Electrical Conductivity of Cr$_2$O$_3$ Doped with La$_2$O$_3$, Y$_2$O$_3$ and NiO*

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In order to obtain a better fundamental understanding of factors responsible for an excellent improving effect of rare earths addition on the high temperature oxidation resistance of Ni-Cr alloys, the electrical conductivities of sintered Cr$_2$O$_3$ doped with various amounts of La$_2$O$_3$, Y$_2$O$_3$ and NiO were measured in the temperature range from 773 to 1473 K at near atmospheric oxygen pressures.

The electrical conductivities of Cr$_2$O$_3$ doped with La$_2$O$_3$ and Y$_2$O$_3$ up to 0.5 mass% gradually increased. The increment in the electrical conductivity by the addition of Y$_2$O$_3$ was larger than that caused by the addition of Y$_2$O$_3$. The electrical conductivities of Cr$_2$O$_3$ undoped and doped with La$_2$O$_3$ and Y$_2$O$_3$ decreased with decreasing partial pressure of oxygen. This result showed that they were p-type semiconductors under the conditions investigated. The pressure dependence of the electrical conductivity of Cr$_2$O$_3$ slightly changed with the addition of La$_2$O$_3$ and Y$_2$O$_3$. The electrical conductivity of Cr$_2$O$_3$ markedly increased with increasing NiO content up to 1 mass%. In contrast, the temperature and pressure dependence of the electrical conductivity of Cr$_2$O$_3$ doped with NiO abruptly changed with the addition of more than 0.2 mass%. The electrical conductivity of Cr$_2$O$_3$ doped with NiO more than 0.2% was independent of the partial pressure of oxygen at all temperatures investigated. Both the magnitude and the temperature and pressure dependence of the electrical conductivities of Cr$_2$O$_3$-1%NiO-1%R$_2$O$_3$ (R: La and Y) were very close to those of Cr$_2$O$_3$-1%NiO. This result suggested that there was little interaction between NiO and R$_2$O$_3$ in Cr$_2$O$_3$.

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I. Introduction

It has been well known that relatively minor additions of rare earths and other reactive elements to Fe–Cr, Ni–Cr and Co–Cr alloys strongly improve the oxidation resistance. Although various hypotheses and explanations have been proposed concerning the mechanism by which the addition of these elements affects the oxidation kinetics and scale adhesion of the alloys, the mechanisms are still not elucidated well.

Footner et al.(1) measured the electrical conductivity of Cr$_2$O$_3$ doped with various amounts of Fe$_2$O$_3$ and compared the result with the oxidation behavior of Fe–Cr alloys with various amounts of Cr. They reported that a minimum in the electrical conductivity was found at about 4 mol% Fe$_2$O$_3$, which was similar to the composition of the scale formed on the alloy of maximum oxidation resistance. They also noted that the sign of the thermoelectric power changed across the minimum in the electrical conductivity, indicating that Cr$_2$O$_3$ changed from a cation deficient p-type to an anion deficient n-type semiconductor. Their results strongly show that the scale composition plays an important role in the oxidation resistance.

Some researchers(2)(3), on the other hand, performed Pt marker experiments on the alloys which form Cr$_2$O$_3$ scale, to study the scale growth mechanism. They reported that the addition of rare earths and some other reactive elements changed the direction of scale growth from outward to inward. The change in the direction of the scale growth was explained by means of the alteration in the defect structure
of the Cr$_2$O$_3$ scale. This explanation is very interesting but is still rather speculative yet, because there have been few data on the defect structure of Cr$_2$O$_3$ doped with rare earths and other reactive elements.

It is the purpose of this investigation to obtain a better fundamental understanding of the factors responsible for the high temperature oxidation resistance of alloys and also verify whether or not these additive elements affect the defect structure of Cr$_2$O$_3$ scale. As preliminaries to a more advanced study of the properties of the actual scale formed on alloys, the electrical conductivity of Cr$_2$O$_3$ doped with various amounts of La$_2$O$_3$, Y$_2$O$_3$ and NiO was measured in the temperature range from 773 to 1473 K at near atmospheric oxygen pressures.

II. Experimental Procedure

For the electrical conductivity measurements, Cr$_2$O$_3$ specimens doped with various amounts of La$_2$O$_3$ (0–2.0 mass%), Y$_2$O$_3$ (0–1.0 mass%) and NiO (0–4.0 mass%) were prepared in the form of rods (20×6×2 mm$^3$) by die-pressing without a binder and sintering in alumina boats in a vacuum of 1.33×10$^{-3}$ Pa at 1773 K for 180–360 ks (50–100 h). The type of oxide powders used, source of supply, and semiquantitative spectrographic analysis data are listed in Table 1. The purities were verified to be above 99.9% in all cases.

