Effect of La, Y and Al Additions on the High-Temperature Oxidation of Ni-20Cr Alloy

By Hiroshi Nagai* and Makoto Okabayashi**

The isothermal oxidation of Ni–20Cr alloys with a simultaneous addition of rare earths (La and Y) and Al was investigated in air at 1273, 1373 and 1473 K. The simultaneous addition of rare earths and Al significantly reduced the oxidation rate of the Ni–20Cr alloy especially at higher temperatures, while singular additions of La and Y lost their improvement effect. The simultaneous addition completely suppressed the spalling of the scale even at 1473 K, where severe spalling was observed in the Ni–20Cr alloys with a singular addition of La, Y and Al. The density of the internal oxide formed beneath the scale was markedly increased by the simultaneous addition, but internal oxidation experiments revealed that the simultaneous addition of rare earths and Al did not accelerate the Al diffusion. There was no apparent correlation between the mass of the spalled scale and the density of the internal oxide. This result suggested that effects other than the “keying” or “pegging” effect might contribute to the scale adhesion.

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I. Introduction

It is well-known that relatively minor additions of rare earths and some reactive elements to Ni–Cr, Co–Cr and Fe–Cr alloys improve their high temperature oxidation resistance. Although various models have been proposed, a mechanism for the improvement has not been elucidated well.

In our previous studies on the oxidation behavior of Fe–20Cr(1)–(3) and Ni–20Cr(4) alloys with 0.7 mass% addition of various rare earths and reactive elements, it was found that the additions of La and Y showed the best improving effect on the oxidation resistance of these two alloys at 1273 K. However, La and Y additions lost their improving effect in both alloys at 1373 and 1473 K, where the best improvement was obtained in the alloys with Al and Si forming a dense internal oxide layer at the scale-alloy interface. From these results and our model proposed previously(2), it was anticipated that a simultaneous addition of rare earths having a strong affinity for oxygen and reactive elements, such as Al and Si, having a high diffusivity in the base alloy would significantly improve the oxidation resistance of both alloys. This anticipation was confirmed on Fe–20Cr alloys with the simultaneous additions of rare earths and reactive elements, La–Al(5), La–Si(6) and Y–Si(6). However, the simultaneous addition of Y–Al unexpectedly increased the oxidation rate of Fe–20Cr alloy. This result seems to show that the excellent improving effect induced by the simultaneous addition of rare earths and reactive elements is not simple.

Furthermore, it is well-known that the oxidation behavior of Ni–Cr alloy is considerably different from that of Fe–Cr alloy due to the essential difference in the physical and chemical properties of the substrate and the scale, for example, the crystal structures, the thermal expansion coefficients of the alloys and scales, the diffusivities of the alloying elements in the alloys, the composition and defect structures of the scales, the ion diffusivities in the scales and so forth. The typical oxidation behavior of Ni–Cr alloy is a severe spalling of the scale, while that of Fe–Cr alloy is a very rapid increment in the oxidation rate (break-away oxidation) after an incubation period. Therefore, it is naturally anticipated that the improving effects of the alloying elements on the oxidation behavior of Ni–20Cr alloy will be different from that of Fe–20Cr alloy.

* Department of Materials Science and Engineering, Faculty of Engineering, Osaka University, Yamada-oka, Suita, Osaka 565, Japan.

** Graduate School, Osaka University, Suita. Present address: AISIN-SEIKI Co., Ltd., Kariya 448, Japan.
In order to obtain a better fundamental understanding of a factor responsible for high-temperature oxidation resistance of the Ni-20Cr alloy, the effects of a simultaneous addition of rare earths (La or Y) with Al both on the oxidation rate and the scale adhesion of Ni-20Cr alloy were examined in this study.

II. Experimental Procedure

Alloys were prepared from electrolytic Ni, electrolytic Cr, La(99%), Y(99%) and Al (99.99%) by non-consumable argon arc-melting. Experimental details relating to alloy and specimen preparation and metallographic techniques have been described previously. The chemical compositions and notations are given in Table 1. The compositions of alloys were determined so as to clarify the difference between the beneficial effects obtained on singular and simultaneous additions.

The specimens were isothermally oxidized in air at 1273, 1373 and 1473 K. Oxidation kinetics were determined by the mass gain measurements. In order to examine the effect of La and Y addition on the diffusion rate of Al in the Ni-20Cr alloy, internal oxidation experiments were carried out. La-Al, Y-Al, 0.7Al and 1.4Al alloys were sealed in a quartz tube with a mixed powder compact of Cr-Cr₂O₃ (2:1 in mass ratio) and held isothermally at 1473 K for various times, and then the internal oxide layer depths were measured with a microscope.

