasing volume and interconnectivity and decreasing frequency when

**Figure 11** Pores average location with proportional volume relative to the other pores. Z distance through oxide indicates how far through oxide the centre of the pore was measured at, starting at 0 µm at the outer magnetite layer and ~115 µm for the substrate below. Magnetite Cr-rich spinel interface is indicated by a red line.

**Figure 12** a The distribution of the 18 largest pores (<10 µm³) and their distribution. Cr-rich spinel magnetite interface is indicated with a red band b diagram showing the location of the 18 largest pores and their relative volume. Magnetite Cr-rich spinel interface is indicated by a red line in both.
possible [21, 35–38]. This can be seen in the middle Cr-rich spinel regions and the Cr-rich spinel regions closer to the substrate, but not near the magnetite interface. From this, it can be suggested that coalescence of the pores is being inhibited towards the outer Cr-rich spinel regions (near magnetite interface), but is taking place at the middle Cr-rich spinel and the substrate.

Figure 13 Comparison between 2 and 3D porosity measurements taken at the fin tip of sample HRA-8547-4580. Percentage through oxide indicates 0 at the outermost region of magnetite and 100% at the 9Cr substrate below where the slice and view were stopped.

Figure 14 Visual example showing the Cr segregation to carbides within the substrate over exposure to a CO₂-rich atmosphere: a as-received, b 2538 h, c 4580 h and d 15,068 h.

Figure 15 shows a series of micrographs taken from the slice and view; within the Cr-rich spinel, a circle feature surrounded by pores can be seen. The circle band has inhibited the complete coalescence of this porosity which surrounds it in three dimensions. These circle features were found in increasing frequency through the oxide towards the Cr-rich spinel and show similar sizes to substrate carbides which
have oxidised [19], so therefore are thought to be Cr rich. To characterise this feature, a TEM lamella was prepared from a second fin tip but at the same location through the oxide as the series of images shown in Fig. 15. The HAADF micrograph and corresponding EDS maps are shown in Fig. 16.

Several of these features can be seen throughout the lamella in Fig. 16a, with one feature highlighted. The EDS maps of this region can be seen with the circle feature showing Cr-rich oxide with Mo present in the centre. This elemental distribution is characteristic of a Cr-rich carbide which has oxidised [19], and from this, it can be concluded that the circle features shown in Fig. 15 are Cr-rich oxide and that the Cr-rich oxide within the Cr-rich spinel inhibits the movement and coalescence of pores in the Cr-rich spinel.

It has been shown that the oldest regions of oxide (nearest to Cr-rich spinel/magnetite interface) show the smallest pores, but the highest frequency of pores. In comparison through the remainder of the oxide, the area frequency of pores decreases with increasing the average size.

As shown in Fig. 14, the Cr is segregating in the form of Cr-rich carbides, increasing volume with exposure time. These elemental distribution changes will lead to changes in the elemental distribution within the Cr-rich spinel as the Cr-rich spinel Cr distribution is dictated by the substrate Cr distribution prior to oxidation. This has potential to alter pore distribution with the Cr-rich oxide regions able to inhibit the development of pores, and examples are shown in Figs. 15 and 16 and previously reported [21].

During early exposure times, Cr is distributed throughout the substrate and a much lower volume is segregated (Fig. 14a). Therefore, as the initial oxide grows, Cr is relatively dispersed throughout the substrate but in smaller particles. This Cr distribution inhibits the migration and coalescence, which results in smaller more frequent pores. This is observed within at the outer Cr-rich spinel near to the magnetite layer and is shown in Fig. 7, region (c).

At later stages of exposure, increased volume Cr is segregated to the carbides, with decreased Cr concentration found elsewhere. This segregation effectively increases the gap between the Cr-rich areas, which upon oxidation would form Cr-rich oxide and inhibit the coalescence of porosity. This means that greater Cr segregation leads to increased average pore size due to the larger spacing between individual Cr-rich oxide regions, which allows the pores to coalesce.

Elemental segregation is also observed within the internal oxidation zone as the Cr-rich regions are oxidised ahead of the main Cr-rich spinel front. Pores also begin to form within the IOZ, and a series of micrographs through the IOZ into the oxide is shown in Fig. 17. The needle-type carbides within the grains and the larger grain boundary carbides can be seen oxidising ahead of the front giving a criss-cross oxide pattern within the IOZ. This criss-cross pattern can also be observed within the newly formed pores, an example of which is highlighted in Fig. 18, further linking porosity within the oxide to substrate carbide distribution.

These criss-cross patterns are seen throughout the Cr-rich spinel oxide scale, indicating their formation throughout the continued oxide growth. The size of these criss-cross patterns varies depending on the region of oxide where the micrograph was taken. Four labelled example slices are shown in Fig. 19.

Figure 19a shows very fine porosity, and this micrograph is taken very close to the Cr-rich spinel.

