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ADDITION: A$_2$O$_3$- FORMING ALLOYS

I. M. Allam, D. P. Whittle and J. Stringer

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IMPROVEMENTS IN OXIDATION RESISTANCE BY DISPERSED OXIDE ADDITION:  
Al₂O₃-FORMING ALLOYS.

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ABSTRACT.

The improvement in oxidation resistance produced by small additions of active elements to Al₂O₃-forming CoCrAl alloys is primarily dependent on the formation of oxide pegs which grow into the alloy around the internal oxide particles of the active element; void formation at the alloy/scale interface is also suppressed. The distribution of these pegs is critical and this paper demonstrates that an internal oxidation pre-treatment can be used to convert the active element to its oxide in a controlled manner, thereby optimising the peg distribution.

Al₂O₃-forming CoCrAl containing 1% Hf or Ce are internally oxidized in a sealed quartz capsule containing a 50/50 powder mixture of CoAl-Al₂O₃; it was not possible to internally oxidize Y-containing alloys. The isothermal and cyclic oxidation resistance of these alloys is superior to alloys not given a prior treatment. Detailed metallographic examination indicates that the prior internal oxidation treatment produces a finer, more uniform distribution of oxide pegs penetrating into the alloy which is more efficient in combatting scale spallation. Furthermore, the lower residual hafnium content in the alloy minimises large Hf₂O₂ precipitates and the formation of gross Al₂O₃ intrusions, which can initiate scale failure. Thus, by internally oxidizing the alloy first, the advantages of a high alloy Hf content (1%) in producing sufficient oxide pegs, but of the right size, coupled with minimal thickening of the surface scale, can be achieved.
INTRODUCTION.

Adhesion between surface scale and alloy substrate is an essential requirement of a material possessing good overall oxidation resistance. Poor adhesion can lead to oxide spallation in response to thermal cycling, or mechanically applied stresses, resulting in enhanced oxidation rates. Marked improvements in scale/substrate adhesion, however, can be achieved via the 'rare earth effect' whereby addition of a small amount of a rare earth element to heat-resisting alloys produces significant increases in the alloys' resistance to cyclic oxidation conditions. This effect is no longer limited to rare-earth elements: additions of other active elements, or of fine distributions of stable oxides are equally, if not more so, efficient.

Many detailed studies have been carried out, particularly with heat-resisting alloys which form Cr$_2$O$_3$ scales (1-9); Al$_2$O$_3$-forming alloys have been studied far less (10-14). Y has been the most common metallic additive used (11-15) and the MCrAlY (M = Fe, Ni, or Co) group of overlay cladding alloys has been an important development. The aspect of particular interest is the improved scale adhesion and a number of theories have been put forward to explain this (12, 15-22). However, more recently, a model has been developed which appears capable of interpreting most aspects of the so-called 'rare-earth effect' (10); two factors emerge as the most significant:

(i) the disappearance of voids at the alloy/scale interface (19), and
more importantly

(ii) the formation of oxide protrusions or pegs at the alloy/scale interface which anchor the scale to the substrate (12, 16-18).

Furthermore, it has been demonstrated (10) that the greatest beneficial effects are achieved when a fine, uniform distribution of small oxide pegs are formed, since these are more efficient in keying the scale to the substrate. Explanations based on increased scale plasticity (21), formation of a compound oxide layer, between scale and substrate, having a thermal expansion coefficient that gradually changes from a value similar to that of the alloy to a value close to that of the scale (graded seal) (20), or on lateral growth of the oxide (22), did not seem pertinent.
On the basis of this model then, it is possible to attempt to design alloys having improved oxidation resistance. This paper is one of a series aimed at the design and optimization of oxidation-resistant alloy compositions based on as fundamental a model as is currently available. It is not the primary aim of this work to elucidate reaction mechanisms, since although detailed identification of the growth processes involved in peg formation, for instance, may be of scientific interest, it is unlikely that such an identification would significantly improve the predictive capability of the model.

THEORETICAL CONSIDERATIONS.

The disappearance of voids at the alloy/scale interface when an active element or oxide dispersion is present in the alloy seems largely independent of the nature of the addition (10). It is generally proposed that the particles of the stable oxide act as sites for the condensation of vacancies injected by the oxidation process itself (19) or by unequal diffusional fluxes of the metallic components in the alloy (14), preventing their condensation at the alloy/scale interface as voids. Unless void formation is particularly critical during the early stages of oxidation, there is little to choose between reactive metal or oxide additions: the reactive metal oxidizes internally ahead of the oxidation front. There has been a suggestion (10) that vacancy injection is greatest during the initial, transient stages before the protective/scale develops; however, this transient stage is curtailed on alloys containing active elements (10,11). It is also possible that the reactive metal atoms themselves act as condensation sites.

