Effect of alloying additions and preoxidation on high temperature sulphidation resistance of iron–chromium alloys

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High temperature corrosion of structural alloys in sulphur bearing environments is many orders of magnitude higher than in oxidising environments. Efforts to increase sulphidation resistance of these alloys include addition of alloying elements. This paper reports the effect of yttrium, aluminium and yttrium plus aluminium addition on the sulphidation behaviour of an Fe–20Cr alloy in H2–2%H2S at 700 and 800°C. The effect of preoxidation of these alloys on sulphidation behaviour was also investigated. The initial stages of sulphidation of these alloys were observed and overall sulphidation kinetics was determined. In the presence of yttrium, the sulphidation rate of the alloy decreased by an order of magnitude, and the sulphide layer on the FeCrY alloy was significantly thinner than that formed on the FeCr alloy. Aluminium addition increased sulphidation resistance even more. The FeCrAl and FeCrAlY alloys exhibited parabolic sulphidation kinetics at the two temperatures. On both alloys, initial chromium sulphide (Cr2S3) formation at grain boundaries and Al2S3 and FeCr2S4 formation over the grains was followed by formation of an outer Cr2S3 layer over a mixed sulphide layer. Preoxidation of the two alloys resulted in an ‘incubation period’ with practically no sulphidation during subsequent exposure to S bearing environments. After this incubation period, the sulphidation behaviour of the FeCr alloy was similar to that when the alloy was not preoxidised. The incubation period of the FeCrAl alloy was significantly longer, over 45 h, compared with 2 h for the Al free alloy. Based on thermogravimetric as well as SEM, energy dispersive spectroscopy (EDS) and X-ray diffraction (XRD) data, sulphidation mechanisms have been proposed for the alloys before and after preoxidation.

Keywords: Sulphidation, iron–chromium alloy, yttrium addition, aluminium addition

Introduction

Degradation resistance of structural alloys in aggressive environments at elevated temperatures usually depends on the ability of the alloys to form and maintain a protective reaction product scale. In most oxidising environments, Cr2O3 is the predominant constituent of the scale on chromium containing iron based alloys. These alloys are used in many high temperature commercial processes such as oil refining, coal gasification and fossil–fuel conversion, which produce complex gaseous environments. These environments are in general, multicomponent mixtures that contain sulphur bearing gases (H2S and SO2) in addition to oxidants (CO2/CO and H2O/H2). High temperature corrosion of various metals and alloys in sulphur bearing environments may be orders of magnitude higher than their oxidation rates.1 This difference is due mainly to the nature of the sulphide scale, which is non-adherent and highly porous, whereas the oxide scale is compact and adherent to the substrate. Sulphides are also thermodynamically less stable, fuse at lower temperatures and reveal significant shifts in stoichiometry, compared with corresponding oxides.2

A number of studies have been carried out with the objective of designing alloys to resist sulphur attack and include those that considered the addition of alloying elements and pretreatments.3–14 Chromium additions were reported to be beneficial. Addition of 3–5 wt-%Al to Fe–17Cr alloys increased sulphidation resistance in H2S environments with sulphur partial pressure Ps2 of $6 \times 10^{-2}$ torr (Ref. 4). Further increase in Al content, as in iron aluminides, increased sulphidation resistance even more at 800°C, and this was attributed to the formation of α-Al2O3 scale.8,9 The benefits of adding reactive elements such as Y, Hf, Ti or Zr, to improve the oxidation resistance of chromium dioxide and alumina forming alloys at high temperatures is quite well documented.10–12 These elements aid the formation of
protective oxide layers and the mechanism by which these elements influence oxidation behaviour is quite similar. The effect of reactive element additions on sulphidation behaviour at high temperatures has received some attention. Improvements in sulphidation resistance of iron based alloys with Y addition have been reported and contrary to this, increase in sulphidation rate with Y additions has also been reported. Saxena et al. observed that the addition of Y and Zr to the alloy did not alter the rate controlling step of the sulphidation reaction.