The electrical conductivity was measured in d.c. current by a 4-probe technique in the temperature range from 773 to 1473 K. The direction of the current was changed several times to cancel the thermoelectrical potential caused by the inevitable difference in the temperature at the two probes. The sample temperature was measured by a Pt–Pt(Rh) thermocouple placed close to the sample. The gas ambients were O$_2$, air, or O$_2$/Ar mixture. The electrical conductivity of Cr$_2$O$_3$ doped with 1%La$_2$O$_3$–1%NiO and 1%Y$_2$O$_3$–1%NiO was also measured to examine the effect of the interaction between rare earth oxides and NiO in the electrical conductivity of Cr$_2$O$_3$.

III. Experimental Results

1. Electrical conductivity of Cr$_2$O$_3$ doped with La$_2$O$_3$, Y$_2$O$_3$ and NiO in air

As a typical example, Fig. 1 shows a plot of the electrical conductivity in air vs 1/T for Cr$_2$O$_3$ doped with 0, 0.2, 0.5, 1.5 and 2.0 mass% La$_2$O$_3$. It should be emphasized here that two straight lines intersect at about 1273 K for all specimens. The addition of La$_2$O$_3$ up to 0.5 mass% increased the electrical conductivity of Cr$_2$O$_3$, especially at lower temperatures, and decreased the activation energy for conduction. However, the addition of La$_2$O$_3$ of more than 0.5% did not change the electrical conductivity significantly. The electrical conductivities of Cr$_2$O$_3$–xLa$_2$O$_3$ in air were plotted against the
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Fig. 2 Electrical conductivity of Cr₂O₃-xLa₂O₃ in the temperature range from 773 to 1473 K in air.

![Graph showing electrical conductivity vs La₂O₃ content for Cr₂O₃-xLa₂O₃.]

Fig. 3 Electrical conductivity of Cr₂O₃-xY₂O₃ in the temperature range from 773 to 1473 K in air.

![Graph showing electrical conductivity vs Y₂O₃ content for Cr₂O₃-xY₂O₃.]

La₂O₃ content in Fig. 2.

Figure 3 shows the dependence of the electrical conductivity in air of Cr₂O₃-xY₂O₃ on the Y₂O₃ content. The electrical conductivity of Cr₂O₃-xY₂O₃ also increased with increasing Y₂O₃ content up to approximately 0.5% and approached constant values. However, the increment in the electrical conductivity due to the addition of La₂O₃ was larger than that due to the addition of Y₂O₃.

Since IMA analyses revealed that the NiO contents of the Cr₂O₃ scale formed on the Ni-20Cr alloys with additional elements were dependent largely on the type and the amounts of the additional elements, the effect of the NiO addition on the electrical conductivity of Cr₂O₃ was examined. Figure 4 shows a plot of the electrical conductivity in air vs 1/T for Cr₂O₃ doped with various amounts of NiO. The electrical conductivity of Cr₂O₃ was significantly increased by the addition of small amounts of NiO. It should be emphasized that the temperature dependence of the electrical conductivity of Cr₂O₃-xNiO abruptly changed between 0.1 and 0.2%NiO, i.e. the activation energies in the higher temperature region for Cr₂O₃ not doped and doped with 0.1%NiO were larger than in the lower temperature region, but those in the higher temperature region for Cr₂O₃ doped with NiO more than...
0.2% became smaller than those in the lower temperature region. Figure 5 shows the dependence of the electrical conductivity in air of Cr$_2$O$_3$-xNiO on the NiO content. The electrical conductivity of Cr$_2$O$_3$ significantly increased with increasing NiO content up to 1%.

2. Dependence of the electrical conductivity on the partial pressure of oxygen

As described in the introduction, it has been reported$^{(2)(3)}$ that the addition of rare earths to the alloys changes the scale growth direction due to the alteration of the defect structure of Cr$_2$O$_3$. The dependence of the electrical conductivity of Cr$_2$O$_3$ not doped and doped with rare earths and NiO on the partial pressure of oxygen was then examined to clarify whether or not the defect structure of Cr$_2$O$_3$ was changed.

