Electrical Conductivity of Cr_2O_3 Doped with La_2O_3 , Y_2O_3 and NiO *

By Hiroshi Nagai**, Takeshi Fujikawa*** and Kei-ichiro Shoji**

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_2O_3 doped with various amounts of La_2O_3 , Y_2O_3 and NiO were measured in the temperature range from 773 to 1473 K at near atmospheric oxygen pressures.

The electrical conductivities of Cr_2O_3 doped with La_2O_3 and Y_2O_3 up to 0.5 mass% gradually increased. The increment in the electrical conductivity by the addition of La_2O_3 was larger than that caused by the addition of Y_2O_3 . The electrical conductivities of Cr_2O_3 undoped and doped with La_2O_3 and Y_2O_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_2O_3 slightly changed with the addition of La_2O_3 and Y_2O_3 . The electrical conductivity of Cr_2O_3 markedly increased with increasing NiO content up to 1 mass%. In contrast, the temperature and pressure dependence of the electrical conductivity of Cr_2O_3 doped with NiO abruptly changed with the addition of more than 0.2 mass%. The electrical conductivity of Cr_2O_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_2O_3 -1% NiO -1% R_2O_3 (R: La and Y) were very close to those of Cr_2O_3 -1% NiO . This result suggested that there was little interaction between NiO and R_2O_3 in Cr_2O_3 .

(Received December 24, 1982)

Keywords: electrical conductivity, chromium oxide, doping effect of rare earths, high temperature oxidation, defect structure of oxide, oxygen pressure dependence

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_2O_3 doped with various

amounts of Fe_2O_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_2O_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_2O_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_2O_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

* This paper was represented at the Annual Meeting of the Japan Inst. Metals in Nov. 1981 (Kyoto).

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

*** Graduate Student, Osaka University, Suita, Osaka, Japan. Present address: Kobe Steel, Ltd., Fujisawa 252, Japan.

of the Cr_2O_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_2O_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_2O_3 scale. As preliminaries to a more advanced study of the properties of the actual scale formed on alloys, the electrical conductivity of Cr_2O_3 doped with various amounts of La_2O_3 , Y_2O_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_2O_3 specimens doped with various amounts of La_2O_3 (0–2.0 mass %), Y_2O_3 (0–1.0 mass %) and NiO (0–4.0 mass %) were prepared in the form of rods ($20 \times 6 \times 2 \text{ mm}^3$) by die-pressing without a binder and sintering in alumina boats in a vacuum of $1.33 \times 10^{-3} \text{ Pa}$ at 1773 K for 180–360 ks (50–100 h). The type of oxide powders used, source of supply, and semi-quantitative 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 tem-

perature 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_2O_3 doped with 1% La_2O_3 –1% NiO and 1% Y_2O_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_2O_3 .

III. Experimental Results

1. Electrical conductivity of Cr_2O_3 doped with La_2O_3 , Y_2O_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_2O_3 doped with 0, 0.2, 0.5, 1.5 and 2.0 mass % La_2O_3 . It should be emphasized here that two straight lines intersect at about 1273 K for all specimens. The addition of La_2O_3 up to 0.5 mass % increased the electrical conductivity of Cr_2O_3 , especially at lower temperatures, and decreased the activation energy for conduction. However, the addition of La_2O_3 of more than 0.5% did not change the electrical conductivity significantly. The electrical conductivities of Cr_2O_3 – $x\text{La}_2\text{O}_3$ in air were plotted against the

Table 1 Semiquantitative spectrographic analysis of the oxide powders. (ppm)

Oxides	Cr_2O_3	NiO	La_2O_3	Y_2O_3
Fe	50	20	20	30
Ca	20	20	30	20
Si	20	20	20	nd
Mg	tr	tr	tr	nd
Cu	tr	tr	nd	tr
Al	tr	tr	tr	tr
other rare earths	nd	nd	<120	<130
source of supply	A	A	B	B

tr: trace, nd: not detected, A: Mitsuwa Pure Chemical Co. Ltd., B: Shin-etsu Chemical Co. Ltd.

Fig. 1 Electrical conductivity of Cr_2O_3 doped with La_2O_3 in the temperature range from 773 to 1473 K in air.