Very low concentrations of additions seem sufficient to eliminate interfacial voids, although there is some evidence to suggest that with low concentrations, saturation can occur and voids re-appear after extended exposures (10).

As indicated earlier, the formation of oxide pegs is the more decisive factor and a fine, uniform distribution of small oxide pegs is the ultimate aim. With metallic additions, this is difficult to control, since essentially the reactive element oxidizes internally during high temperature exposure and these internally precipitated oxides form the nuclei around which the protective oxide (Cr$_2$O$_3$ or Al$_2$O$_3$) forms the pegs. Clearly the distribution of internal oxides, and subsequently the pegs, depends on the exposure conditions and is thus not directly controllable. Nevertheless, it has been shown (10) that Hf additions are far preferable to the widely used Y additions, principally because the latter tend to segregate to alloy grain boundaries forming intermetallics with the base metal, and the distribution of this intermetallic pre-determines the distribution of the internal oxides, and thus the pegs. Hf is completely soluble in matrices of this type and consequently gives a far better distribution of internal oxide.
An oxide dispersion, as opposed to a reactive metal addition might produce further benefits: with Cr$_2$O$_3$-forming alloys it has been shown (23) that the amount of chromium required in the alloy to form a continuous, external protective scale is reduced in the presence of a dispersoid, but not for alloys containing active elements (23): the protective scale is also more readily established in the early stages of oxidation. Both these phenomena are related to a model (5) in which it is suggested that the dispersoid particles at the alloy surface act as nucleation sites for all the oxide phases, producing a finer grained initial oxide film, which can then achieve its steady state configuration more rapidly.

Overall, then, in terms of potential improvements in oxidation resistance, oxide dispersions are to be preferred. If the active element is present already as an oxide dispersion, then control of the dispersion morphology and distribution allows an optimum peg configuration at the alloy/scale interface to be achieved during subsequent exposure: this is the overriding factor. The traditional powder preparation methods, such as ball-milling, co-precipitation or colloidal mixing, followed by mechanical alloying to produce oxide dispersion-containing alloys do not generally allow such fine control. The present work attempts to use a controlled internal oxidation pre-treatment developed for Cr$_2$O$_3$-forming alloys (23), in which it was demonstrated that internal oxidation of Co-Cr alloys containing small addition of an active element (Hf, Ti or Zr) was able to produce a stable oxide dispersion. This internal oxidation was carried out in a sealed quartz tube containing a mixture of Cr/Cr$_2$O$_3$ powders which maintained the oxygen activity at a level below that required for Cr$_2$O$_3$ formation on the alloy, yet sufficient to oxidize the active elements Hf, Ti or Zr. The conditions are more stringent to prevent Al$_2$O$_3$-formation, but this should be possible using a CoAl/Al$_2$O$_3$ mixture. Ti and Zr are not suitable as active elements, however, in these alloys, since they have a lower stability than Al$_2$O$_3$: Hf, Ce and Y should be suitable.

**EXPERIMENTAL.**

The alloys used in this study were identical to those used earlier (10): these are Co-10Cr-11Al alloys containing 0.05 - 1 Hf (wt.%) and Co-10Cr-7Al, Co-15Cr-6Al, Co-6Cr-6Al, Co-10Cr-5Al all containing 1 Hf. In addition a Co-10Cr-11Al-1Ce alloy was included. All these alloys form an external scale of $\alpha$-Al$_2$O$_3$ over the temperature range studied, although breakdown to a greater or lesser extent of this oxide can result in the formation of other oxidation products. The Y-containing alloys of the previous study were not included, primarily because attempts to produce a Y-rich oxide dispersion using the "Rhines Pack" as described below, were unsuccessful. Note, however, that Y was less effective in improving the oxidation resistance, because it tends to segregate to alloy grain boundaries as Y-rich intermetallics and as such provides a poor site distribution for oxide pegs (10). Equally, this segregated distribution of Y would pre-determine the distribution of any internal oxides, giving a very poor dispersion.
Oxidation experiments were of two types: (a) isothermal exposure and (b) repeated thermal cycles of 20 h duration each. Details of these along with the techniques of sample examination have been given (10). As indicated, the detailed morphology of the alloy/scale interface was studied by stripping the scale and examining its underside and, when possible, the exposed surface of the alloy. Scales were stripped either mechanically by quenching in liquid nitrogen, or with particularly adherent scales the substrate was dissolved away using 10% bromine-methanol solutions.