Figure 6 shows the dependence of the electrical conductivity of Cr$_2$O$_3$ not doped on the partial pressure of oxygen in the temperature range from 773 to 1473 K. The numbers on each line are the values of 1/n when the pressure dependence can be expressed by $\sigma \propto P_{O_2}^{1/n}$. The slopes of these lines increased with decreasing temperature but were smaller than 3/16, and this will be mentioned below. The electrical conductivity of Cr$_2$O$_3$ decreased with decreasing partial pressure of oxygen. This means that Cr$_2$O$_3$ is a p-type semiconductor.

Figures 7 and 8 show the dependence of the electrical conductivity of Cr$_2$O$_3$ doped with 1%La$_2$O$_3$ and 1%Y$_2$O$_3$ on the partial pressure of oxygen, respectively. The slopes at higher temperatures were larger than those of undoped Cr$_2$O$_3$, but the slopes became smaller than those of undoped Cr$_2$O$_3$ at lower temperatures. It should be emphasized at this point that both Cr$_2$O$_3$-1%La$_2$O$_3$ and Cr$_2$O$_3$-1%Y$_2$O$_3$ show a p-type behavior like that of undoped Cr$_2$O$_3$.

As an example, Fig. 9 shows the dependence of the electrical conductivity of Cr$_2$O$_3$ doped with 0.1 and 0.2%NiO on the partial pressure of oxygen. The electrical conductivity of Cr$_2$O$_3$ doped with 0.1%NiO was very slightly dependent of the partial pressure of oxygen. However, those of Cr$_2$O$_3$ doped with NiO...
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Fig. 7 Electrical conductivity of \( \text{Cr}_2\text{O}_3 - 1\%\text{La}_2\text{O}_3 \) as a function of the partial pressure of oxygen at temperatures up to 1473 K.

Fig. 8 Electrical conductivity of \( \text{Cr}_2\text{O}_3 - 1\%\text{Y}_2\text{O}_3 \) as a function of the partial pressure of oxygen at temperatures up to 1473 K.

more than 0.2\% were independent of the partial pressure of oxygen at all temperatures concerned.

3. Electrical conductivity of \( \text{Cr}_2\text{O}_3 - \text{NiO-R}_2\text{O}_3 \) (R: La and Y)

IMA analyses revealed that the \( \text{Cr}_2\text{O}_3 \) scale formed during the early stage of oxidation of Ni–Cr alloys with rare earths contained both NiO and rare earths. Furthermore, the effect of NiO addition on the electrical conductivity of \( \text{Cr}_2\text{O}_3 \) was markedly different from those of the rare earths addition, as seen in Figs. 1–9. The effect of simultaneous addition of NiO and rare earths on the electrical conductivity of \( \text{Cr}_2\text{O}_3 \) was then examined.

As a typical example, Fig. 10 shows a plot of the electrical conductivity in air vs \( 1/T \) for \( \text{Cr}_2\text{O}_3 - 1\%\text{NiO-1}\%\text{R}_2\text{O}_3 \). For comparison, the electrical conductivities of \( \text{Cr}_2\text{O}_3 \) undoped and doped with 1\%La\(_2\)O\(_3\), 1\%Y\(_2\)O\(_3\) and 1\%NiO were also included in this figure. As can be seen in this figure, both the magnitude and the temperature dependence of the electrical conductivities of \( \text{Cr}_2\text{O}_3 - 1\%\text{NiO-1}\%\text{R}_2\text{O}_3 \) were very close to that of \( \text{Cr}_2\text{O}_3 \) doped with 1\%NiO. It can be concluded that the electrical conductivities of \( \text{Cr}_2\text{O}_3 - 1\%\text{NiO-1}\%\text{R}_2\text{O}_3 \) are solely determined by the NiO content. It should be noted that the electrical conductivity of \( \text{Cr}_2\text{O}_3 - 1\%\text{NiO-1}\%\text{R}_2\text{O}_3 \) were independent of the partial pressure of oxygen at all temperatures.

IV. Discussion

As can be seen from the temperature de-
Fig. 10 Electrical conductivity of Cr$_2$O$_3$ doped with Y$_2$O$_3$, La$_2$O$_3$ and NiO in the temperature range from 773 to 1473 K in air.