In the light of the above contributions, in this investigation the effect of Y, Al and Y plus Al additions to Fe–20Cr on the sulphidation behaviour in H₂–H₂S environments at 700 and 800°C has been studied. The effect of preoxidation of the alloys on sulphidation behaviour has also been studied.

Methods and materials
Iron–chromium (FeCr), iron–chromium–yttrium (FeCrY), iron–chromium–aluminium (FeCrAl) and iron–chromium–aluminium–yttrium (FeCrAlY) alloy ingots with compositions, as shown in Table 1, were prepared in a vacuum induction furnace. These ingots were hot forged at 980°C, specimens cut to size and ground to 220 mesh. The specimens were exposed to flowing H₂–2%H₂S mixture at 800°C before exposure to the flowing H₂–2%H₂S mixture at 800°C. The surfaces of specimens from the different tests were examined in a scanning electron microscope (SEM), and the composition of the reaction products determined using energy dispersive spectroscopic (EDS) analysis and X-ray diffraction (XRD) analysis.

Results and discussion
The weight gain curves of the FeCr and FeCrY alloys as a function of sulphidising time at 700 and 800°C are shown in Fig. 1. The FeCr alloy exhibited parabolic behaviour at 700°C and linear behaviour at 800°C, and the sulphidation rate of the Y containing alloy was significantly lower than that of the Y free alloy. The sulphidation rate constants are shown in Table 2.

The sulphidation curves of the FeCrAl and FeCrAlY alloys at 700 and 800°C are shown in Fig. 2. The sulphidation rate constants of these two alloys are also given in Table 2 indicating parabolic behaviour at the two temperatures. The influence of Y in the Al containing alloys was slight, indeed increasing the overall weight gain of the alloy at the two temperatures. Similar increases in weight with Y additions were reported by Godlew ska et al.

The surface of the FeCr alloy sulfidised for 5 min is shown in Fig. 3a. Formation of ridges can be observed. After 15 min of sulphidation, as shown in Fig. 3b, the surface is undulating with coalesced ridges. EDS analysis and X-ray diffraction (XRD) analysis were performed to determine the composition of the reaction products. EDS analysis indicated the presence of oxygen and sulphur in the reaction products, with a small amount of iron. X-ray diffraction analysis confirmed the presence of iron sulphide and iron oxide in the reaction products.

Table 1 Chemical composition of alloys

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Element</th>
<th>Cr</th>
<th>Al</th>
<th>Y</th>
<th>Fe</th>
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<tr>
<td>FeCr</td>
<td></td>
<td>19.74</td>
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<tr>
<td>FeCrY</td>
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<td>...</td>
<td>...</td>
<td>0.69</td>
</tr>
<tr>
<td>FeCrAl</td>
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<td>18.44</td>
<td>4.96</td>
<td>...</td>
<td>Bal.</td>
</tr>
<tr>
<td>FeCrAlY</td>
<td></td>
<td>18.70</td>
<td>5.40</td>
<td>0.58</td>
<td>Bal.</td>
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</table>

Table 2 Sulphidation rate constants of alloys

<table>
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<tr>
<th>Test temperature, °C</th>
<th>Alloy</th>
<th>Kp, g² cm⁻⁴ s⁻¹</th>
<th>Ki, g cm⁻² s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>700</td>
<td>FeCr</td>
<td>1.08 x 10⁻⁸</td>
<td>...</td>
</tr>
<tr>
<td>800</td>
<td>FeCr</td>
<td>1.68 x 10⁻⁶</td>
<td>...</td>
</tr>
<tr>
<td>700</td>
<td>FeCrY</td>
<td>3.25 x 10⁻⁹</td>
<td>...</td>
</tr>
<tr>
<td>800</td>
<td>FeCrY</td>
<td>6.92 x 10⁻⁷</td>
<td>...</td>
</tr>
<tr>
<td>700</td>
<td>FeCrAl</td>
<td>4.81 x 10⁻¹¹</td>
<td>...</td>
</tr>
<tr>
<td>800</td>
<td>FeCrAl</td>
<td>9.62 x 10⁻¹⁰</td>
<td>...</td>
</tr>
<tr>
<td>700</td>
<td>FeCrAlY</td>
<td>5.32 x 10⁻¹¹</td>
<td>...</td>
</tr>
<tr>
<td>800</td>
<td>FeCrAlY</td>
<td>7.62 x 10⁻¹⁰</td>
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measurements revealed high Fe content on this surface, and the dark regions contained more Cr than the light regions. After 30 min of sulphidation, as shown in Fig. 3c, a significant amount of sulphide spalled. The EDS measurements on this surface revealed an iron rich external layer with some Cr and a Cr rich internal layer (below the scaled regions).

