The Role of Rare Earths and Reactive Elements in High-Temperature Oxidation Behavior of Fe–20Cr Alloy*

By Hiroshi Nagai**, Teruyuki Murai*** and Hiroyasu Mitani**

The isothermal oxidation behavior of Fe–20Cr alloys with various amounts of lanthanum and with constant amounts of various reactive elements (Y, Gd, La, Al, Zr, Ti and Si) was studied in air at 1273 K.

The oxidation behavior of the alloys with various amounts of La suggested that the improving mechanism of oxidation resistance was different from those proposed previously. Seven alloying elements of 0.7% resulted in a remarkable improvement of oxidation resistance. The extent of beneficial effect of each element considerably depended on its affinity for oxygen, but the effect of La and Si additions deviated from this tendency. Internal oxidation layers were observed beneath the scale in all the oxidized alloys except for the La-containing alloys, which showed the least improving effect.

As the result, it was found that these elements had two main beneficial effects on the improvement of oxidation resistance. The first was the stabilization of the Cr2O3 scale with dissolving the alloying element which was followed by a drop in dissociation oxygen pressure of the scale and the second was the formation of an internal oxidation layer which was enriched under the lowered dissociation oxygen pressure induced by the first effect.

It was assumed from the thermochemical considerations that the alloying elements having strong affinity for oxygen and also high mobility in the base alloy would be more effective in the improvement of oxidation resistance.

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I. Introduction

It has been well known that small additions of reactive elements such as rare earths Y, Al and Si, singly or together, to Fe–Cr, Ni–Cr and Co–Cr alloys play a crucial role in improving their oxidation resistance. Although various hypothesis and explanations(1)–(17) on the improving mechanism have been proposed, the mechanism has not been clearly understood. The significant mechanisms proposed are as follows:

1. The oxide layer of the reactive element formed beneath the scale acts as a physical barrier to inhibit the diffusion of metal from alloy to scale and reduces the rate of scale growth(1)–(10).

2. Diffusion of desirable elements is enhanced by changing the properties of the base alloy(11) such as an expansion of the lattice by the addition of elements with a large atomic volume. It promotes the formation of the protective Cr2O3 scale or the protective internal oxidation layer of the reactive element added together with rare earths.

3. A complicated alloy-scale interface formed by preferential oxidation at grain boundary improves the scale adherence, so-called “key-on” effect(11)–(13).

4. Internal oxide particles act as vacancy sinks and absorb inward flowing vacancies, thus preventing void formation at the alloy-scale interface(14)–(16).

5. Dissolution of additive elements into scale improves the sintering and plasticity of the scale and consequently prevents the mechanical failure of the scale(16)(17).

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The purpose of this study was to obtain a better understanding of the improving mechanism of oxidation resistance by comparing the oxidation behavior of Fe–20Cr alloys with various amounts of lanthanum and also with constant amounts of various elements. Lanthanum was selected because it has a large atomic volume and does not form any intermetallic compounds with Fe\(^2\) and Cr\(^3\). The other additional elements which are in a wide range of affinity for oxygen were used.

**II. Experimental Procedure**

All alloys with an addition were prepared by non-consumable arc-melting. Fifty gram buttons were arc-melted on a water-cooled copper hearth in an argon furnace. The argon atmosphere was purified by melting a zirconium button and allowing it to react with residual oxygen and nitrogen. These alloys were then given a preliminary annealing treatment in vacuum at 1273 K for 72 h to promote homogeneity. Each specimen was hot-rolled at 873 K into 1 mm thickness and cut into 10×10×1 mm. The specimens were abraded on silicon carbide paper and annealed in vacuum at 1273 K for 24 h to relieve stress and minimize grain growth effects in the subsequent oxidation process. The chemical compositions of the alloys are listed in Tables 1 and 2. After degreasing and weighing, the specimens were put in an alumina crucible suspended with fine Pt and quartz wires.

The specimens were isothermally oxidized at 1273 K in air. Oxidation kinetics were determined by the weight gain measurements. The surface topography of the oxidized specimens was examined by scanning electron microscopy. Standard X-ray diffraction techniques were employed for phase identification of the oxidation products in situ. Traverse sections of the specimens were subsequently prepared by standard metallographic techniques and examined by microphotography and EPMA.

In order to study the formation process of internal oxidation layer beneath the scale, the encapsulation method was employed. Specimens of L07, Y07, A07 and S07 alloys designated in Table 2 were sealed at one end of a quartz capsule containing a mixed powder compact of Cr–Cr\(_2\)O\(_3\) (2:1 in weight ratio) and Cr–Cr\(_2\)O\(_3\)(Y\(_2\)O\(_3\))(2:1) at the other end of the capsule respectively. The Cr\(_2\)O\(_3\)(Y\(_2\)O\(_3\)) powders were prepared as follows. Cr\(_2\)O\(_3\) and Y\(_2\)O\(_3\) powders (9:1 in mole ratio) were thoroughly mixed and cold pressed into disk form at a pressure of 588 MPa and fired at 1273 K for 72 h in air. The resulting oxide was ground to –325 mesh in an agate mortar. The capsule was held isothermally at 1273 K for several hours to allow internal oxidation to occur. The cross sections of the specimens internally oxidized were then examined optically and the depth (\(\xi\)) of the internal oxidation layer was measured with a microscope. Measurements of \(\xi\) were made at points away from grain boundaries. The samples were etched by swabbling for 15 s to 1 min with a mixture of nitric and hydrochloric acids, plus a few drops of glycerin, until the internal oxidation interface could be seen on the microscope.