Fig. 2 Electrical conductivity of $\text{Cr}_2\text{O}_3\text{-xLa}_2\text{O}_3$ in the temperature range from 773 to 1473 K in air.

Fig. 3 Electrical conductivity of $\text{Cr}_2\text{O}_3\text{-xY}_2\text{O}_3$ in the temperature range from 773 to 1473 K in air.

La_2O_3 content in Fig. 2.

Figure 3 shows the dependence of the electrical conductivity in air of $\text{Cr}_2\text{O}_3\text{-xY}_2\text{O}_3$ on the Y_2O_3 content. The electrical conductivity of $\text{Cr}_2\text{O}_3\text{-xY}_2\text{O}_3$ also increased with increasing Y_2O_3 content up to approximately 0.5% and approached constant values. However, the in-

Fig. 4 Electrical conductivity of Cr_2O_3 doped with NiO in the temperature range from 773 to 1473 K in air.

crement in the electrical conductivity due to the addition of La_2O_3 was larger than that due to the addition of Y_2O_3 .

Since IMA analyses revealed that the NiO contents of the Cr_2O_3 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 Cr_2O_3 was examined. Figure 4 shows a plot of the electrical conductivity in air vs $1/T$ for Cr_2O_3 doped with various amounts of NiO . The electrical conductivity of Cr_2O_3 was significantly increased by the addition of small amounts of NiO . It should be emphasized that the temperature dependence of the electrical conductivity of $\text{Cr}_2\text{O}_3\text{-xNiO}$ abruptly changed between 0.1 and 0.2% NiO , i.e. the activation energies in the higher temperature region for Cr_2O_3 not doped and doped with 0.1% NiO were larger than in the lower temperature region, but those in the higher temperature region for Cr_2O_3 doped with NiO more than

Fig. 5 Electrical conductivity of $\text{Cr}_2\text{O}_3\text{-xNiO}$ at 773 and 1473 K in air.

0.2% became smaller than those in the lower temperature region. Figure 5 shows the dependence of the electrical conductivity in air of $\text{Cr}_2\text{O}_3\text{-xNiO}$ on the NiO content. The electrical conductivity of Cr_2O_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_2O_3 . The dependence of the electrical conductivity of Cr_2O_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_2O_3 was changed.

Figure 6 shows the dependence of the electrical conductivity of Cr_2O_3 not doped on the

Fig. 6 Electrical conductivity of pure Cr_2O_3 as a function of the partial pressure of oxygen at temperatures up to 1473 K.

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 $\sigma \propto P_{\text{O}_2}^{1/n}$. 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_2O_3 decreased with decreasing partial pressure of oxygen. This means that Cr_2O_3 is a p-type semiconductor.

Figures 7 and 8 show the dependence of the electrical conductivity of Cr_2O_3 doped with 1% La_2O_3 and 1% Y_2O_3 on the partial pressure of oxygen, respectively. The slopes at higher temperatures were larger than those of undoped Cr_2O_3 , but the slopes became smaller than those of undoped Cr_2O_3 at lower temperatures. It should be emphasized at this point that both $\text{Cr}_2\text{O}_3\text{-1%La}_2\text{O}_3$ and $\text{Cr}_2\text{O}_3\text{-1%Y}_2\text{O}_3$ show a p-type behavior like that of undoped Cr_2O_3 .

As an example, Fig. 9 shows the dependence of the electrical conductivity of Cr_2O_3 doped with 0.1 and 0.2% NiO on the partial pressure of oxygen. The electrical conductivity of Cr_2O_3 doped with 0.1% NiO was very slightly dependent of the partial pressure of oxygen. However, those of Cr_2O_3 doped with NiO

Fig. 7 Electrical conductivity of Cr_2O_3 -1% La_2O_3 as a function of the partial pressure of oxygen at temperatures up to 1473 K.

Fig. 8 Electrical conductivity of Cr_2O_3 -1% Y_2O_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 Cr_2O_3 -NiO- R_2O_3 (R: La and Y)

IMA analyses revealed that the Cr_2O_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

Fig. 9 Electrical conductivity of Cr_2O_3 doped with 0.1 and 0.2%NiO as a function of the partial pressure of oxygen at 1473, 1273 and 1073 K.