INTERNAL OXIDATION.

Alloy samples, after surface preparation, were placed into one arm of a dumb-bell shaped quartz tube, the other arm of which contained a mixture of equal weights of Co-aluminide (Co-20Al) and Al₂O₃ powders. The capsules were then evacuated to 10⁻⁵ Torr prior to sealing. The sealed capsule was then placed into another quartz tube containing small amounts of Ta metal in order to reduce the possibility of atmospheric oxygen passing through the wall at temperature. The outer tube was also sealed under vacuum (10⁻⁵ Torr). Internal oxidation was then carried out at 1100 and 1200°C for different periods of time.

The ratio of CoAl/Al₂O₃ is not critical providing there is sufficient Al to getter the oxygen remaining in the quartz tube. There did not appear to be any transfer of Al from the 'pack' to the samples: however, the samples were usually kept separate from the mixture.

Ce-containing alloys were internally oxidized in the same way: attempts to internally oxidize Y-containing alloys were unsuccessful, as mentioned above.

MORPHOLOGY OF THE INTERNAL OXIDES.

Thin tarnish films were formed on all the alloy samples during the pre-oxidation treatment: this did not seem to inhibit the internal oxidation, or have any great effect on the surface composition; very little depletion of the CoAl phase was detected. Both tarnish layer and any depletion were always removed by mechanical polishing before subsequent oxidation experiments.

HfO₂ particles were formed right through the sample cross-sections, surprisingly with no defined internal oxidation front. Figure 1 shows a typical example. The density of the spherical HfO₂ particles is higher near to the specimen surface than in the interior. Particles are randomly distributed through both α and CoAl phases. The size and number of particles varies also with Hf content: there are more HfO₂ particles in the alloy of highest Hf content, but there is not a direct correlation. Reduction in the Al content of the alloy also results in the formation of a larger number of finer particles. In addition, for a given alloy, the size of the HfO₂ particles decreases as the pre-oxidation
Figure 1. Cross-section of a Co-10Cr-11Al-1Hf sample internally oxidized in CoAl/Al$_2$O$_3$ pack for 68 h at 1200$^\circ$C (x 175).
temperature increases, but increases with increasing time of treatment at a fixed temperature. Internal oxidation of the Ce-containing alloy for 120 h at 1200°C produced relatively few, large CeO$_2$ precipitates, mainly in a band near the surface.

**THE INTERNAL OXIDATION PROCESS.**

If the internal oxidation process were controlled by diffusion of oxygen into the alloy, then increasing the time of internal oxidation would only result in the front of precipitation advancing into the alloy. The density of particles near to the surface would not be expected to alter. However, no internal oxidation front is ever observed and internal oxide particles are formed completely through the sample cross-section. Thus, it seems likely that with the low oxygen activity in the 'Rhines Pack' the supply of oxygen to the alloy surface, possibly through a tarnish film of Al$_2$O$_3$, is much lower than the diffusional flux of dissolved oxygen in the alloy. As a result, there is only a very shallow concentration gradient of oxygen through the alloy section, and the solubility product of HfO$_2$ is exceeded virtually simultaneously throughout the alloy. Increase in the time of internal oxidation then, produces more and more HfO$_2$ precipitates and lowers the Hf concentration remaining in solid solution: the density of internal oxide particles will not necessarily be directly proportional to the alloy Hf content until internal oxidation is complete.

**ISOTHERMAL OXIDATION KINETICS.**

Figure 2 shows the effect of variable pre-oxidation treatments on the oxidation behaviour of the alloy Co-10Cr-11Al-1Hf. The Hf addition itself produces a reduction in growth rate in comparison with the undoped alloy (10), without any internal oxidation treatment. However, internal oxidation produces even further reductions in the growth rates. The improvement in oxidation resistance is greatest for alloys given the most extensive internal oxidation pre-treatment: highest temperature and longest duration. Internal oxidation of 150 h at 1100°C is equivalent to about 40 h at 1200°C in terms of diffusion distance (23); however, as discussed earlier, diffusion of oxygen into the alloy may not be the rate-controlling factor.