**III. Experimental Results**

1. **Fe–20Cr–xLa alloys**

Figure 1 depicts weight gain-time curves in

<table>
<thead>
<tr>
<th>Alloys</th>
<th>Intended composition</th>
<th>Fe (wt%)</th>
<th>Cr (wt%)</th>
<th>La (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>L 0</td>
<td>Fe–20Cr</td>
<td>Bal.</td>
<td>19.23</td>
<td></td>
</tr>
<tr>
<td>L02</td>
<td>Fe–20Cr–0.2La</td>
<td>Bal.</td>
<td>20.57</td>
<td>0.17</td>
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<tr>
<td>L05</td>
<td>Fe–20Cr–0.5La</td>
<td>Bal.</td>
<td>19.82</td>
<td>0.53</td>
</tr>
<tr>
<td>L07</td>
<td>Fe–20Cr–0.7La</td>
<td>Bal.</td>
<td>20.30</td>
<td>0.72</td>
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<tr>
<td>L10</td>
<td>Fe–20Cr–1.0La</td>
<td>Bal.</td>
<td>19.48</td>
<td>1.04</td>
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<tr>
<td>L13</td>
<td>Fe–20Cr–1.3La</td>
<td>Bal.</td>
<td>20.60</td>
<td>1.36</td>
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</table>

<table>
<thead>
<tr>
<th>Alloys</th>
<th>Alloying elements</th>
<th>Fe (wt%)</th>
<th>Cr (wt%)</th>
<th>M (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y07</td>
<td>Y</td>
<td>Bal.</td>
<td>20.16</td>
<td>0.69</td>
</tr>
<tr>
<td>G07</td>
<td>Gd</td>
<td>Bal.</td>
<td>19.93</td>
<td>0.65</td>
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<tr>
<td>L07</td>
<td>La</td>
<td>Bal.</td>
<td>20.30</td>
<td>0.72</td>
</tr>
<tr>
<td>A07</td>
<td>Al</td>
<td>Bal.</td>
<td>19.88</td>
<td>0.71</td>
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<tr>
<td>Z07</td>
<td>Zr</td>
<td>Bal.</td>
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<td>0.69</td>
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<td>T07</td>
<td>Ti</td>
<td>Bal.</td>
<td>20.24</td>
<td>0.62</td>
</tr>
<tr>
<td>S07</td>
<td>Si</td>
<td>Bal.</td>
<td>20.56</td>
<td>0.68</td>
</tr>
</tbody>
</table>
Role of Rare Earths and Reactive Elements in High-Temperature Oxidation Behavior of Fe-20Cr Alloy

Fig. 1 Isothermal oxidation of Fe-20Cr-xLa alloys in air at 1273 K.

air at 1273 K for Fe-20Cr alloys with additions of 0, 0.2, 0.5, 0.7, 1.0 and 1.3 wt%La. All alloys showed approximately parabolic weight gains in the first 4 h. The parabolic rate constants for these alloys were in the range between $2.7 \times 10^{-2}$ and $0.3 \times 10^{-2}$ g²/m⁴. Although both of L0 and L02 alloys showed severe oxidation after only 4 h oxidation, but it is evident from a comparison of the oxidation rate on these two alloys that 0.2%La addition slightly improved the oxidation resistance. The improvement of oxidation resistance was more remarkable on alloys with 0.5%La or more and these alloys exhibited a negative deviation from parabolic behavior after 4 h oxidation.

Photograph 1 shows the typical surface topography of L0–L10 alloys after 20 h oxidation at 1273 K in air. The structure was quite similar on the alloys with 0.5%La or more and consisted of a more or less uniform layer with small oxide grains. In comparison with those alloys, the contrast is striking on L0 and L02 alloys where extremely large oxide grains were observed. The time dependency of the superficial appearance of the scales corresponded with the time dependency of weight gain shown in Fig. 1. Scales formed during the first 4 h oxidation were quite similar in all alloys. On L0 and L02 alloys, however, large oxide grains initiated to grow from the fine-grained surface after 10 h oxidation and then grew up to quite large oxide grains after 20 h oxidation. In contrast, fairly fine-grained oxide surface was maintained in the alloys with 0.5%La or more during the oxidation period examined.