Figures 4a and 4b are SEMs of the FeCrY alloy sulphidised at 700°C for 5 and 30 min. EDS analysis of the large particle (region 1) in Fig. 4a revealed, besides S, high Fe and low Cr contents. At regions 2 and 3 in the same micrograph, the Fe and Cr contents were close to those of the alloy. On the surface of the FeCrY alloy sulphidised for 30 min (Fig. 4b) much of the sulphide spalled. The grain boundaries, seen in Fig. 4b, revealed high Y and equal amounts of Fe and Cr. At regions away from the grain boundary, no Y was detected, and the Cr content was higher than the Fe content. Even though no Y was detected in the sulphide formed at the grain boundary after 5 min of exposure, large amounts of Y were detected in the grain boundary region under the spalled sulphide after 30 min of sulphidation, indicating diffusion of Y from the grain to the grain boundary and then to the metal/sulphide interface.

Figure 5 shows a cross-section of FeCr sulphidised at 700°C. The average total thickness of the sulphide layer was 120 μm, and it consisted of two ‘sublayers’. The metal/sulphide interface was planar. The external sublayer consisted of alternated light and dark lamellae.
EDS analysis revealed that the dark lamellae were richer in chromium than the light lamellae. The external sublayer also revealed a large number of cracks. The sulphide grains were also columnar, indicating predominant unidirectional diffusion. The elemental profile, determined by EDS, revealed that the inner sublayer (close to the metal/sulphide interface) contained chromium and some iron. The external layer contained only iron and sulphur. The XRD data confirmed this observation and indicated the presence of Fe$_{1-x}$S in the external layer and Fe$_{1-x}$S, FeS$_6$ and Cr$_2$S$_3$ in the inner layer. The formation of sulphide lamellae probably occurred during decomposition of the sulfospinel (Fe$_2$Cr$_x$S$_4$) during cooling.\textsuperscript{16}

Figure 6a shows a cross-section of the FeCrY alloy sulphidised for 2 h at 700˚C. The light regions within the alloy (arrows) were identified by EDS to be the Fe–Y phase. In the sulphide layer, the presence of this phase (in sulphidised form) was observed up to a certain depth. In the external sublayer, where EDS analysis was carried out, only Fe$_{1-x}$S formed. Thus it can be stated that sulphidation occurred initially by predominant cationic diffusion, forming the external layer and then by predominant anionic diffusion, with the sulphidation front progressing into the alloy. The Fe–Y phase acted as a "marker", indicating the direction of growth of the sulphide. A cross-section of the FeCrY alloy sulphidised at 700˚C for 10 h is shown in Fig. 6b. The average thickness of the layer was 75 µm, thinner than that formed on the FeCr alloy, under identical sulphidation conditions. The sulphide/alloy interface was undulating, quite different from that in the Y free alloy (Fig. 5), where it was planar. The light regions within the sulphide layer were rich in yttrium, and such regions were not observed in the external sublayer. The phases detected in the reaction product that remained adhering to the surface of the FeCrY alloy sulphidised for 5 h at 700˚C were Fe$_{1-x}$S, Cr$_2$S$_3$ and Y$_2$S$_3$.

The FeCr and FeCrY alloys spalled considerably. A large number of cracks, both intergranular and transgranular were observed on the surfaces of these alloys. The sulphide grains on the FeCrY alloy were smaller than those on the FeCr alloy.