NiO addition on the electrical conductivity of Cr_2O_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 Cr_2O_3 was then examined.

As a typical example, Fig. 10 shows a plot of the electrical conductivity in air vs $1/T$ for Cr_2O_3 -1%NiO-1% R_2O_3 . For comparison, the electrical conductivities of Cr_2O_3 undoped and doped with 1% La_2O_3 , 1% Y_2O_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 Cr_2O_3 -1%NiO-1% R_2O_3 were very close to that of Cr_2O_3 doped with 1%NiO. It can be concluded that the electrical conductivities of Cr_2O_3 -1%NiO-1% R_2O_3 are solely determined by the NiO content. It should be noted that the electrical conductivity of Cr_2O_3 -1%NiO-1% R_2O_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_2O_3 doped with Y_2O_3 , La_2O_3 and NiO in the temperature range from 773 to 1473 K in air.

pendence of the electrical conductivity of Cr_2O_3 undoped and doped with La_2O_3 (Fig. 1), two straight lines intersect at about 1273 K. The same tendency was reported on Cr_2O_3 by various investigators^{(4)–(8)}. Results of reported studies of the electrical conductivity of undoped Cr_2O_3 are summarized in Fig. 11. In the higher temperature region, both the conductivity magnitude and the activation energies are in fair agreement with each other, while in the lower temperature region, the results of the different studies show large discrepancies.

From the smaller dependence of the electrical conductivity of Cr_2O_3 on oxygen partial pressure, it is generally concluded that the high temperature region reflects the intrinsic electronic equilibrium in the oxide^{(5)–(9)}. The reason for the transition to the low temperature region is not clear. For a sufficiently low temperature, a proposed explanation is that the concentration of electronic defects produced by the intrinsic electronic equilibrium becomes so small that

Fig. 11 Electrical conductivity of Cr_2O_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.

their concentration is determined by unavoidable impurities, such as Na, Ca, etc. The presence of lower valent metals may determine the concentration of electron holes, e.g. $[\text{Ca}'_{\text{Cr}}] = p$ or $2[\text{Na}''_{\text{Cr}}] = p$. This may explain the facts that undoped Cr_2O_3 is found to be a p-type semiconductor in the low temperature region and that the measured electrical conductivities in this region may differ by several orders of magnitude from one study to another. The impurity level of Cr_2O_3 used in this study was as low as that used by Crawford and Vest⁽⁷⁾, who made their studies on a high purity single crystal. However, as seen in Fig. 11, the electrical conductivity of undoped Cr_2O_3 used in this study was larger than that of Crawford and Vest at lower temperatures than 1273 K, and the difference became larger with decreasing temperature. This difference strongly suggests that the electrical conductivity of undoped Cr_2O_3 used in this study might be affected by the existence of grain boundary, where the impurities

tend to be enriched. In general, the concentration of impurities at the grain boundary increases with decreasing temperature. This may explain the fact that the $1/n$ value gradually increased with decreasing temperature (Fig. 6). However, the $1/n$ value approaches $3/16$, which is rationalized on the basis of a Cr vacancy defect equilibrium

This result shows that the defect structure of Cr_2O_3 is very complex and is not clear yet, as Kofstad pointed out⁽⁹⁾. Further detailed studies using higher purity materials are planned to carry out to clarify the defect structure of Cr_2O_3 and the effect of impurities and grain boundary on it. It can be concluded at least that undoped Cr_2O_3 is a p-type semiconductor in the temperature and oxygen pressure range investigated in this study.