X-ray diffraction analyses of the oxide scales in situ were carried out. Table 3 summarizes the oxide phases identified in the scales formed on L0–L13 alloys oxidized in air at 1273 K for 20 h. α-Fe₂O₃ and spinel phases were detected on L0 and L02 alloys which exhibited severe oxidation. The intensity of α-Fe₂O₃

<table>
<thead>
<tr>
<th>Alloys</th>
<th>Oxides</th>
</tr>
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<tbody>
<tr>
<td>L0</td>
<td>α-Fe₂O₃(s) (s) spinel⁴(m)</td>
</tr>
<tr>
<td>L02</td>
<td>α-Fe₂O₃(s) (s) spinel(m)</td>
</tr>
<tr>
<td>L05</td>
<td>spinel(s), Cr₂O₃(s), α-Fe₂O₃(m)</td>
</tr>
<tr>
<td>L07</td>
<td>Cr₂O₃(m), α-Fe₂O₃(w)</td>
</tr>
<tr>
<td>L10</td>
<td>Cr₂O₃(m), α-Fe₂O₃(w)</td>
</tr>
<tr>
<td>L13</td>
<td>Cr₂O₃(m), α-Fe₂O₃(w)</td>
</tr>
</tbody>
</table>

* ³Fe₂O₄ and FeCr₂O₄
(s) strong, (m) medium, (w) weak

Photo. 1 SEM photographs of oxides surface formed on Fe-20Cr-xLa alloys in air at 1273 K.
and spinel phases decreased with increasing La content accompanied by a simultaneous increase in the intensity of \( \text{Cr}_2\text{O}_3 \). \( \text{Cr}_2\text{O}_3 \) phase was safely maintained during the oxidation period on the alloys with 0.5\%La or more which showed good oxidation resistance. It seems apparent that the presence of \( \text{Cr}_2\text{O}_3 \) is the essential element of a satisfactory scale and more than 0.5\%La additions stabilizes the \( \text{Cr}_2\text{O}_3 \) phase. Table 4 summarizes the X-ray diffraction results of the scales formed on L02 alloy oxidized in air at 1273 K for 2, 4, 10 and 20 h. \( \text{Cr}_2\text{O}_3 \) is the main reaction product with small amounts of spinel and \( \alpha\text{-Fe}_2\text{O}_3 \) phases in the first 2 h oxidation. The intensity of \( \alpha\text{-Fe}_2\text{O}_3 \) and spinel phases increases as oxidation proceeded, then no peak of \( \text{Cr}_2\text{O}_3 \) phase was detected after 10 and 20 h, when severe oxidation occurred. It seems apparent that small weight gain is maintained as far as the \( \text{Cr}_2\text{O}_3 \) scale exists and severe oxidation occurs as soon as the \( \text{Cr}_2\text{O}_3 \) scale disappears. As can be seen from Tables 3 and 4, no lanthanum oxide, such as \( \text{La}_2\text{O}_3 \) or \( \text{LaCrO}_3 \), was detected on L05–L13 alloys which exhibited good oxidation resistance, whose formation had been proposed as one of the most significant mechanisms by which oxidation resistance was improved.

As a typical example, Photo. 2 shows electron probe microanalyses of scales formed on L0, L02, and L07 alloys oxidized at 1273 K for 20 h. Multi-layered scales similar to those in Photo. 2(a) (b) formed on L0 and L02 alloys after only 4 h oxidation. The most outer layer of the stratified scales consists solely of iron oxide while the inner layer consists of both Fe and Cr which were substantiated by X-ray diffraction to be \( \alpha\text{-Fe}_2\text{O}_3 \) and (Fe, Cr)-spinel respectively.

As described above, in La containing alloys, any layer possible to inhibit the diffusion of metals from alloy to scale and the reaction between alloy and scale was not observed beneath the scale. In addition, judging from the line analyses by EPMA, the depletion of Cr at the interface did not depend on La content, which meant La with a large atomic volume did not enhance the Cr diffusion. A complicated alloy-scale interface, which is expected to key the scale on the alloy, was observed on L0 and L02 alloys rather than on the alloys which exhibited good oxidation resistance. However, very thin \( \text{Cr}_2\text{O}_3 \) scale was safely maintained on the alloys which exhibited good oxidation resistance even after 20 h oxidation. Since these results seemed to suggest that the improving effect of La addition on the oxidation resistance might be considerably different from those proposed in the previous work(1)–(17), the oxidation behavior of the alloys with constant amount of various elements was compared.

### 2. Fe–20Cr–0.7M alloys

Figure 2 depicts weight gain-time curves at 1273 K for Fe–20Cr alloys with 0.7 wt\% of Y, Gd, La, Al, Zr, Ti and Si, whose affinities for oxygen are in a wide range. The reproducibility obtained was reasonably close. Although all the additional elements resulted in the remarkable improvement of oxidation resistance, La addition showed the least improving effect on the oxidation resistance.

Since authors predicted that the improvement effect of the alloying element would depend on its affinity for oxygen, weight gains at 1273 K for 20 h were plotted against the standard free energies of formation \( (-\Delta G_{\text{MO}_{\text{ox}}}) \) of each oxide \( (\text{MO}_{\text{ox}}) \) in Fig. 3. As can be seen from Fig. 3, there is a tendency that the stronger affinities for oxygen the alloying elements have, i.e. the larger the value of \( -\Delta G_{\text{MO}_{\text{ox}}} \), the greater is the improvement effect of oxidation resistance with the exception of La and Si additions. Although La has strong affinity for oxygen \( (\Delta G_{\text{La}_2\text{O}_3} = -955 \text{ kJ/mol})^{(20)} \), the improvement effect of La on the oxidation resistance was the least among the alloying