Pre-oxidation of alloys containing 0.3 and 1% Hf produces more reduction in growth rate in comparison to the alloy of lower Hf content, 0.1%.

The presence of the dispersoid also influences the initial, transient stages of oxidation, as did the addition of metallic Hf (10). Its presence speeds up the approach to “steady state” scaling conditions - growth of a continuous Al$_2$O$_3$ scale. The greater the density of internal oxide precipitates, the more curtailed is the transient stage. However, differences in overall weight gain after 120 h at 1100°C are not only due to differences in
Figure 2. Iso-thermal oxidation of Co-10Cr-11Al-1Hf at 1100°C after receiving different internal oxidation treatments.
weight gain during the initial stages. Table I compares the weight gains after the transient period (approximately 1 h) and the total weight gains after 120 h exposure.

**TABLE I**

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Internal Oxidation Pretreatment</th>
<th>Weight Gain, mg/cm²</th>
<th>1 h</th>
<th>120 h</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co-10Cr-11Al</td>
<td>None</td>
<td></td>
<td>0.15</td>
<td>0.9</td>
</tr>
<tr>
<td>Co-10Cr-11Al-0.1Hf</td>
<td>None</td>
<td></td>
<td>0.14</td>
<td>0.23</td>
</tr>
<tr>
<td></td>
<td>300 h at 1200°C</td>
<td></td>
<td>0.12</td>
<td>0.21</td>
</tr>
<tr>
<td>Co-10Cr-11Al-0.3Hf</td>
<td>None</td>
<td></td>
<td>0.20</td>
<td>0.52</td>
</tr>
<tr>
<td></td>
<td>120 h at 1200°C</td>
<td></td>
<td>0.14</td>
<td>0.22</td>
</tr>
<tr>
<td></td>
<td>300 h at 1200°C</td>
<td></td>
<td>0.09</td>
<td>0.18</td>
</tr>
<tr>
<td>Co-10Cr-11Al-1.0Hf</td>
<td>None</td>
<td></td>
<td>0.17</td>
<td>0.7</td>
</tr>
<tr>
<td></td>
<td>150 h at 1100°C</td>
<td></td>
<td>0.13</td>
<td>0.52</td>
</tr>
<tr>
<td></td>
<td>120 h at 1200°C</td>
<td></td>
<td>0.13</td>
<td>0.42</td>
</tr>
<tr>
<td></td>
<td>300 h at 1200°C</td>
<td></td>
<td>0.12</td>
<td>0.26</td>
</tr>
<tr>
<td>Co-10Cr-11Al-1.0Hf</td>
<td>None</td>
<td></td>
<td>0.35</td>
<td>1.0 (90 h)</td>
</tr>
<tr>
<td></td>
<td>300 h at 1200°C</td>
<td></td>
<td>0.21</td>
<td>0.42</td>
</tr>
<tr>
<td>Co-10Cr-5Al-1Hf</td>
<td>None</td>
<td></td>
<td>0.20</td>
<td>0.75</td>
</tr>
<tr>
<td></td>
<td>300 h at 1200°C</td>
<td></td>
<td>0.18</td>
<td>0.42</td>
</tr>
<tr>
<td>Co-10Cr-11Al-1Ce</td>
<td>None</td>
<td></td>
<td>0.41</td>
<td>1.7</td>
</tr>
<tr>
<td></td>
<td>120 h at 1200°C</td>
<td></td>
<td>0.38</td>
<td>1.25</td>
</tr>
</tbody>
</table>

The effect of the internal oxidation treatment on alloys of lower Al content is even more significant. Both Co-10Cr-7Al and Co-10Cr-5Al are more susceptible to scale breakaway at temperature than the previous alloy containing 11% Al. Furthermore, the results of scale breakaway are more significant with borderline Al₂O₃-forming alloys and nodules containing spinel (Co₃Al₂O₄) and CoO can form, particularly at specimen edges and corners. As a result the weight gain data are of low reproducibility, and do not form the best basis to characterize the behaviour. Minor scale breakaway near specimen edges can result in relatively high weight gains, even though protective Al₂O₃ is formed over most of the specimen surface. Nevertheless, the amount of CoO and Co₃Al₂O₄ formation on either Co-10Cr-7Al-1Hf or Co-10Cr-5Al-1Hf was markedly reduced by internal oxidation. Co-15Cr-6Al-1Hf behaves similarly.
Figure 3 shows the behaviour of the Ce-containing alloy. Even after internal oxidation for 120 h at 1200°C the Ce-containing alloy oxidized at a much faster rate than a Hf-containing alloy, even when the latter had not been internally oxidized. The internally oxidized Ce-containing alloy was slightly better than the same alloy not internally oxidized: there was considerable spinel and CoO formation with this alloy as a result of scale breakaway at temperature.