Fig. 11 Electrical conductivity of Cr$_2$O$_3$ as a function of the reciprocal absolute temperature. Results by Hauffe and Block$^{(4)}$, Fischer and Lorenz$^{(5)}$, Hay et al.$^{(8)}$, Hagel and Seybolt$^{(6)}$, and Crawford and Vest$^{(7)}$ are also included.
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Kofstad and Lillerud\(^{(10)}\) demonstrated that Cr$_2$O$_3$ contains excess metal ions at oxygen pressures near the decomposition pressure of Cr$_2$O$_3$, and the major defects are probably oxygen vacancies. In the oxidation process of metals and alloys, since the oxygen potential varies through the scale from the ambient oxygen pressure to the decomposition pressure of the scale at the scale/metal interface, it is necessary to take into account the effect of the dopants on the defect structure of Cr$_2$O$_3$ over a wide range of oxygen pressures. A study of the effect of various dopants on the electrical conductivity of Cr$_2$O$_3$ in the lower oxygen pressure range is now planned.

The effect of NiO addition on the electrical conductivity of Cr$_2$O$_3$ was significant. It is reasonable that the electrical conductivity of Cr$_2$O$_3$ is increased by the addition of divalent Ni ions to p-type Cr$_2$O$_3$. However, it should be emphasized that both the temperature and the pressure dependences of the electrical conductivity of Cr$_2$O$_3$ were markedly changed by the addition of only 0.2 mass% NiO. Davies and Smeltzer\(^{(11)}\) reported that the solubility of NiO in Cr$_2$O$_3$ was 0.2 mass% at 1273 and 1373 K, which was in fair agreement with the NiO content at which the abrupt changes in the temperature and pressure dependence of the electrical conductivity occurred. Although this result shows that the solubility of NiO in Cr$_2$O$_3$ is around 0.2 mass% near the atmospheric oxygen pressure, further detailed research is required before concluding the precise solubility of NiO in Cr$_2$O$_3$.

This study revealed that both the conductivity magnitude and the dependence of the electrical conductivity on the temperature and oxygen pressure of Cr$_2$O$_3$-1%NiO-1%R$_2$O$_3$ were very close to those of Cr$_2$O$_3$-1%NiO. This result also suggests that the additions of La$_2$O$_3$ and Y$_2$O$_3$ do not affect the defect structure of Cr$_2$O$_3$ more than the addition of NiO does near the atmospheric oxygen pressure. However, as described above, further research in the lower oxygen pressure region is required before concluding whether or not the improvement in oxidation resistance by the addition of rare earth is due to the alteration in the defect structure of Cr$_2$O$_3$ scale.
V. Conclusion

The electrical conductivities of Cr$_2$O$_3$ doped with various amounts of La$_2$O$_3$, Y$_2$O$_3$ and NiO were measured in the temperature range from 773 to 1473 K at near atmospheric oxygen pressures. The results obtained were as follows:

1. The temperature dependence for Cr$_2$O$_3$ undoped and doped with La$_2$O$_3$ and Y$_2$O$_3$ can be divided into two main regions. The activation energy in the higher temperature region above 1273 K was larger than that in the lower temperature region.

2. La$_2$O$_3$ and Y$_2$O$_3$ additions up to 0.5 mass% gradually increased the electrical conductivity of Cr$_2$O$_3$ especially at lower temperatures. The increment in the conductivity caused by the addition of La$_2$O$_3$ was larger than that caused by the addition of Y$_2$O$_3$.

3. The electrical conductivities of Cr$_2$O$_3$ undoped and doped with La$_2$O$_3$ and Y$_2$O$_3$ decreased with decreasing partial pressure of oxygen. This result showed that they were p-type semiconductors under the conditions investigated. However, the pressure dependence of their electrical conductivities was very small especially at higher temperatures.

4. The electrical conductivity of Cr$_2$O$_3$ significantly increased with increasing NiO content up to 1 mass%. The temperature dependence of the electrical conductivity abruptly changed with the addition of NiO of more than 0.2 mass%.

5. The electrical conductivity of Cr$_2$O$_3$ doped with NiO more than 0.2 mass% was independent of the partial pressure of oxygen at all temperatures concerned. The solubility of NiO was estimated to be 0.1–0.2 mass% near the atmospheric oxygen pressure.

6. Both the magnitude and the temperature and pressure dependences of the electrical conductivities of Cr$_2$O$_3$–1%NiO–1%R$_2$O$_3$ (R: La and Y) were very close to those of Cr$_2$O$_3$–1%NiO. This result showed that the addition of NiO more strongly affected the defect structure of Cr$_2$O$_3$ than did the additions of La$_2$O$_3$ and Y$_2$O$_3$ at least near the atmospheric oxygen pressure region.

REFERENCES