**Figure 15** Four slices taken from the slice and view showing a Cr-rich oxide inhibiting pore coalescence within the oxide scale. (1) is the first slice in the series through to (4).
interface and would have formed initially in the early stages of oxidation. Deeper into the substrate, Fig. 19b shows larger pores with the pattern easier to identify, and the same is shown in Fig. 19c with larger more pronounced pores present. In Fig. 19d, the porosity is far lower in volume, but this micrograph is taken from the internal oxidation zone as the main substrate begins to oxidise. Both the pattern in the pores and the substrate carbides (highlighted with an arrow) which have begun to oxidise show the criss-cross pattern. The pores within the Cr-rich spinel oxide varying in size corresponds with the development of the carbides in the substrate with previous work also observing porosity development relating to the porosity development [17, 19, 21, 34].

The smaller criss-cross patterns are associated with the Cr-rich spinel oxide regions which have formed earliest (nearest to the interface), and the size of the criss-cross patterns increases towards the substrate, where the carbides have increased in both size and frequency (see Fig. 14 for the carbide size development and Fig. 19 for the criss-cross pattern size development through the oxide scale).

A simplified schematic of the proposed mechanism for porosity variation across the scale is shown in Fig. 20. Figure 20a shows the detail of the Cr development within the substrate forming larger Cr-rich carbides within the substrate (based off previous work [20]). And Fig. 20b shows how this affects the pore morphology within the oxide based off the substrate microstructure at the time of oxidation. The more frequent Cr-rich regions inhibit the coalescence, leading to the finer porous structure observed near to the magnetite/Cr-rich spinel interface. As the Cr forms larger carbides, this leads to more available space for the large pores to form leading to the less frequent larger pores which are observed through the Cr-rich spinel oxide layer. This is seen to the right in Figure 16 TEM HAADF micrographs with corresponding EDS maps showing a circle feature within the oxide of sample HRA-8547-4580.
The larger pores can be seen towards the steel substrate below, increasing size from near to the magnetite interface where the porosity is fine due to the Cr being dispersed within the substrate prior to oxidation. Moving through the oxide towards the substrate, the pores increase in size due to the elemental segregation of the Cr within the substrate prior to oxidation allowing for the pores to coalesce and form larger more interconnected regions of porosity. The development of the carbides within the substrate has been previously been discussed by the authors and the effect it has on the oxidation characteristics of the steel [20, 34].

This mechanism can be summed up as follows:

1. During exposure to a carburising atmosphere, segregation of Cr to carbides within the substrate increases and these form typically along grain boundaries, especially in longer exposed samples [17, 33].
2. The Cr distribution in the substrate dictates Cr distribution in the Cr-rich spinel oxide layer with shadows of the prior Cr distribution visible through EDS in the newly formed Cr-rich spinel. Cr-rich regions inhibit the movement and coalescence of pores within the Cr-rich spinel.
3. During early exposure, the bands of Cr are more frequent/dispersed across the substrate and therefore oxide. This inhibits larger pore coalescence, leading to high area fraction of smaller pores. This is seen near the magnetite interface in Figs. 5 and 10.
4. As more Cr is segregated to grain boundaries, the regions where pores can coalesce increases in size. This allows the pores to increase in average size but decrease in frequency due to coalescence.
Figure 19 Various graphs showing the criss-cross pattern which can be seen throughout the Cr-rich spinel oxide scale at various locations. (a)→(d) indicate deeper into the oxide from the outer magnetite layer. Examples of the patterns are circled in each micrograph.

Figure 20 Schematic showing the proposed mechanism of porosity development. a shows the substrate development with the Cr forming larger carbides and b shows how the Cr elemental segregation affects the pore size.
5. The spacing between the Cr rich, pore inhibiting, oxide changes with exposure. This leads to undulation of both pore size and pore frequency through the oxide scale. This is shown in Fig. 10 with each increase in average pore size associated with a decrease in pore frequency.

Conclusions

The oxide scale formed on 9Cr–1Mo steel has been characterised through the use of a PFIB to investigate large regions of material. The porosity within both the Cr-rich spinel and the magnetite layer has been examined, and the presence of carbides within the substrate has been discussed. The various oxide morphologies through the oxide scale have been discussed, and a mechanism for the various formations has been proposed.

From this experimental work, the following conclusions can be drawn:

- Measurements of the area fraction are similar for both 2D SEM and 3D FIB techniques. This means that for future work, if the pore area fraction is the desired measurement, this can be performed using SEM which is far faster than the FIB slice and view. If the 3D morphology of the pores is required, 3D FIB is still required.
- No network of porosity spanning across the oxide scale was observed. Had one been observed it may have given insight into breakaway oxidation initiation due to the change in kinetics with increased CO₂, leading to more rapid oxidation taking place.
- Four distinct regions of varying porosity have been identified, the magnetite, near magnetite/ Cr-rich magnetite interface within the magnetite, micro-porosity near to the interface within the Cr-rich spinel and the larger pores found within the body of the Cr-rich spinel. A mechanism has been proposed for the various different pore types observed within the oxide. This mechanism links the Cr distribution within the substrate and how this changes with exposure time leading to the various pore types found in the oxide. One limitation, albeit for all lift-out quantifications, is that some of the larger pores spanned the total region where the lift-out was performed. Because of this, the interconnectivity of the pores may be higher than is reported in this report (pores might connect outside of the region examined).

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Declarations

Conflict of interest  The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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