**CYCLIC OXIDATION KINETICS.**

Cyclic oxidation tests were carried out at 1200°C with samples cooled to room temperature every 20 h. Primarily, this examines the adherence of the $\text{Al}_2\text{O}_3$ scales to the substrate and the effects of differing levels of Hf additions and different internal oxidation conditions. However, in considering the results a further factor must also be considered: in addition to improving the adhesion between $\text{Al}_2\text{O}_3$ and the substrate, the presence of the oxide dispersion (or possibly Hf alone) may also encourage the re-formation of $\text{Al}_2\text{O}_3$ after spalling on alloys which in its absence would form spinel or other faster growing scales.

Internal oxidation of the 0.1 and 0.05 Hf alloy has virtually no effect on its thermal cycling behaviour. Pre-oxidation of the 0.3 and 1% Hf alloys, on the other hand, reduces the overall weight gain during thermal cycling: Figure 4 shows the behaviour of the 1% alloys. As noted earlier in the isothermal tests, this is partially related to the lower growth rate of the $\text{Al}_2\text{O}_3$ scale following internal oxidation, but in addition, and more importantly, the tendency for scale spallation has been reduced.

With the borderline alloys of lower Al content, internal oxidation can be more beneficial in retaining the $\text{Al}_2\text{O}_3$ on the surface, or encouraging it to reform after spallation. Figure 5 shows the behaviour of Co-10Cr-7Al. Without Hf the alloy suffers rapid scaling after the first cycle: with 1% Hf but no internal oxidation, rapid oxidation commences only after 5 cycles. An internal oxidation pre-treatment reduces the overall scaling rate but the results are not reproducible: this is a reflection of the rather spasmodic scale spallation. Much the same sort of behaviour is observed with Co-10Cr-5Al and Co-15Cr-6Al. Pre-oxidation has no effect on the thermal cycling behaviour of the Ce-containing alloy: scale adherence on this alloy was relatively poor in comparison to the Hf-containing alloys, even under isothermal conditions. Table II summarises the weight gains of all the alloys under thermal cycling conditions.
Figure 3. Comparison of the isothermal oxidation kinetics at 1100°C for Co-10Cr-11Al containing 1 wt% Ce or 1 wt% Hf with and without internal oxidation in CoAl/Al₂O₃ mixtures (120 h at 1200°C).
Figure 4. Weight gain/time curves for Co-10Cr-11Al-1Hf with and without internal oxidation (150 h at 1100°C, 200 or 300 h at 1200°C in CoAl/Al₂O₃ mixtures) oxidized at 1200°C under cyclic conditions (20 h cycles).
Figure 5. Weight gain/time curves for Co-10Cr-7Al-1Hf with and without internal oxidation (120 or 300 h at 1200°C in CoAl/Al2O3 mixtures) oxidized at 1200°C under cyclic conditions (20 h cycles).
TABLE II
WEIGHT GAIN DATA AT 1200°C - THERMAL CYCLING EXPOSURE

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Internal Oxidation Pre-treatment</th>
<th>Weight gain, mg/cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co-1OCr-11Al-0.3Hf</td>
<td>None</td>
<td>3.7</td>
</tr>
<tr>
<td></td>
<td>68 h at 1100°C</td>
<td>2.1</td>
</tr>
<tr>
<td></td>
<td>300 h at 1200°C</td>
<td>1.0</td>
</tr>
<tr>
<td>Co-1OCr-11Al-1.0Hf</td>
<td>None</td>
<td>3.0</td>
</tr>
<tr>
<td></td>
<td>150 h at 1100°C</td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td>200 h at 1200°C</td>
<td>1.6</td>
</tr>
<tr>
<td></td>
<td>300 h at 1200°C</td>
<td>1.0</td>
</tr>
<tr>
<td>Co-1OCr-7Al-1Hf</td>
<td>None</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>120 h at 1200°C</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>300 h at 1200°C</td>
<td>22</td>
</tr>
<tr>
<td>Co-1OCr-5Al-1Hf</td>
<td>None</td>
<td>170 (4 x 20 h)</td>
</tr>
<tr>
<td></td>
<td>120 h at 1200°C</td>
<td>140 (4 x 20 h)</td>
</tr>
<tr>
<td></td>
<td>300 h at 1200°C</td>
<td>120 (6 x 20 h)</td>
</tr>
<tr>
<td>Co-15Cr-6Al-1Hf</td>
<td>None</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>120 h at 1200°C</td>
<td>34</td>
</tr>
<tr>
<td>Co-1OCr-11Al-1Ce</td>
<td>None</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td>120 h at 1200°C</td>
<td>14</td>
</tr>
</tbody>
</table>