The surface of FeCrAl sulphidised for 15 min at 700˚C is shown in Fig. 7a revealing preferential grain boundary attack. The EDS measurements at the grain boundary revealed (by weight) 55.8%S, 26.2%Cr, 12.3%Fe and 5.5%Al. This suggests a higher Cr diffusion rate compared with that of Fe or Al along the grain boundaries. Figure 7b shows the surface of this alloy sulphidised for 30 min. The EDS measurements carried out on the grain boundary revealed (by weight) 8.8%S, 60.8%Cr, 16.3%Fe and 14.1%Al and on the grain, 1.2%S, 28.2%Cr and 27.2%Al. This indicated that Al and Cr ions diffuse not only along the grain boundaries, but also from within the grain. The sulphide formed after 30 min did not spall and the surface continued to reveal a mirror like finish.

The surface of the FeCrAlY alloy sulphidised for 15 min at 700˚C is shown in Fig. 8a. Sulphur attack
along the grain boundary is marked. The EDS measurements on the grain boundary revealed 16.4% Al and 60.2% Cr. No Y was detected at this grain boundary. On the grain, the Al content was very high (24.4%), almost 6 times that present in the alloy. The Cr content in the grain was also high (30.3%), ~50% more than that in the alloy. The Cr and S contents at the grain boundary of the specimen sulphidised for 30 min at 700 °C (Fig. 8b) were 50 and 30.4% respectively. The Cr content was 2.5 times that in the alloy and Y was detected at the grain boundary. The grain revealed 27.3% Cr and 25.1% Al. This Al content is 7 times that in the alloy. These results indicate that Al and Cr diffuse preferentially and much faster than Fe, both along the grain boundaries and in the grains. On the grains, very little S was detected, 2.3 and 1.5% after 15 and 30 min sulphidation respectively. The high Al and Cr contents detected by EDS probably correspond to that in the alloy, as the depth of penetration of electrons, used in EDS, exceeds the thickness of the sulphide layer. The varying amounts of Al and Cr, at different regions, reflect diffusion of Al\(^{3+}\) and Cr\(^{3+}\) to the interface. The low S contents can be also attributed to the same reason. The surface reaction product did not spall and the surface was quite bright even after 30 min of sulphidation at 700 °C.

A cross-section of the FeCrAl specimen sulphidised for 5 h at 700 °C is shown in Fig. 9a. The sulphide layer is thin, irregular and revealed regions where the sulphide had penetrated into the alloy, probably at grain boundaries. The phases Al\(_2\)S\(_3\), Cr\(_2\)S\(_3\) and FeCr\(_2\)S\(_4\) were revealed by XRD. A cross-section of FeCrAlY alloy sulphidised for 5 h at 700 °C is shown in Fig. 9b. A fine but irregular layer of sulphide is seen, similar to that on the Y free alloy, with it penetrating into the alloy at some regions. The phases detected in the surface of this alloy by XRD were FeCr\(_2\)S\(_4\), Al\(_2\)S\(_3\), Fe\(_{1-x}\)S and Cr\(_2\)S\(_3\). The Fe\(_{1-x}\)S phase, not present in the FeCrAl alloy indicates slightly higher Fe diffusion in the Y containing alloy.

**Preoxidation of alloys**

The four alloys were isothermally oxidised for 4 h at 1000 °C as these parameters correspond to a steady state region in the parabolic oxidation weight gain versus time curves of these alloys. The oxides on the surface of FeCr and FeCrY were found to be Cr\(_2\)O\(_3\) and FeCr\(_2\)O\(_4\). That on the surface of FeCrAl contained \(\alpha\)-Al\(_2\)O\(_3\), \(\theta\)-Al\(_2\)O\(_3\), Cr\(_2\)O\(_3\) and FeCr\(_2\)O\(_4\). The oxide on the surface of the FeCrAlY alloy contained \(\alpha\)-Al\(_2\)O\(_3\), \(\theta\)-Al\(_2\)O\(_3\) and Cr\(_2\)O\(_3\).