<table>
<thead>
<tr>
<th>Oxidation time</th>
<th>Oxides</th>
</tr>
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<tbody>
<tr>
<td>2 h</td>
<td>( \text{Cr}_2\text{O}_3 )(m), spinel*( (\text{w}) ), ( \alpha\text{-Fe}_2\text{O}_3 )(w)</td>
</tr>
<tr>
<td>4 h</td>
<td>spinel(s), ( \text{Cr}_2\text{O}_3 )(m), ( \alpha\text{-Fe}_2\text{O}_3 )(m)</td>
</tr>
<tr>
<td>10 h</td>
<td>( \alpha\text{-Fe}_2\text{O}_3 )(s), spinel(m)</td>
</tr>
<tr>
<td>20 h</td>
<td>( \alpha\text{-Fe}_2\text{O}_3 )(s), spinel(m)</td>
</tr>
</tbody>
</table>

* \( \text{Fe}_2\text{O}_3 \) and \( \text{FeCr}_2\text{O}_4 \)
(s) strong, (m) medium, (w) weak
elements investigated in this study. On the other hand, S07 alloy exhibited relatively good oxidation resistance in spite of the weakest affinity for oxygen \((\Delta G_{\text{FeO}} = -653 \text{ kJ/mol})\) in this study. Figure 3 indicates that the improvement effect of alloying elements depends not only on their affinities for oxygen but also on the other factors.

Table 5 summarizes the oxide phases identified in the alloys oxidized at 1273 K for several hours. Generally, all the alloys showed the same tendency that \(\text{Cr}_2\text{O}_3\) was the main reaction product and the weak lines of the oxides of each alloying element were observed except for L07 alloy.

For typical example, Photo. 3(a), (b) and (c) show the optical microscope pictures of metallographic cross sections of A07, Y07 and S07 alloys oxidized in air at 1273 K for 20 h respectively. As can be seen from Photo. 3(a), inner layer beneath the scale was clearly observed on A07 alloy, and the X-ray diffraction
identification substantiated that the inner layer was internal oxidation layer of $\alpha$-Al$_2$O$_3$. The internal oxidation layer was not observed directly on the other alloys, but after etching, the samples except for S07 and L07 alloys revealed an internal oxidation layer similar to that in Photo. 3(b). Although the internal oxidation layer was not observed on S07 alloy even after etching, the EPMA line analysis of Si showed an thin layer enriched in Si beneath the scale, which was substantiated to be SiO$_2$ by X-ray diffraction. While any lanthanum oxide and internal oxidation layer was not detected on the oxidized L07 alloy as described above.

Although the addition of La more than 0.5% completely suppressed the break-away and maintained the Cr$_2$O$_3$ scale safely, L07 alloy in which the internal oxidation layer was not observed exhibited the least oxidation resistance among the alloys investigated. In contrast, the alloys in which the internal oxidation layer formed exhibited good oxidation resistance, even though the alloying elements had relatively weak affinities for oxygen. Then it was considered that the alloying elements had two main beneficial effects on the improvement of oxidation resistance; first is the stabilization effect of the main Cr$_2$O$_3$ scale and second is the formation of the internal oxidation layer.

| Table 5 Oxides detected by X-ray diffraction of Fe–20Cr–0.7M alloys oxidized in air at 1273 K. |
|---|---|---|---|---|
| Alloy | Oxidation time (h) | 2 h | 4 h | 10 h | 20 h |
| L07 | Cr$_2$O$_3$(m) | Cr$_2$O$_3$(m) | Cr$_2$O$_3$(m) | Cr$_2$O$_3$(m) | Cr$_2$O$_3$(m) | \(\alpha\)-Fe$_2$O$_3$(vw) | \(\alpha\)-Fe$_2$O$_3$(w) |
| Y07 | Cr$_2$O$_3$(s) | YCrO$_3$(w) | Cr$_2$O$_3$(s) | YCrO$_3$(m) | Cr$_2$O$_3$(s) | YCrO$_3$(m) |
| G07 | Cr$_2$O$_3$(s) | Gd$_2$O$_3$(w) | Cr$_2$O$_3$(s) | Gd$_2$O$_3$(w) | Cr$_2$O$_3$(s) | Gd$_2$O$_3$(w) |
| T07 | Cr$_2$O$_3$(m) | TiO$_2$(vw) | Cr$_2$O$_3$(s) | TiO$_2$(w) | Cr$_2$O$_3$(s) | TiO$_2$(w) |
| Z07 | Cr$_2$O$_3$(s) | ZrO$_2$(vw) | Cr$_2$O$_3$(s) | ZrO$_2$(vw) | Cr$_2$O$_3$(s) | ZrO$_2$(vw) |
| A07 | Cr$_2$O$_3$(m) | \(\alpha\)-Al$_2$O$_3$(w) | Cr$_2$O$_3$(s) | \(\alpha\)-Al$_2$O$_3$(w) | Cr$_2$O$_3$(s) | \(\alpha\)-Al$_2$O$_3$(w) |
| S07 | Cr$_2$O$_3$(s) | Si$_2$O$_3$(w) | Cr$_2$O$_3$(m) | Si$_2$O$_3$(w) | Cr$_2$O$_3$(m) | Si$_2$O$_3$(w) |

(s) strong, (m) medium, (w) weak, (vw) very weak
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Photo. 3 Microphotographs of external scales and internal oxidation layers formed on the alloys oxidized for 20 h in air at 1273 K.
(a) Fe-20Cr-0.7Al alloy (no etch)
(b) Fe-20Cr-0.7Y alloy (etched with HCl-HNO3-glycerin)
(c) Fe-20Cr-0.7Si alloy (no etch)

beneath the scale.