SCALE MORPHOLOGY.

Primarily, all the alloys studied form Al₂O₃ scales; however, there are a number of detailed differences in the morphology and these will be outlined in this section. Firstly the behaviour of undoped alloys and doped alloys not given the internal oxidation treatment is briefly summarised (10).

During isothermal exposure, scale spallation on the Co-1OCr-11Al (10) alloy was not particularly critical. When it does occur, primarily near to specimen edges and corners, the alloy contains sufficient Al to re-form Al₂O₃ resulting in multilayered scales. Under thermal cycling conditions the relatively poor adherence of the Al₂O₃ to this alloy became apparent and scale spallation was more extensive. As a result, the faster growing CoO and spinel phases developed after repeated loss of the Al₂O₃-scale. Alloys of lower Al content were even more susceptible to rapid oxidation after scale spallation and nodules of CoO and spinel were observed even after isothermal exposure. Virtually no protective Al₂O₃ was observed during cyclic exposure.
After isothermal exposure, all the Co-10Cr-11Al alloys containing Hf showed single layers of Al₂O₃. In addition, internal oxidation of the Hf occurred, forming relatively coarse precipitates of HfO₂ near the scale/alloy interface; these precipitates were almost invariably enveloped by Al₂O₃ which apparently grew inwards from the surface scale. Some oxide stringers penetrated deeply into the alloy, particularly with alloys of lower Al content.

Under thermal cycling conditions the 0.05 and 0.1% Hf alloys were more susceptible to scale spallation and some nodular growth of CoO was evident near specimen corners. The 0.3 and 1.0% Hf alloys remained protected by an Al₂O₃ scale; spallation was much less severe, and when it did occur, Al₂O₃ was re-formed, except on occasional sites near specimen corners.

There are marked changes in the morphology of the oxide intrusions penetrating into the alloy when the Hf-containing alloys are given a prior internal oxidation treatment, converting the Hf into an HfO₂ dispersion. Figure 6 compares the underside of the stripped scale from two Co-10Cr-11Al-1Hf alloys, one (Figure 6a) having been given an internal oxidation treatment of 200 h at 1200°C prior to oxidation; both samples were oxidized for 1000 h at 1200°C. In the pre-oxidized sample, the oxide intrusions are all of fairly similar size and present a relatively homogeneous distribution. In contrast, with the un-preoxidized alloys, the distribution is much more irregular, and as noted earlier, some of the intrusions can be very long indeed. X-ray energy dispersive analysis of these intrusions formed on the dispersoid-free alloy shows a high Hf content.

Figure (7a) shows the Al₂O₃ scale formed on the Co-10Cr-11Al-1Hf alloy pre-oxidized for 200 h at 1200°C and then subjected to 17 x 20 h cycles at 1200°C. The scale is thin, and relatively compact. The same alloy oxidized for an identical period, but without an initial internal oxidation treatment, is shown in Figure 7b. By comparison, the Al₂O₃ surface scale is thicker, shows considerably more apparent porosity and a much greater density of oxide intrusions penetrating into the alloy.

Similar behaviour is also observed with Co-10Cr-7Al-1Hf alloy. Here the oxide intrusions are thinner, but again there are less in the alloy which has been internally oxidized. The external scale tends to spall above large intrusions of oxide penetrating into the alloy, no matter what the type of addition, or the preoxidation treatment. Figure 8 is an example of this showing that the surface scale above the long intrusion has flaked off, obviously during cooling. The implication is that more spallation is likely on alloys which were not exposed to pre-oxidation treatment, since these contain more long intrusions.
Figure 7. Cross-section of the scale formed on Co-10Cr-11Al-1Hf oxidized for 17 x 20 h cycles at 1200°C:

(a) sample internally oxidized in CoAl/Al₂O₃ mixture for 200 h at 1200°C (x 600).