**Sulphidation of preoxidised alloys**

The isothermal sulphidation curves of the four alloys preoxidised for 4 h at 1000 °C and sulphidised at 800 °C are shown in Fig. 10. The mass gain and sulphidation rate of the preoxidised FeCr and FeCrY alloys reveal a rate transition after ~2 h. During this period, the oxide on the alloy surface protects the alloy in the sulfidising environment. After this initial ‘incubation period’, the sulphidation rate of the alloy increases. The preoxidised
FeCrAl alloy exhibits parabolic sulphidation kinetics and the oxide layer formed during preoxidation protects the alloy for at least 45 h at 800°C in the sulphidising environment. The α-Al2O3 layer formed on the FeCrAl and FeCrAlY alloys during preoxidation is more compact and contains fewer defects compared with the Cr2O3 formed on the FeCr alloy during preoxidation. This results in lower diffusion rates of species across the oxide layer and longer incubation period during sulphidation.

The surface of FeCr preoxidised and sulphidised at 800°C is shown in Fig. 11a. The sulphide layer has spalled in some regions. EDS analysis in the unspalled region revealed the outer layer to be rich in Cr and Fe. At various regions on this specimen, EDS measurements revealed that the S and Fe contents decreased in the direction of the sulphide/alloy interface. This revealed that S did not diffuse easily through the oxide layer, and that the sulphides formed preferentially at the gas interface. The Cr content increased towards the interface with the alloy. Various phases present on the surface of the pre-oxidised and sulphidised FeCr alloy were revealed by XRD analysis. Besides the Cr2S3 and FeCr2S4, Cr2O3 formed during the preoxidation stage was also detected. The surface of FeCrY preoxidised and sulphidised at 800°C is shown in Fig. 11b. Energy dispersive spectroscopy on the surface indicated high oxygen content, suggesting the presence of Cr2O3, formed during the preoxidation.

Figure 11c shows the cross-section of the same specimen. Three layers can be observed. The thin top layer, close to the sulphide/gas interface, is Cr2O3 (arrows) formed during preoxidation. Just below this layer, the sulphide layer with the light and dark lamellae can be seen. The dark layer is the specimen mounting resin and the layer below that adheres to the alloy substrate. EDS measurements were carried out at regions marked with numbers 1–5 in Fig. 11c. The EDS and XRD results indicated the phases to be FeCr2S4, FeCr2O4 and Cr2O3. Comparison of the cross-sectional micrographs of the FeCrY specimen preoxidised and sulphidised with that just sulphidised, as shown in Fig. 6b, revealed differences in the microstructure. In the preoxidised specimens the outer Fe1−xS layer, that normally permits rapid cation transport, did not form.

The surface of FeCrAl preoxidised for 4 h at 1000°C and then sulphidised at 800°C for 45 h is shown in Fig. 12a. The EDS data on different regions of this specimen revealed high Al content and oxygen in region 1 (the back ground). On some regions nodule formation was observed (region 2). A region within this nodule revealed the presence of Fe, Cr, S and some Al. Some sulphide nuclei can be seen at various points on the surface of the specimen shown in Fig. 12a. XRD analysis of the surface of this alloy revealed besides FeCr2S4, the oxides α-Al2O3, Cr2O3 and FeCr2O4, formed during preoxidation. These observations are coherent with the model proposed by Stott et al. Sulphide formation occurred at specific regions and not all over the surface, as observed on the surface of the alloy that was not preoxidised. On the basis of these observations it can be stated that the preoxidised alloy would not be resistant to the sulphidising environment.
for very long times. Nevertheless, preoxidation of Al containing FeCr alloy would extend the life of components made with this alloy and exposed to sulphidising environments. Figure 12b shows the surface of the FeCrAlY alloy preoxidised for 4 h at 1000°C and then sulphidised at 800°C for 45 h. Different sulphide grain morphologies can be observed. In this alloy no large nodules were observed, as they were in the Y free alloy. Only α-Al₂O₃ was revealed by XRD analysis.