The internal oxidation layer is considered to be formed under the dissociation oxygen pressure of the Cr$_2$O$_3$ scale lowered by dissolving the alloying element in the scale, which was detected by an ion microanalyser (IMA) of the scales formed on each alloy. Therefore, in order to obtain a better understanding of the effects of dissolving the alloying element in the scale on the formation process of the internal oxidation layer, encapsulation oxidation experiments were carried out. As described above, L07, Y07, A07 and S07 alloys were encapsulated in a quartz tube with Cr-Cr$_2$O$_3$ and Cr-Cr$_2$O$_3$(Y$_2$O$_3$) mixed powder compacts respectively and oxidized under each equi-

librium oxygen pressure at 1273 K for several hours.

In the case of L07 alloy, no internal oxidation layer was detected, in contrast, white external scale of SiO$_2$ was observed on S07 alloy under both oxygen pressures. In the case of Y07 and A07 alloys, on the other hand, internal oxidation layers were observed and the depth ($\xi$) of the internal oxidation layers grew with time. In Fig. 4, the results are given in the form $\xi^2$ vs time for both alloys at 1273 K. The rates of growth of the internal oxidation layer were parabolic under both oxygen pressure, in addition, the rates were significantly decreased by dissolving of Y$_2$O$_3$ in Cr$_2$O$_3$ and also there were considerable differences in the rates between A07 and Y07 alloys under the same oxygen pressure. The results in Fig. 4 indicate that the dissolution of Y$_2$O$_3$ into Cr$_2$O$_3$ considerably decreases the dissociation oxygen pressure of Cr$_2$O$_3$, ie Cr$_2$O$_3$ is stabilized thermochemically, and at the same time the formation process of the internal oxidation layer depends on the characteristics of the alloying elements, probably on the mobility of the alloying element in the base alloy.

IV. Discussion

As the results described above, it was con-

![Fig. 4 Variation of internal oxidation layer depth with time for Y07 and A07 alloys oxidized in Cr$_2$O$_3$-Cr and Cr$_2$O$_3$(Y$_2$O$_3$)-Cr mixed powder compacts at 1273 K respectively.](image-url)
sidered that the alloying elements investigated had two main beneficial effects on the improvement of oxidation resistance; the first was the stabilization of the main Cr$_2$O$_3$ scale with dissolving the alloying element in the scale, and the second was the formation of internal oxidation layer beneath the scale.

In order to obtain an exact understanding of these two effects, it will be discussed here how the main Cr$_2$O$_3$ scale is stabilized and the formation process of internal oxidation layer is affected by the characteristics of alloying elements and why L07 and S07 alloys exhibited the unexpected oxidation behavior.

Severe oxidation (Break-away) was completely suppressed and the Cr$_2$O$_3$ scale was safely maintained on the alloys with 0.5%La or more in spite that internal oxidation layer was not observed. Then, the effect of the reactive elements addition to suppress “Break-away” will be discussed in some detail at first.

The oxidation rate of Fe-Cr alloys with 13–25Cr at high temperature shows a rapid increase after an induction period during which Cr$_2$O$_3$ is present, and the protective scale is suddenly replaced by non-protective spinel scale in which metallic ions have faster movilities than in Cr$_2$O$_3$ scale. The mechanism of this sudden change in oxidation kinetics, generally termed “Break-away” has been the subject of some controversy(22)(23). Two main theories have been proposed to account for break-away. First is a “chemical transformation” where the initial chromium oxide scale is attacked from within by the Cr-depleted alloy and second is a “mechanical failure” of the protective scale, exposing fresh, Cr-depleted alloy surface to the hot-oxidizing gases. Whittle et al.(24) reported that the determined Cr concentration at the alloy-scale interface was much higher than the calculated limiting value (5×10$^{-3}$ wt %Cr at 1273 K) above which Cr$_2$O$_3$ is thermochemically stable and then concluded that the chemical transformation from Cr$_2$O$_3$ to spinel by reaction (1) was not deemed to occur as reported by Whittle et al., if the following processes accompanying with the diffusion process are considered, the chemical transformation is thermochemically possible.