III. Experimental Results

Figure 1 shows the mass gain-time curves at 1273 K for the alloys listed in Table 1 with the mass of the spalled scale. As can be seen from this figure, since the mass gains of the alloys with the singular addition of La, Y and Al were quite small, the effects of simultaneous additions of rare earths with Al were not clear at this temperature. Although it was reported previously that the spalling of the scale was not observed at 1273 K for the alloys with and without the singular addition of various elements, repeated and detailed measurements revealed that very small amounts

<table>
<thead>
<tr>
<th>Alloy No.</th>
<th>Ni (mass %)</th>
<th>Cr (mass %)</th>
<th>La or Y (mass %)</th>
<th>Al (mass %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-Cr</td>
<td>Ni-20Cr</td>
<td>Bal.</td>
<td>20.72</td>
<td></td>
</tr>
<tr>
<td>0.7La</td>
<td>Ni-20Cr-0.7La</td>
<td>Bal.</td>
<td>20.42</td>
<td>0.64</td>
</tr>
<tr>
<td>0.7Y</td>
<td>Ni-20Cr-0.7Y</td>
<td>Bal.</td>
<td>20.31</td>
<td>0.68</td>
</tr>
<tr>
<td>0.7Al</td>
<td>Ni-20Cr-0.7Al</td>
<td>Bal.</td>
<td>19.89</td>
<td>0.71</td>
</tr>
<tr>
<td>La-Al</td>
<td>Ni-20Cr-0.7La-0.7Al</td>
<td>Bal.</td>
<td>20.31</td>
<td>0.68</td>
</tr>
<tr>
<td>Y-Al</td>
<td>Ni-20Cr-0.7Y-0.7Al</td>
<td>Bal.</td>
<td>19.28</td>
<td>0.65</td>
</tr>
<tr>
<td>1.4Al</td>
<td>Ni-20Cr-1.4Al</td>
<td>Bal.</td>
<td>20.05</td>
<td>1.32</td>
</tr>
</tbody>
</table>

Fig. 1 Isothermal oxidation of Ni-20Cr alloys with La, Y and Al at 1273 K.
of the spalled scale were detected on the Ni–20Cr alloys with and without the singular addition of 0.7%La and 0.7%Y at this temperature. In contrast, the simultaneous addition of rare earths with Al completely suppressed the spalling of the scale. The improving effect of the simultaneous addition of rare earths and Al both on the oxidation rate and the spalling of the scale was clearer at 1373 K than at 1273 K, as shown in Fig. 2. Although the alloys with the singular addition of 0.7%La or 0.7%Y showed a rapid increase in the oxidation rate after 36 ks (10 h) at this temperature, further addition of Al to these alloys significantly suppressed the rapid increase in the oxidation rate in spite of the fact that the alloy with 1.4%Al showed a large mass gain. Suppression of the spalling of the scale by the simultaneous addition was significant, and no spalling of the scale was observed in La–Al, Y–Al and 0.7Al alloys. It is interesting to emphasize that the spalling of the scale for 1.4Al was very large at 1373 K, but no spalling of the scale was observed at 1273 K.

Since it was found that the oxidation rate and the spalling of the scale were significantly dependent on the oxidation temperature, from the results at 1273 and 1373 K, the mass gain and the mass of the spalled scale after 72 ks (20 h) oxidation at 1273, 1373 and 1473 K were compared in Figs. 3 and 4.

As can be seen in Fig. 3, the increments in the mass gains with increasing oxidation temperature were significant in the 0.7La, 0.7Y, 0.7Al and 1.4Al alloys, especially in the 0.7La and 0.7Y alloys. Although the mass gains of the 0.7La and 0.7Y alloys were the smallest at 1273 K, it was surprising that they became larger than that of the Ni–20Cr alloy at 1473 K. The improving effect of the simultaneous additions La–Al and Y–Al was excellent and became clearer at higher temperatures.

