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THE OXIDATION BEHAVIOUR OF Fe-Cr ALLOYS CONTAINING HfO$_2$-DISPERSED PHASE

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ABSTRACT

The present investigation examines the high temperature oxidation behaviour of Fe-Cr ferritic alloys containing 1.0% Hf which has been converted into an oxide dispersion. The oxide dispersions were produced by an internal oxidation treatment using a 50/50 Cr/Cr$_2$O$_3$ powder mixture in a sealed quartz capsule at 1100°C; the samples were not in direct contact with the powders. The effect of the dispersed oxide was spectacular under isothermal oxidation conditions, but it had almost no effect during thermal cycling conditions. Unlike the TiO$_2$ containing Fe-Cr ferritic alloys, virtually no particle coarsening was observed. The absence of the coarse particles caused poor thermal cycling behaviour, whereas in TiO$_2$-containing ferritic alloys, coarse particles acted as oxide pegs giving a keying-on effect.

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INTRODUCTION

In previous papers, (1-3) the influence of TiO$_2$ or TiN dispersed phases on the oxidation behaviour of ferritic Fe-Cr and austenitic Fe-Cr-Ni alloys in the temperature range 1000-1200°C were reported.

The internal oxidation treatment produces a significant improvement in both the isothermal and the cyclic oxidation behaviour of the Fe-Cr alloys containing 0.5 or 1.0 wt.% Ti. Nitride dispersions seemed to operate in an essentially similar manner to oxide dispersions but were less effective, and it is probable that they were oxidized during the course of exposure. Considerable particle coarsening occurs during exposure of both oxide and nitride dispersions in ferritic Fe-Cr alloys, and this was particularly true at elevated temperatures.

In austenitic alloys, the presence of dispersed oxides significantly improved the thermal cycling behaviour brought about by an increase in scale-metal adhesion. However, the additional presence of nickel in the alloy is also important. (2) The increasing nickel content itself improves the scale-alloy adhesion: the lower inter-diffusion rate in the alloy coupled with the higher oxygen solubility and diffusivity in austenite in comparison to ferrite results in the development of a more irregular alloy/scale interface—a keying-on effect.

Increasing contents of nickel in the alloy reduces the oxidation rate. (5) However, interestingly, with alloys given prior internal
oxidation treatment, the parabolic rate constants for continued 
Cr$_2$O$_3$ growth are virtually independent of nickel content.

In austenitic alloys, where, because of the lower diffusivity of 
solute atoms, coarsening was absent. (2)

The present work examines the oxidation behaviour of ferritic 
Fe-Cr alloys containing Hf as solute element, since HfO$_2$ is more 
stable than TiO$_2$, particle coarsening is expected to be absent.
EXPERIMENTAL PROCEDURE

Table I shows the nominal compositions of the alloys studied.

Alloy samples were prepared as described previously. (1-2) The internal oxidation pretreatment involved sealing the sample in one arm of an evacuated dumb-bell shaped quartz tube, the other arm containing a mixture of approximately equal parts of Cr and Cr₂O₃ powders. The internal oxidation treatment was carried out for 120h at 1100°C. After the pre-oxidation, samples were cleaned by light abrasion.

Isothermal and cyclic oxidation studies were carried out as previously. (1-4) For the latter a cycle time of 3h was used: results are presented as weight gains since all the spalled scale was collected and weighed with the samples.
<table>
<thead>
<tr>
<th>Fe</th>
<th>Cr</th>
<th>Hf</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bal</td>
<td>18</td>
<td>1.0</td>
</tr>
<tr>
<td>Bal</td>
<td>14</td>
<td>1.0</td>
</tr>
<tr>
<td>Bal</td>
<td>12</td>
<td>1.0</td>
</tr>
</tbody>
</table>
EXPERIMENTAL RESULTS

(i) Morphology of the Internal Oxides

The internal oxide morphology is somewhat different from those observed in the titanium-containing alloys. The particles are comparatively finer, but there is, however, a slight indication of a relatively coarse grain boundary network of internal oxides, together with a fine distribution throughout the grains.

(ii) Isothermal Oxidation Kinetics

Figure 1 shows the oxidation kinetics of the internally oxidized Fe-18, 14 and 12 Cr-1.0Hf alloys at 1100°C. The 18 and 14% Cr containing alloys oxidize almost at the same rate. The 12% Cr containing alloy shows an initial protective scaling which then is followed by a rapid breakthrough.