A Cr$_2$O$_3$ scale formed at the start of the high-temperature oxidation of Fe–20Cr alloy is containing a very small amount of iron oxides and then is not considered to be in equilibrium with the Cr-depleted alloy at the interface(25)(26). Then the situation at the interface is like that of a diffusion couple of Cr$_2$O$_3$ and Cr-depleted alloy, where the Cr-depleted alloy supplies iron to the scale and both tend to approach the equilibrium state according to reaction (2).

\[ 2Fe + 3/O_2 + Cr_2O_3 = (Cr_2O_3)(Fe_2O_3). \] (2)

If the Cr$_2$O$_3$ scale formed on Fe–20Cr binary alloy is denoted as Cr$_2$O$_3'$ and the standard free energy of formation of Cr$_2$O$_3'$ is assumed to be written as eq. (3), then the dissociation oxygen pressure is given by eq. (4).

\[ \Delta G^0_{(Cr_2O_3')} = N_{Fe_2O_3} \Delta G^0_{Fe_2O_3} + (1 - N_{Fe_2O_3}) \Delta G^0_{Cr_2O_3}, \] (3)
\[ P_{O_2(Cr_2O_3')} = P_{O_2(Fe_2O_3)}^0 P_{O_2(Fe_2O_3)}^{0(1 - N_{Fe_2O_3})}, \] (4)

where $\Delta G^0_{Fe_2O_3}$, $\Delta G^0_{Cr_2O_3}$ and $P_{O_2(Fe_2O_3)}^0$ are the standard free energies of formation and the dissociation pressure of pure Fe$_2$O$_3$ and Cr$_2$O$_3$, respectively. Equation (4) shows that the dissociation oxygen pressure of Cr$_2$O$_3$ increases with increasing Fe$_2$O$_3$ content in the Cr$_2$O$_3$ phase, it means that the Fe$_2$O$_3$ content at the outer portion of the scale must be higher than that at the inner portion. Therefore, although Fe$_2$O$_3$ content in the Cr$_2$O$_3$ scale is considered to be uniform at the start of oxidation, the faster diffusing iron ions segregate at the outer scale surface because this distribution favored thermochemically. When the Fe$_2$O$_3$ content in the Cr$_2$O$_3$ arrives at a limiting value, a spinel will form at the outer portion of the scale rather than the Fe$_2$O$_3$ content continues to increase because the value of the free energy change for the spinel formation given by eq. (5) becomes negative.

\[ 2Cr_2O_3 + Fe_2O_3 = 2FeCr_2O_4 + 1/O_2, \] (5)
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Fe$^{+1/2}$O$_2$ + Cr$_2$O$_3$ = FeCr$_2$O$_4$,

$\Delta G_{sp}^o = -275310 - 50.63T(27)$, (J)

2Fe + 3/2O$_2$ = Fe$_2$O$_3$,

$\Delta G_{Fe_2O_3}^o = -809140 - 255.4T(21)$, (J)

$\Delta G_5 = 2\Delta G_{sp}^o - \Delta G_{Fe_2O_3}^o$,

$\Delta G_5 = \Delta G_5^o - RT\ln K_5$

$= 2\Delta G_{sp}^o - \Delta G_{Fe_2O_3}^o$ + $RT\ln(P_{O_{1/2}}^{1/2}(a_{FeCr_2O_4}/a_{Cr_2O_3}a_{Fe_2O_3}))$,

$\Delta G_5(1273K) = 62300 + 4.184RT\ln(P_{O_{1/2}}^{1/2}/a_{Fe_2O_3})$. (J)

The value of $x$ in the spinel phase, denoted as FeFe$_{2x}$Cr$_{2-2x}$O$_4$ ($0 \leq x \leq 1$), increases through the scale and becomes unity (ie. Fe$_3$O$_4$) at the outermost part of the spinel layer. This is further oxidized to Fe$_2$O$_3$ at the scale surface in a manner similar to that formed on pure iron. The situation described above is schematically shown in Fig. 5.

Since the scale is very thin as far as the Cr$_2$O$_3$ layer exists, the concentration profiles and phase distribution have not been determined satisfactorily. But IMA results revealed a considerable enrichment of iron at the scale surface and seemed to support this consideration. However, since no quantitative results were obtained in this study, further detailed researches are required.

As iron ions diffuse to the outer layer, Fe$_2$O$_3$ and the spinel layer grow, and consequently the interfaces of Fe$_2$O$_3$-spinel and spinel-Cr$_2$O$_3$ are considered to move towards the alloy surface as shown in Fig. 5. Although the oxidation is considerably suppressed as far as the Cr$_2$O$_3$ layer exists, as soon as the spinel layer arrives at the alloy surface, rapid oxidation with the formation of a thick stratified scale (break-away) will occur because of the faster diffusion of iron ions in the spinel phase.

On the other hand, the addition of the reactive elements investigated completely suppressed the break-away. The IMA studies showed the alloying elements existed in the Cr$_2$O$_3$ scale formed on all alloys which exhibited good oxidation resistance. These results suggest that the dissolution of the alloying elements in the Cr$_2$O$_3$ scale suppressed the transformation from Cr$_2$O$_3$ to spinel or the growth of the spinel layer. Thus, if the scale containing alloying element is denoted by Cr$_2$O$_3^*$ and the standard free energy of formation of Cr$_2$O$_3^*$ is assumed to be written as eq. (6), then the dissociation oxygen pressure of Cr$_2$O$_3^*$ is given by eq. (7).