The spalling of the scale was also apparently dependent on the oxidation temperature. The difference in the spalling of the scale among

![Fig. 2 Isothermal oxidation of Ni-20Cr alloys with La, Y and Al at 1373 K.](image)

![Fig. 3 Mass gains of Ni-20Cr alloys with La, Y and Al oxidized in air for 72 ks at 1273, 1373 and 1473 K.](image)
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Fig. 4 Mass of spalled oxide of Ni-20Cr alloys with La, Y and Al oxidized in air for 72 ks at 1273, 1373 and 1473 K.

various alloys was quite striking at 1473 K, as shown in Fig. 4. The simultaneous additions of La–Al and Y–Al completely suppressed the spalling of the scale even at 1473 K, whereas the addition of 0.7Al and 1.4Al had almost no effect at this temperature. In contrast, the addition of 0.7Y and 0.7La significantly enhanced the spalling of the scale at 1473 K. The mass of the spalled scale (210 g/m²) for the 0.7La alloy means that most of the scale formed on this alloy spalled off. It should be emphasized that the simultaneous addition of rare earths with Al was very effective both on the reduction in the oxidation rate and the suppression in the spalling of the scale, especially at higher temperatures.

In our previous study⁵ on the oxidation of Fe–20Cr alloys with an addition of 0.7Al, 1.4Al, La–Al and Y–Al, there seemed to be a general correlation between the oxidation resistance and the structure of the internal oxide of Al₂O₃ formed beneath the scale. Therefore, the EPMA microstructure of the cross-section of the 0.7Al, 1.4Al and Y–Al alloys oxidized in air at 1373 K for 72 ks (20 h) were compared in Photo. 1. As can be seen from these photographs, the internal oxides of Al₂O₃ were clearly observed in all of these alloys, but there seemed to be no correlation between the structure of the internal oxide and the oxidation resistance. That is to say, the accumulation of the internal oxides in the 1.4Al alloy was higher than that in the Y–Al and 0.7Al alloys, but the mass gain and the mass of the spalled scale in the 1.4Al alloy were the largest among these three alloys. The accumulation of the internal oxides formed at 1473 K was slightly higher than at 1373 K, but its dependence on the type of the alloys was the same as that at 1373 K. Although there was no obvious difference in the accumulation of the internal oxides for the Y–Al and 0.7Al alloys, both of the mass gain and the mass of the spalled scale for the 0.7Al alloy markedly increased and became equivalent to those for the 1.4Al alloy at 1473 K. These observations seem to suggest that the suppression of the spalling may be due not to the “key-on” effect but to another effect.

As can be seen from the composition image of Photo. 1, the addition of La and Y to 0.7Al alloy seemed to change the shape and the depth of the internal oxide layer of Al. Therefore, in order to examine the effect of La and

Fig. 5 Variation in internal oxide layer depth ξ with time for Ni–20Cr–0.7Al–0.7M alloys oxidized under the equilibrium oxygen pressure of Cr₂O₃–Cr at 1473 K. (M: Al, Y, La).
Y additions on the diffusion rate of Al in the alloy, internal oxidation experiments were carried out. The 0.7Al, 1.4Al, La-Al and Y-Al alloys were oxidized under the equilibrium oxygen pressure of Cr–Cr₂O₃ at 1473 K for various periods.

Figure 5 shows a plot of the internal oxide layer depth vs time for these alloys. The rates of the layer growth were approximately parabolic in all alloys. There was no significant
difference in the rate among the 0.7Al, La–Al and Y–Al alloys, which were much faster in the rate than the 1.4Al alloy. This result suggests that La and Y additions do not enhance the Al diffusion rate in the alloy as reported previously\(^{(5)(6)}\) in Fe–20Cr alloy, although the shape and the depth of the internal oxide layer of Al were changed by the simultaneous addition of rare earths with Al.

IV. Discussion

It was found in this study that the simultaneous addition of Y or La with Al significantly improved the oxidation resistance of Ni–20Cr alloy. The effect of the simultaneous addition on the spalling of the scale was especially excellent at a higher temperature (1473 K), where the singular addition of rare earths and Al lost its improving effect or rather accelerated the spalling of the scale.

Several explanations have been proposed to account for the improvement in the scale adhesion. One of the most significant explanations is the so-called “keying” or “pegging” effect\(^{(7)-(13)}\) of the internal oxide of the additional elements penetrating into the substrate from the scale. However, the results obtained in this study seem to suggest that the excellent suppression of the spalling of the scale induced by the simultaneous addition of rare earths with Al can not be explained only by the “keying” or “pegging” effect. That is to say, although the density of the internal oxide particles formed in the 1.4Al alloy was much higher than that in the 0.7Al and R–Al alloys, the mass of the spalled scale for the 1.4Al alloy was much larger than the masses for the 0.7Al and R–Al alloys. Furthermore, in our recent study on the oxidation of Ni–20Cr alloys with the dispersion of various reactive metal oxides, it was found that the mass of the spalled scale was apparently dependent on the type of the dispersed oxides. The addition of La\(_2\)O\(_3\) to Ni–20Cr alloy markedly suppressed the spalling of the scale but the additions of SiO\(_2\) and TiO\(_2\) significantly accelerated it. These results suggest that some effect other than the “keying” or “pegging” effect must contribute to the scale adhesion, although the “keying” or “pegging” effect is considered to contribute to the scale adhesion in some extent.