As described in the introduction, Giggins and Pettit⁽²⁾ and Michels⁽³⁾ proposed that the scale growth direction was changed by the addition of rare earths and other reactive elements from outward to inward. There are two possibilities which account for the change in the direction of the scale growth. That is, since Cr_2O_3 is a p-type semiconductor, the diffusion rate of metal ions through the scale is decreased or that of oxygen ions is accelerated by the addition of rare earth elements. Michels proposed that Y_2O_3 , La_2O_3 , ThO_2 and Al_2O_3 added to the alloy occupied cation vacancies in the Cr_2O_3 scale. This will reduce the total defect in Cr_2O_3 and lower the diffusion rate of the cation, and as a result the oxidation resistance is improved. Occupying cation vacancies is considered to decrease the electrical conductivity, but the results were completely reversed, as can be seen in Figs. 2 and 3. If Cr_2O_3 is changed from a p-type to an oxygen deficient n-type semiconductor by dissolving the additional elements, the diffusion rate of oxygen ions will be accelerated. But, as can be seen in Figs. 6, 7 and 8, the additions of La_2O_3 and Y_2O_3 did not change the defect structure of Cr_2O_3 from p-type to n-type in the oxygen pressure range of this investigation. Although the electrical conductivity has not been studied at partial pressures close to the decomposition of Cr_2O_3 ,

Kofstad and Lillerud⁽¹⁰⁾ demonstrated that Cr_2O_3 contains excess metal ions at oxygen pressures near the decomposition pressure of Cr_2O_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_2O_3 over a wide range of oxygen pressures. A study of the effect of various dopants on the electrical conductivity of Cr_2O_3 in the lower oxygen pressure range is now planned.

The effect of NiO addition on the electrical conductivity of Cr_2O_3 was significant. It is reasonable that the electrical conductivity of Cr_2O_3 is increased by the addition of divalent Ni ions to p-type Cr_2O_3 . However, it should be emphasized that both the temperature and the pressure dependences of the electrical conductivity of Cr_2O_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_2O_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_2O_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_2O_3 .

This study revealed that both the conductivity magnitude and the dependence of the electrical conductivity on the temperature and oxygen pressure of Cr_2O_3 -1 % NiO -1 % R_2O_3 were very close to those of Cr_2O_3 -1 % NiO . This result also suggests that the additions of La_2O_3 and Y_2O_3 do not affect the defect structure of Cr_2O_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_2O_3 scale.

V. Conclusion

The electrical conductivities of Cr_2O_3 doped with various amounts of La_2O_3 , Y_2O_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_2O_3 undoped and doped with La_2O_3 and Y_2O_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_2O_3 and Y_2O_3 additions up to 0.5 mass% gradually increased the electrical conductivity of Cr_2O_3 especially at lower temperatures. The increment in the conductivity caused by the addition of La_2O_3 was larger than that caused by the addition of Y_2O_3 .

(3) The electrical conductivities of Cr_2O_3 undoped and doped with La_2O_3 and Y_2O_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_2O_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_2O_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_2O_3 –1% NiO –1% R_2O_3 (R: La and Y) were very close to those of Cr_2O_3 –1% NiO . This result showed that the addition of NiO more strongly affected the defect structure of Cr_2O_3 than did the additions of La_2O_3 and Y_2O_3 at least near the atmospheric oxygen pressure region.

REFERENCES

- (1) P. K. Footner, D. R. Holmes and D. Mortimer: *Nature*, **216** (1967), 54.
- (2) C. S. Giggins and F. S. Pettit: *Met. Trans.*, **2** (1971), 1071.
- (3) H. T. Michels: *ibid.*, **7A** (1976), 379.
- (4) K. Hauffe and J. Block: *Z. Phys. Chem.*, **198** (1961), 232.
- (5) W. A. Fisher and G. Lorenz: *Arch. Eisenhüttenw.*, **28** (1957), 497.
- (6) W. C. Hagel and A. U. Seybolt: *J. Electrochem. Soc.*, **108** (1961), 1146.
- (7) J. A. Crawford and R. W. Vest: *J. Appl. Phys.*, **35** (1964), 2413.
- (8) K. A. Hay, F. G. Hicks and D. R. Holmes: *Werkst. Korros.*, **21** (1970), 917.
- (9) P. Kofstad: *Nonstoichiometry, Diffusion, and Electrical Conductivity in Binary Metal Oxides*, Wiley-Interscience, N.Y. (1972), p. 207.
- (10) P. Kofstad and K. P. Lillerud: *J. Electrochem. Soc.*, **127** (1980), 2410.
- (11) H. Davies and W. W. Smeltzer: *ibid.*, **121** (1974), 543.