$$
\Delta G_{Cr_2O_3^*} = N_{MO_3}\Delta G_{MO_3}^o + N_{Fe_2O_3}\Delta G_{Fe_2O_3}^o + (1 - N_{MO_3} - N_{Fe_2O_3})\Delta G_{Cr_2O_3^*}^o. \quad (6)
$$

$$
P_{O_2(Cr_2O_3^*)} = P_{O_2(MO_3)}^{1-N_{MO_3}} P_{O_2(Fe_2O_3)}^{1-N_{Fe_2O_3}} P_{O_2(Cr_2O_3)} P_{O_2(Cr_2O_3^*)}. \quad (7)
$$

where $P_{O_2(MO_3)}$ is the dissociation pressure of pure MO$_3$. From eq. (7), it can be seen that the larger the values of $-\Delta G_{MO_3}^o$ and $N_{MO_3}$ the lower becomes the dissociation oxygen pressure of Cr$_2$O$_3^*$. It means that reaction (1) would move to the left side due to the lowered oxygen pressure and the dissolution of iron into Cr$_2$O$_3$ scale as Fe$_2$O$_3$ is prevented and then the alloys with the reactive elements exhibit good oxidation resistance. Thus the alloying elements with the stronger affinities for oxygen show a larger improving effect on the oxidation resistance.

On the other hand, as described above, the internal oxidation layer of each alloying element was observed beneath the scale. When a continuous internal oxidation layer formed beneath the scale, it would improve the oxidation resistance. If the volume fraction of the oxide particles in the layer is large, even a discontinuous layer as observed in this study
can be expected to act as a physical barrier and inhibit the movement of metals from alloy into the scale\(^{(28)(29)}\). Therefore, the factors which affect on the volume fraction of the oxide particles in the internal oxidation layer was discussed using Wagner's theory\(^{(28)}\).

Wagner's theory is concerning on the internal oxidation of binary alloys, however, this theory is considered to be available to the ternary alloys at very low oxygen pressure where only a reactive element is oxidized. Under the condition where diffusion in the solid is rate controlling, the depth, \(\xi\), of the internal oxidation layer should increase with time, \(t\), according to

\[ \xi = 2\gamma(D_0 t)^{1/2}. \]  

Here \(D_0\) is the diffusion coefficient of oxygen in the alloy and \(\gamma\) is a dimensionless parameter. Wagner showed that the quantities of \(\gamma\) and enrichment factor \(f'/N_{O}^{(0)}\) could be evaluated by eqs. (9) and (10) respectively under the low oxygen pressure, where \(\gamma \ll 1\) and \(\gamma\phi^{1/2} \ll 1\) are valid. Then the volume fraction of oxide in the internal oxidation layer, \(g\), is given by eq. (11)\(^{(29)}\).

\[ \gamma = \pi^{1/2} \phi^{1/2} N_0^{(s)} / 2v N_{M}^{(0)}. \]  

\[ f'/N_{O}^{(0)} = 2v N_{M}^{(0)} D_M / \pi N_{O}^{(s)} D_0. \]  

\[ g = f(V_{ox}/V) = 2v N_{M}^{(0)} D_M V_{ox}/\pi N_{O}^{(s)} D_0 V. \]  

Here \(N_{O}^{(s)}\): concentration of oxygen at the scale-alloy interface.  
\(N_{M}^{(0)}\): concentration of alloying element in the alloy.  
\(D_M\): diffusion coefficient of alloying element in the alloy.  
\(f\): mole fraction of oxide particles in the internal oxidation layer.  
\(v\): stoichiometric ratio of oxygen and metal in the internal oxide.  
\(\phi\): \(D_0/D_M\).  
\(V_{ox}\) and \(V\): molar volume of the oxide and alloy respectively.

Although the volume fraction of the oxide, \(g\), depends on several factors, the larger the value of \(g\), the stronger the effect to inhibit the diffusion process of iron from alloy to scale and eventually prevent the rapid growth of scale as observed on the Fe–20Cr binary alloy. Since the standard free energies of formation of \(\text{Cr}_2\text{O}_5^*\) and \(\text{Cr}_2\text{O}_3\) scales formed on Fe–20Cr alloys with and without the reactive element were assumed as eqs. (3) and (6) respectively, the ratio of the oxygen concentrations beneath the scale, \(N_{O}^{(s)}/N_{O}^{(s)'}\), can be represented by eq. (12) using Sievert's law:

\[ N_{O}^{(s)}/N_{O}^{(s)'} = \exp \{ N_{MO_2}(\Delta G_{MO_2} - \Delta G_{\text{Cr}_2\text{O}_3})/2RT \}. \]  

As can be seen from eq. (12), when the alloying element with the larger negative value of the free energy of formation of its oxide than that of \(\text{Cr}_2\text{O}_3\) is added to Fe–20Cr alloy, since \(N_{O}^{(s)}\) becomes smaller than \(N_{O}^{(s)'}\), the \(\text{Cr}_2\text{O}_3\) scale would be stabilized thermochemically. Furthermore, as can be seen from eq. (11), since \(g\) value becomes larger at lower \(N_{O}^{(s)}\), the internal oxidation layer with the larger volume fraction of the oxide particles would form beneath the \(\text{Cr}_2\text{O}_3\) scale and then prevent the diffusion of iron from alloy to the scale. Thus alloying elements have two beneficial effects on the oxidation resistance.