**Sulphide scale formation and development**

Based on the results shown so far, a schematic representation of sulphide scale formation and its growth as a function of time on the FeCr and FeCrY alloys at 700°C in H₂–H₂S is shown in Figs. 13 and 14 respectively. In the initial stages of sulphidation of the FeCr alloy, as shown in Fig. 13a, owing to easy access of S to the alloy surface, Fe₁₋ₓS nuclei form. These grow rapidly because of its non-stoichiometry. The Cr present on the surface is also readily sulphidised, provoking diffusion of more Cr to the alloy surface. The diffusion at this stage is mainly cationic. Subsequently, the phases Cr₂S₃ and/or FeCr₂S₄ grow as shown in Fig. 13b, at a slightly lower rate, compared with the Fe₁₋ₓS. These also form within the alloy owing to internal sulphidation. After some time, as shown in Fig. 13c, the Fe₁₋ₓS phase grows rapidly and the different nuclei coalesce forming an external layer of Fe₁₋ₓS. Under this layer, internal sulphidation progresses and the Cr₂S₃ islands join together forming the inner Cr₂S₃ or the mixed sulphide FeCr₂S₄ layer. This inner layer grows slowly, because the diffusion of species through this layer is

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**12 Surfaces of alloys preoxidised and sulphidised at 800°C for 45 h**

![Image](natural_text.png)

(a) FeCrAl; (b) FeCrAlY

13 Schematic diagram of sulphide layer growth on FeCr alloy at 700°C

**13 Schematic diagram of sulphide layer growth on FeCr alloy at 700°C**

(a) formation of Fe₁₋ₓS; (b) formation of Cr₂S₃ and/or FeCr₂S₄; (c) blocking of preferential cationic diffusion paths by Y³⁺ ions; (d) diffusion becomes predominantly anionic and regions with internally sulphidised Cr appear; (e) formation of continuous layer of Cr₂S₃ near alloy/sulphide interface

**14 Schematic diagram of sulphide layer growth on FeCr/Y alloy at 700°C**
much slower, and the compounds in this layer are more stoichiometric. The overall sulphidation rate decreases and follows a parabolic rate. At this stage the growth of the sulphide layer depends on the diffusion of the different ions, Cr$^{3+}$, Fe$^{2+}$, Fe$^{3+}$ and S$^{2-}$.

In the initial stages of sulphidation of the Y containing alloy (Fig. 14a), easy access of S results in formation of Fe$_{1-x}$S at grain boundaries and on the Fe–Y phase. After a certain time (Fig. 14b), large quantities of Cr diffuse to the surface, both along the grain boundaries and through the grain, to form Cr$_2$S$_3$ and/or FeCr$_2$S$_4$. These sulphides fuse together to form a layer and the sulphidation rate decreases. The Y$^{3+}$ ions also diffuse through the grains to the alloy/sulphide interface and block the diffusion of other cations (Fig. 14c). Consequently, anion diffusion becomes predominant (Fig. 14f). The growth of the sulphide layer decreases and the growth of islands of Cr$_2$S$_3$ within the alloy increases (Fig. 14f). The Cr$_2$S$_3$ nuclei within the alloy grow to form steps. At regions where the critical volume for growth of sulphide is not reached, internal sulphidation continues to progress towards the alloy interior, following a mechanism quite similar to the internal sulphidation model for internal oxidation in Ni–Cr proposed by Stott. Thus, a relatively compact layer of Cr$_2$S$_3$ forms on the alloy surface as shown in Fig. 14f. The main defects in Fe$_{1-x}$S are cationic vacancies and with the inhibition of cation diffusion by Y$^{3+}$, the velocity of growth of Fe$_{1-x}$S in this alloy decreases.

The sulphide layer formation on FeCrAl and FeCrAlY at 700°C probably follows a sequence as shown schematically in Fig. 15. Initially, chromium sulphide formation takes place at the grain boundaries along with Al$_2$S$_3$ and FeCr$_2$S$_4$ formation over the grains, as shown in Fig. 15a. Growth of the nuclei of these three sulphides, as shown in Fig. 15a, is considered to lead to the formation of an outer Cr$_2$S$_3$ layer over a mixed sulphide layer (Al$_2$S$_3$ and FeCr$_2$S$_4$), a consequence of continuous diffusion of cations from the alloy close to the interface and as shown in Fig. 15b. The Cr$_2$S$_3$ transport through the scale is probably a rate limiting step.