Figure 2 (a-b) compares the isothermal oxidation kinetics of the preoxidized Fe-18 and 14% Cr alloys containing HfO₂ or TiO₂. HfO₂ containing alloys show superior isothermal oxidation resistance to those containing TiO₂. Figure 2(b) shows a similar set of results at 1000°C and clearly indicates that the difference is almost the same even at lower temperatures. Table II summarizes the parabolic rate constants, Kₚ, and compares with that of the alloys containing TiO₂.

As is shown in Table II, HfO₂--dispersoids cause a significant reduction in the oxidation rate in comparison to TiO₂--dispersoids. The oxidation rate of simple binary alloys are also given for comparison.
<table>
<thead>
<tr>
<th>Alloy</th>
<th>Temperatures</th>
<th>$K_p$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$-2 \cdot 10^{-4} \text{ cm}^{-2} \cdot \text{sec}^{-1}$</td>
</tr>
<tr>
<td>(Fe Base), wt.%</td>
<td>1000°C</td>
<td>0.93x10^{-12}</td>
</tr>
<tr>
<td>14 Cr - 1.0 Hf</td>
<td></td>
<td>54x10^{-12}</td>
</tr>
<tr>
<td></td>
<td>1100°C</td>
<td>3.3x10^{-12}</td>
</tr>
<tr>
<td>14 Cr - 1.0 Ti</td>
<td></td>
<td>0.44x10^{-12}</td>
</tr>
<tr>
<td>18 Cr - 1.0 Hf</td>
<td></td>
<td>8x10^{-12}</td>
</tr>
<tr>
<td></td>
<td>2.25x10^{-12}</td>
<td></td>
</tr>
<tr>
<td>18 Cr - 1.0 Ti</td>
<td></td>
<td>120x10^{-12}</td>
</tr>
<tr>
<td></td>
<td>from literature</td>
<td></td>
</tr>
<tr>
<td>14 Cr</td>
<td></td>
<td>54x10^{-12}</td>
</tr>
<tr>
<td>18 Cr</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table II

Parabolic Rate Constants for the Oxidation of the Preoxidized Fe-Cr Alloys
(iii) **Cyclic Oxidation Kinetics**

Figure 3 shows the cyclic oxidation kinetics of the preoxidized Fe-18, 14 and 12 Cr - 1.0 Hf alloys at 1200°C. In contrary to the isothermal oxidation kinetics, HfO₂ containing alloys show poorer thermal cycling resistance than TiO₂-containing alloys. After the first cycle all the alloys have shown spallation and 12 and 14 Cr alloys have failed to form a new Cr₂O₃ protective layer and have show stratified scale formation. The 18% Cr alloy has also shown spallation but during the subsequent cycle always formed Cr₂O₃. The oxidation kinetics of these alloys are given in details elsewhere. (4)

(iv) **Scale Morphology and Composition**

The morphology and composition of the scale formed on these alloys were much the same as those formed on TiO₂-containing alloys, and this is given elsewhere. (1-4)

Figure 4 a-b compare the scales formed on the TiO₂-dispersoid containing Fe-18Cr-1.0Ti and the HfO₂-dispersoid containing Fe-18Cr-1.0Hf alloys respectively. The scale composition in both alloys is the same: mostly Cr₂O₃. In agreement with the kinetic data, the scale formed on the TiO₂-dispersoid containing alloy is much thicker. It is also quite adherent to the substrate mainly it seems because in a number of places the surface scale links up with the almost complete sub-surface layer of TiO₂ which has formed due to the coalescence of the internal oxide particles. The very thick almost unobservable in cross section, Cr₂O₃ scale in the
HfO$_2$-containing alloy is no longer adherent to the substrate. As indicated earlier (Figure 3) this alloy has poor resistance to thermal cycling and the scale presumably spalled from the surface on cooling down after the 50h exposure. The most interesting feature, however, is that the HfO$_2$-dispersoid particles do not show any coarsening and the particle size is almost the same as the original size. As was shown earlier, TiO$_2$ particles continuously coarsen during oxidation.