(b) no internal oxidation treatment (x 600).
Figure 8. Cross sample of the scale formed on Co-10Cr-7Al-1Hf internally oxidized in CoAl/Al₂O₃ for 50 h at 1100°C and oxidized for 17 x 20 h cycles at 1200°C (x 600).
Figures 9 and 10 present a comparison of the X-ray maps of the alloys in cross section: these samples have been oxidized for 17 x 20 h cycles at 1200°C. The Al₂O₃ scale on the untreated alloy is more irregular and there is some evidence of spallation. In addition, as noted earlier, relatively long fingers of Al₂O₃ protrude deeply into the alloy, usually enveloping coarse precipitates of HfO₂. There is also a higher concentration of Hf-rich oxide precipitates near the scale/alloy interface.

No CoO formation at all is observed with 0.3 and 1.0% Hf alloys which have been internally oxidized: not even at the susceptible areas near the edges of the sample or when samples are thermally cycled.

Internal oxidation does not have a great deal of effect on the alloys of lower Hf content (less than 0.3 wt. %): as with the untreated alloys, there is a still limited CoO formation over parts of the surface.

With Ce-containing alloys, internal oxidation produced no beneficial effects on the oxidation behaviour. CoO, which forms during initial stages of oxidation or after Al₂O₃-scale breakaway during the oxidation of the base Co-10Cr-11Al alloy, is formed abundantly during the oxidation of the Co-10Cr-11Al-1Ce alloy.

Figure 11 shows a cross section of the alloy Co-10Cr-11Al-1Ce pre-oxidized for 120 hours at 1200°C then isothermally oxidized for 100 h at 1200°C. The large CeO₂ particles formed during the pre-oxidation treatment, like the finer HfO₂ particles earlier, were encapsulated in Al₂O₃, forming very coarse oxide intrusions; the Al₂O₃ scale usually spalled from most of the sample surface during cooling.

DISCUSSION.

The addition of the active element Hf and to a lesser extent Y or Ce to Al₂O₃-forming CoCrAl alloys, produce marked improvements in their oxidation resistance (10). Here it has been shown that internal oxidation of the Hf-containing alloy and conversion of the Hf to a dispersion of HfO₂ particles increases the beneficial effect: this is not the case with Y or Ce.

The presence of Hf, or the HfO₂ dispersion, produces three main effects:

(a) It speeds up the formation of a continuous layer of Al₂O₃ when the alloys are first exposed, or during exposure when spallation of the Al₂O₃-scale occurs.

(b) It decreases the apparent growth rate of the Al₂O₃-scales.

(c) It enhances the adhesion between scale and substrate.
Figure 9. Electron probe microanalysis of the scale formed on Co-10Cr-11Al-1Hf without any internal oxidation treatment, oxidized at 1200°C for 17 x 20 h cycles (x 600).
Figure 10. Electron probe microanalysis of the scale formed on Co-10Cr-11Al-1Hf internally oxidized in CoAl/Al₂O₃ for 200 h at 1200°C and oxidized at 1200°C for 17 x 20 h cycles (x 600).
Figure 11. Cross-section of Co-10Cr-11Al-1Ce internally oxidized in CoAl/Al$_2$O$_3$ mixture for 120 h at 1200°C then oxidized for 100 h at 1200°C (x 375).
From the kinetic results presented, it is clear that the greater the density of internal oxide precipitates near the surface of the alloy, the more curtailed is the transient stage. This is substantially in agreement with the model referred to earlier, in which it is suggested that the dispersed particles at the alloy surface act as nucleation sites producing a finer grained, initial oxide film, which can then achieve its steady state configuration more rapidly. The additional presence of Hf in the alloy, with its high affinity for oxygen, may assist in this more rapid initial nucleation: the more so, the higher the Hf content. More importantly, however, when the alloys have been pre-internally oxidized they already contain the dispersoid, and the transient stage is reduced even more. Again, the higher the Hf content, the greater is the beneficial effect.

It has also been shown that internal oxidation at high temperature and for long times, produces the greatest effect on the initial formation of Al₂O₃, which is again related to the increased number of dispersoid particles at the alloy surface. The internal oxidation process does not appear to be diffusion-controlled and continued oxide precipitation occurs throughout the sample during the pre-treatments.