Shewmon\(^{(30)}\) has briefly explained the reason why Cu–Zn–Al alloy shows good oxidation resistance as follows; The alloy forms an external scale of ZnO on heating. Under a low oxygen pressure of ZnO, Al is not oxidized internally but diffuses to the surface where it combines with a small amount of oxygen in solution and reduces the ZnO to form a protective layer of \(\text{Al}_2\text{O}_3\). Although our explanations described above seems to be phenomenally similar to his explanation, there are obviously some essential differences between them. A very important point of our explanations is that the alloying element dissolves into the \(\text{Cr}_2\text{O}_3\) scale and considerably lowers the oxygen concentration in the alloy beneath the \(\text{Cr}_2\text{O}_3\) scale to prevent the dissolution of Fe from alloy to scale and also to enhance the enrichment of the internal oxidation layer as described above.

S07 alloy showed far better oxidation resistance than that expected from the affinity for oxygen. Judging from the results of encapsulation oxidation experiments, in which external oxide of SiO\(_2\) formed instead of internal oxidation layer on S07 alloy, it is considered
that the diffusivity of Si in Fe–20Cr alloy is extremely large compared with those of the other alloying elements. Extremely large mobility of Si in Fe–20Cr alloy would be probably reasonable because \( D_{\text{Si}} \) in \( \alpha\text{-Fe} \) is larger than \( D_{\text{Al}} \) and \( D_{\text{Ti}} \) in \( \alpha\text{-Fe} \) by about one order of magnitude. When \( D_{\text{Si}} \) is very large in eq. (11), since \( g \) becomes large, it can be easily understood that the effect of the internal oxidation layer is considerably large on S07 alloy and then S07 alloy shows relatively good oxidation resistance.

On the other hand, La showed the least improvement effect of oxidation resistance. If the diffusivity of La with a large atomic volume of 1.87 \( \times 10^{-10} \text{ m} \) in Fe–20Cr alloy is extremely small like that of Hf in \( \alpha\text{-Fe} \), for instance, the growth rate of internal oxidation layer is considered to be quite slow because of very small \( N_{\text{MO}} \). In fact, the weak peaks of \( \text{La}_2\text{O}_3 \) were detected by X-ray diffraction and very thin internal oxidation layer was observed on L07 alloy oxidized for longer than 95 h at 1273 K. From the results, it was found that the formation rate of internal oxidation layer on La containing alloy were much slower than on the other alloys. Thus, since La has only the first improving effect, La was considered to show the least improvement in oxidation resistance. But further studies are necessary because no data are available for the diffusivities of rare earths in this alloy.

The values of \( N_{\text{MO}} \) were assumed to be constant on all alloys here, but these values would change depending on the affinities of alloying elements for oxygen and also on the solubilities of their oxides in \( \text{Cr}_2\text{O}_3 \). Detailed studies on this problem are under way.

On the other hand, oxidation behavior during relatively short period was studied in this investigation, when the spalling of the scale did not occur. Several papers have reported that the alloying elements such as rare earths remarkably inhibit the spalling of the scale. Further researches are needed concerning this problem.

V. Conclusion

The isothermal oxidation behavior of Fe–20Cr alloys with various amounts of La and with constant amounts of different elements (Y, Gd, La, Al, Zr, Ti and Si) was studied in air at 1273 K using the thermogravimetric method, X-ray diffraction, electron probe microanalysis and microscopy. The results obtained are as follows:

1. The alloys with additions of 0.2% La or less exhibited severe oxidation with the formation of thick stratified scales of \( \alpha\text{-Fe}_2\text{O}_3 \) and spinel oxide after 4 h oxidation. On the other hand, the alloys with additions of 0.5% La or more exhibited good oxidation resistance, where the \( \text{Cr}_2\text{O}_3 \) scale was retained stably in spite of the fact that there is no evidence to improve the oxidation resistance in the literature.

2. Seven alloying elements of 0.7 wt% resulted in a remarkable improvement of oxidation resistance. The beneficial effects of each alloying elements on the improvement of oxidation resistance considerably depended on its affinity for oxygen, but the effect of La and Si addition deviated from the tendency.

3. The internal oxidation layer was observed beneath the scale of each oxidized alloys except for L07 alloy. La addition showed the least improvement effect on oxidation resistance among the alloying elements investigated in this study. While the alloy with Si showed better oxidation resistance than that predicted from its affinity for oxygen.

4. The alloying elements were detected in the \( \text{Cr}_2\text{O}_3 \) scale by an ion microanalyser. Combining with the results of encapsulation internal oxidation experiments, it was found that dissolving the reactive element in the \( \text{Cr}_2\text{O}_3 \) scale decreased the dissociation oxygen pressure considerably, i.e. stabilization of the \( \text{Cr}_2\text{O}_3 \) scale, and eventually affected also on the formation process of the internal oxidation layer beneath the scale.

5. It was found that the reactive alloying elements had two beneficial effects on the improvement of oxidation resistance of Fe–20Cr alloy. The first effect is stabilization of the \( \text{Cr}_2\text{O}_3 \) scale by dissolving the alloying element. The second effect is the formation of the internal oxidation layer with a high volume fraction of oxide particles, which acts as a
barrier for diffusion of metals from alloy to scale.

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