Figure 5 shows the behavior of the alloy, Fe-18Cr-1.0Hf with and without the internal oxidation pre-treatment to convert the Hf to an oxide dispersion. Without the internal oxidation treatment the alloy on being exposed at 1100°C shows rapid breakdown of the Cr$_2$O$_3$ protective scale and scales in a manner similar to an alloy of lower Cr content. Samples given a pre-oxidation treatment do not show this rapid scaling, although the Cr$_2$O$_3$ scale is not especially adherent, Figure 5b. This may be related to the apparent lower overall growth of the Cr$_2$O$_3$ on the dispersion-containing alloy producing less Cr-depletion at the alloy surface, and hence being able to reform Cr$_2$O$_3$ when the scale spalls. If this is the case, and spalled oxide, identified as Cr$_2$O$_3$ was collected from these samples, it implies that the occurrence of scale spallation is not as critical with this alloy.

Fe-14Cr-1.0Hf without any pre-treatment is not able to maintain a protective Cr$_2$O$_3$ scale and suffers rapid attack even under isothermal conditions; pre-internal oxidized samples, however, do maintain the protective scale, but not on thermal cycling.
DISCUSSION

In agreement with the results reported for TiO$_2$ dispersoid containing Fe-Cr alloys,\textsuperscript{(1,3)} the minimum chromium concentration necessary to form a stable protective Cr$_2$O$_3$ scale in isothermal oxidation lies also between 12 and 14\% Cr. This is also in agreement with those reported for Co- and Ni- base alloys.\textsuperscript{(6)}

The observation of interfacial voids suggest that the vacancy condensation model suggested by Stringer et al\textsuperscript{(6)} is not very effective in the present alloys. The observation of convoluted morphology suggests that stresses are produced during oxidation.

The ferritic alloys containing HfO$_2$ as dispersoids do not show any particle coarsening as was observed in TiO$_2$ containing Fe-Cr alloys. This is probably due to the higher negative free energy of formation of HfO$_2$ in comparison to TiO$_2$, which leads to a higher binding energy and reduces the solubility limit, and thus the particle coarsening does not occur when hafnium is used as a solute element.

Although, HfO$_2$ containing alloys have shown a spectacular increase in isothermal oxidation resistance, their resistance to scale spallation during thermal cycling was not greatly improved. The poor cyclic oxidation resistance is due to the absence of the oxide pegs at the alloy-scale interface. As earlier work\textsuperscript{(1-2)} has shown, Cr$_2$O$_3$ does not form intrusions around the dispersed particles as observed in dispersoids containing CoCrAl systems.\textsuperscript{(7)} TiO$_2$ containing Fe-Cr alloys show better metal-scale adhesion which is due to a continuous coarsening of the TiO$_2$ particles during oxidation.
and coarse particles act as oxide pegs and improve the metal-scale adhesion. Nevertheless, scale spallation on the Fe-18Cr-Hf alloys may be less critical, since rapid scaling does not seem to take place. This may be related to a lesser Cr-depletion at the alloy surface as a result of the slower overall growth rate of the Cr$_2$O$_3$. 

ACKNOWLEDGEMENTS

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REFERENCES

FIGURE CAPTIONS

Figure 1 Isothermal oxidation kinetics of pre-internally oxidized Fe-18, 14 and 12Cr-1.0Hf alloys at 1100°C.

Figure 2 A comparison of the isothermal oxidation kinetics of pre-internally oxidized Fe-Cr alloys containing Ti and Hf
a) 1100°C
b) 1000°C

Figure 3 Cyclic oxidation kinetics of pre-internally oxidized Fe-18, 14 and 12Cr-1.0Hf alloys at 1100°C.

Figure 4 Cross-section of the Cr₂O₃ scale formed after 50h isothermal oxidation for 50h at 1100°C.
a) Pre-internally oxidized Fe-18Cr-1Ti
b) Pre-internally oxidized Fe-18Cr-1Hf.

Figure 5 Cross-section of the scale formed on Fe-18Cr-1Hf after 10x3h cycles at 1100°C.
a) Untreated
b) Pre-internally oxidized.
Internally Oxidised

Fig. 1

Weight Gain (mg cm$^{-2}$) vs Time (h)

$12\text{ Cr}-1.0\text{ Hf}$

$14\text{ Cr}-1.0\text{ Hf}$

$18\text{ Cr}-1.0\text{ Hf}$

$n = 0.5$

XBL 7911-12817
Fig. 2
Fig. 3
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