Hf and HfO₂ additions decrease the overall oxidation rate and this is primarily associated with the improvement in scale adhesion. With Hf-containing alloys it was suggested that there could also be some reduction in the actual transport rate through the Al₂O₃ scale, (10), either lattice diffusion or via some short circuit paths: it is doubtful that there would be any further reduction with oxide-containing alloys.

Two factors are responsible for the improved adhesion. Firstly, the presence of HfO₂ particles in the alloy, formed either during exposure or prior to it, in the internal oxidation treatment, eliminate the formation of interfacial voids. The generally accepted mechanism is that the internal oxide particles act as vacancy sinks, preventing gross loss of contact between alloy and scale. Very low Hf, or dispersion contents are completely sufficient for this.

Interestingly the voids re-appeared after extended periods of oxidation at high temperature, in alloys containing metallic additions (10); this was not so with alloys that had received a prior internal oxidation, there is considerable solute (Hf) enrichment in the zone of internal oxidation formed during exposure, and many of the oxide particles eventually do become incorporated into the scale. They can no longer act as vacancy sinks: this is not the case when the internal oxide is distributed throughout the alloy.
The second, and perhaps more important factor contributing to improved scale adhesion is the formation of oxide intrusions at the scale/alloy interface, which key the scale to the alloy substrate. The incoherent boundary between the HfO$_2$ precipitate and the matrix promotes inward growth of Al$_2$O$_3$ at these points, eventually encapsulating the internal oxide. The Al$_2$O$_3$ intrusions, in general, remain attached to the surface scale.

The higher the Hf content of the alloy, the more of these intrusions are formed and the better should be the scale adhesion. However, high Hf contents lead to the large type of stringers which can actually act as initiation sites for scale cracking. Furthermore, formation of these inwardly growing stringers contributes significantly to the overall weight gain, and consequently under isothermal conditions where scale spallation is not very severe, alloys of low Hf content are more oxidation resistant. It might be argued that since conversion of Hf to HfO$_2$ also involves oxygen pick-up, and would be reduced in alloys of low Hf content, that this might account for overall weight gain differences. This is not the case: scale thickness measurements confirm that the difference is primarily due to the reduced tendency of the Al$_2$O$_3$ to envelop the internal oxides.

Under thermal cycling conditions, scale spallation is far more critical and sufficient oxide intrusions are not formed in the low Hf alloys to ensure good scale retention. Thus, there are conflicting requirements: low Hf contents minimize thickening of the Al$_2$O$_3$ scale by inward growth around the internal oxide particles, and prevent the formation of large oxide pegs, whereas higher Hf contents are required to ensure sufficient pegs needed for efficient scale retention.

However, prior internal oxidation provides an even better compromise. Internal oxidation reduces the Hf content in the alloy, and forms a fine dispersion of HfO$_2$. This fine distribution results in a more uniform distribution of oxide pegs penetrating into the alloy which are more efficient in combatting scale spallation. Furthermore, the lower Hf content in the matrix precludes further internal oxidation of Hf during exposure, conditions which lead to solute enrichment, large HfO$_2$ precipitates and the formation of gross Al$_2$O$_3$ intrusions. Thus, by internally oxidizing the alloy first, the advantages of a high alloy Hf content in producing sufficient oxide pegs, but of the right size, coupled with minimal thickening of the surface scale can be achieved.

CONCLUSION.

One of the original aims of the present work was to establish the critical factors responsible for the improvements in overall oxidation resistance,
especially under cyclic conditions, produced by additions of small amounts of reactive element or of a stable oxide dispersion to heat-resistant alloys. The major factor appears to be the distribution of the oxide particles and for this reason oxide dispersions are more efficient than active metals, since although the latter are internally oxidized during exposure, the distribution of the resulting oxides is dictated by the exposure conditions. In this work an internal oxidation technique has been used to produce the oxide dispersion, although it is unlikely that this method would be suitable as a commercial process. However, because of the importance of the distribution, other methods of production of dispersed oxide-containing alloys ought to be examined more closely.

Equally it appears that the composition of the dispersion is not critical. Nitrides, for example, have been used in austenitic and ferritic stainless steels (24): although they are not as efficient as oxides. Carbides or even stable intermetallic compounds may be other possibilities since in general the following factors seem important:

(a) the dispersoid must be very stable so that it does not dissociate or dissolve in the matrix, and it is better if it does not oxidize;
(b) it is better also if the dispersoid does not contain the constituent that is going to form the protective scale; and
(c) it is possible to disperse the phase within the matrix in the right configuration.

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References.

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