Other explanations for the improvement in scale adhesion are generally based on the suppression of void formation at the alloy-scale interface. The first explanation is that the Cr\(_2\)O\(_3\) scale is formed by the outward diffusion of Cr ions through the scale, and as a consequence, a vacancy flux directed toward the alloy-scale interface is generated. The internal oxide particles or the dispersed oxide particles in the alloy act as vacancy sinks and thereby prevent void formation at the alloy-scale interface, which induces the spalling of the scale\(^{(14)-(16)}\). The second explanation is that the incorporation of rare earths and other additional elements in the scale causes a change in the direction of the scale growth due to the change in the defect structure of the scale or in the morphology of the scale growth.

If the first explanation is true, the mass of the spalled scale will be small on the alloy with higher density of internal oxide particles or the dispersed particles. However, the mass of the spalled scale was larger in the 1.4Al alloy than in the R–Al and 0.7Al alloys in spite of the fact that the density of the internal oxide particles in the 1.4Al alloy was higher than that in the R–Al and 0.7Al alloys. Furthermore, as described above, our recent studies\(^{(17)(18)}\) on the oxidation of Ni–20Cr alloys with the dispersion of various reactive metal oxides revealed that the spalling of the scale was dependent not on the amount but on the type of the dispersed oxides. These results show that the vacancy sink model (first explanation) may not account for the improvement in the scale adhesion.

Several investigators\(^{(19)-(23)}\) performed marker experiments on the alloy with rare earths and other reactive elements, and then found that the direction of the scale growth was changed from outward to inward by these elements. There are two possibilities which can account for the change in the direction of the scale growth from outward to inward. The diffusion rate of oxygen ions is speeded up or otherwise that of Cr ions is slowed down. Although the mechanism of the change in the
direction of the scale growth is still not clarified, the model (second explanation) seems to be rather acceptable. In our recent studies(17)(18) on the oxidation characteristics of the Ni–20Cr alloys with Ti and TiO2 and on the electrical resistivity measurements of Cr2O3 doped with various amounts of TiO2, it was found that there was an obvious correlation among the oxidation rate of the Ni–20Cr alloys with Ti and TiO2, the TiO2 content of the scale formed on these alloys and the electrical resistivity of the Cr2O3 doped with TiO2. This result shows that the incorporation of TiO2 into Cr2O3 scale changes the defect structure of the scale and the oxidation behavior of the Ni–20Cr alloy. Although the additions of Ti and TiO2 to Ni–20Cr alloy showed deleterious effect on the oxidation rate of the Ni–20Cr alloy, this result suggests that the incorporation of the additional elements other than TiO2 to the scale changes the defect structure of the Cr2O3 scale and affects the oxidation resistance of the alloys. In order to clarify whether or not the defect structure of the scale is changed by the addition of rare earths and other reactive elements and the change in the defect structure of the scale plays a crucial role in the oxidation resistance of alloys, detailed analyses of the scale and the electrical resistivity measurements of Cr2O3 doped with various oxides are now being carried out.

V. Conclusion

The isothermal oxidation behavior of Ni–20Cr alloys with a simultaneous addition of rare earths (La and Y) and Al was investigated in air at 1273, 1373 and 1473 K. The results obtained were as follows;

(1) Simultaneous addition of rare earths with Al significantly improved the oxidation resistance of Ni–20Cr alloy especially at higher temperature (1473 K), where singular addition of La and Y lost their improvement effect.

(2) Excellent suppression in the spalling of the scale was obtained by the simultaneous addition of rare earths with Al. The mass of the spalled scale of the alloys with the simultaneous addition was negligible even at 1473 K, where the singular addition of 0.7La, 0.7Y, 0.7Al and 1.4Al was no effect or rather accelerated the spalling of the scale.

(3) The density of the internal oxide particles of Al2O3 was markedly increased by the simultaneous addition of rare earths with Al. However, internal oxidation experiments revealed that the simultaneous addition of rare earths with Al did not accelerate the Al diffusion.

(4) The density of the internal oxide particles was much higher in the 1.4Al alloy than in the R–Al and 0.7Al alloys. However, the mass of the spalled scale was much larger on the former alloy than on the latter alloys. This result suggests that some other effect than the “keying” or “pegging” effect must contribute to the scale adhesion.

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