In the Y containing alloy, Y segregates to grain boundaries in the initial stages of sulphidation. With time more sulphide nuclei form and the sulphide layer thickens. Because experimental data showed no significant differences in the sulphidation kinetics between FeCrAl and FeCrAlY, the rate controlling step for sulphidation of the two alloys is probably the same.

**Growth sequence of sulphides on preoxidised FeCr and FeCrAl alloys**

A schematic representation of sulphide layer growth on FeCr preoxidised at 1000°C for 4 h and sulphidised at 800°C is shown in Fig. 16. On the preoxidised FeCr alloy, during sulphidation, Fe$^{2+}$, Fe$^{3+}$ and Cr$^{3+}$ diffuse through the oxide layer as shown in Fig. 16a and sulphides nucleate at the oxide/gas interface (Fig. 16b). With the time and temperature, an outer sulphide layer forms and S diffuses through the oxide layer and forms sulphides within the oxide layer (Fig. 16c). With continued exposure to the sulphidising environment, S continues to diffuse through the oxide layer to form sulphides at the oxide/metal interface, as shown in Fig. 16d, and signals the end of the incubation period.

Sulphidation of the preoxidised FeCrAl alloy can be considered to follow a sequence quite similar to that presented in Fig. 16 for the FeCr alloy. After extended periods of exposure the aluminium oxide layer formed on the FeCrAl alloy surface remains unattacked. With the time and temperature, S ions penetrate the alumina layer, reach the alloy surface and react with Fe and Cr to form their sulphides. These sulphides push outwards and protrude through the alumina, rather than spread laterally along the oxide/alloy interface. After extended exposure (>45 h) to the sulphidising environment at 800°C, the number of sulphide protrusions could increase causing breakdown of the ‘protective’ alumina layer.

The weight gain of different alloys after 5 h of sulphidation at 700 and 800°C is shown in Fig. 17. Significant reductions in sulphidation rates can be
observed with addition of Y, Al and preoxidation. The conjoint effect of Y and Al addition along with preoxidation resulted in the sulphidation rate of the FeCr alloy at 800°C decreasing by a factor of 70.

Conclusions

1. Growth of the sulphide layer on FeCr at 700°C takes place by predominant cation diffusion.
2. On the FeCr alloy, initial Fe$_{1-x}$S nuclei formation and growth are followed by formation of Cr$_2$S$_3$ or FeCr$_2$S$_4$. These sulphides grow and extend laterally to form a layer below the Fe$_{1-x}$S layer and reduce the overall sulphide growth rate.
3. On the FeCrY alloy, initial sulphide formation takes place at grain boundaries and on the Fe–Y phase followed by formation of Fe$_{1-x}$S and Cr$_2$S$_3$ and/or FeCr$_2$S$_4$, quite similar to that in the Y free alloy.
4. The overall decrease in growth rate of sulphides on the Y containing alloy is attributed to the migration of Y$^{3+}$ ions to the grain boundaries in the alloy and blocking of the diffusion paths of Cr$^{3+}$ to the metal/sulphide interface. Thus, anion diffusion becomes predominant.
5. The addition of Y to the FeCrAl alloy did not cause any significant change in the sulphidation behaviour.
6. In the initial stages of sulphidation of the FeCrAl alloy, Cr$_2$S$_3$ formed at grain boundaries with a mixture of Al$_2$S$_3$ and FeCr$_2$S$_4$ on the grains. Subsequently, aided by the high diffusion rates of Cr and Al from the alloy, a compact and adherent layer made up of the three sulphides formed on the alloy surface.
7. The FeCr alloy preoxidised for 4 h at 1000°C showed an incubation period of ~2 h during subsequent sulphidation at 800°C. After this incubation period, the sulphidation behaviour was similar to that of the alloy that had not been preoxidised. Sulphide growth occurred at the oxide/gas interface.
8. Preoxidation of the FeCrAl alloy at 1000°C for 4 h significantly increased its resistance to sulphidation. An incubation period of at least 45 h in a sulfidising environment at 800°C has been observed.
9. The marked increase in sulphidation resistance of the FeCr alloy with Al addition and preoxidation indicates that preoxidised alumina forming alloys can be considered for components exposed to high temperature in low to medium S partial pressure atmospheres.

References