High Temperature Oxidation of Ni-20Cr- x TiO₂ Alloys

By Hiroshi Nagai*, Makoto Okabayashi** and Tomohiro Murakami***

The isothermal oxidation behavior of Ni-20Cr alloys with various amounts of TiO₂ was investigated in air at 1273, 1373 and 1473 K. The oxidation rate was minimum in the alloys with 0.7 mass%TiO₂ at 1373 and 1473 K and with 0.3%TiO₂ at 1273 K. The oxidation rate markedly increased with increasing TiO₂ content when the TiO₂ content exceeded the one corresponding to the minimum oxidation rate, and then the TiO₂ addition showed a deleterious effect on the oxidation resistance of Ni-20Cr alloy. Spalling behavior of the scale was also significantly dependent on the TiO₂ content of the alloy. The composition of Cr₂O₃ scales formed on the Ni-20Cr- x TiO₂ alloys during the early stage of oxidation was determined by IMA, which revealed that the scales contained NiO and TiO₂. In order to clarify the relation between the TiO₂ content of the scale and the oxidation behavior of Ni-20Cr- x TiO₂ alloys, the electrical resistivity of the sintered Cr₂O₃- x TiO₂ was measured in the temperature range from 873 to 1473 K in air. The electrical resistivity of the Cr₂O₃- x TiO₂ was strongly dependent on the TiO₂ content. The resistivity had a maximum at 0.1–0.2 mass%TiO₂ and then gradually decreased beyond this TiO₂ content. IMA results of the scale were used to correlate the oxidation behavior of the alloys with the electrical resistivity of the sintered Cr₂O₃- x TiO₂. Consequently it was found that the TiO₂ content of the scale formed on the alloy with the minimum oxidation resistance corresponded with the TiO₂ content of the sintered Cr₂O₃- x TiO₂ with the maximum electrical resistivity. These results suggested that the oxidation behavior of the alloy changed due to the alteration in the defect structure of the Cr₂O₃ scale by the introduction of Ti.

(Received May 23, 1982)

I. Introduction

It was reported previously⁽¹⁾ that the dispersion of various reactive metal oxides (0.7 mass%) significantly improved the high temperature oxidation resistance of the Ni-20Cr alloy. Although TiO₂ dispersion also reduced the oxidation rate of the Ni-20Cr alloy, the oxidation behavior of the Ni-20Cr alloy with TiO₂ deviated from the parabolic rate law in spite of the fact that the alloys with other oxides generally obeyed the law. These results suggested that the effect of TiO₂ dispersion on the oxidation behavior was significantly different from that of other oxides.

On the other hand, as reported previously⁽²⁾, the addition of Ti in a metallic form significantly increased the oxidation rate of the Ni-20Cr alloy. The results of IMA and EPMA

analyses of the Cr₂O₃ scale formed during the early stage of oxidation of Ni-20Cr- x Ti alloys suggested that the increment in the oxidation rate might be due to the alteration in the defect structure of the scale by the dissolution of Ti into the scale. If this is true, the oxidation rate of the Ni-20Cr alloy seems to be increased by the TiO₂ addition, but the result was completely reverse.

The purpose of this investigation is to clarify the effect of TiO₂ dispersion on the high temperature oxidation resistance of the Ni-20Cr alloy and to find the reason why the effect of TiO₂ addition was different from that of Ti addition.

In this study, the high temperature oxidation behavior in air of the Ni-20Cr alloys with various amounts of TiO₂ was investigated in the temperature range from 1273 to 1473 K. The electrical resistivity of Cr₂O₃ doped with various amounts of TiO₂ was measured in the temperature range from 873 to 1473 K in air.

II. Experimental Procedure

The starting materials included nickel powder

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

** Graduate School, Osaka University, Suita. Present address: AISIN-SEIKI Co., Ltd., Aichi Japan.

*** Graduate School, Osaka University, Suita.

of -100 mesh, chromium powder of -325 mesh and TiO_2 powder ranging from 10^{-7} to 10^{-8} m in diameter. Ni-20Cr alloys with 0, 0.3, 0.7, 1.4, 2.0 and 6.0 mass % TiO_2 were prepared by the conventional sintering and rolling procedures. Experimental details relating to the preparation of alloys and specimens and the metallographic techniques have been described previously⁽¹⁾.

The specimens were isothermally oxidized in air in the temperature range from 1273 to 1473 K. The oxidation kinetics was determined by the mass gain measurements. The standard X-ray diffraction technique was employed for the phase identification of oxidation products. Transverse sections of the oxidized specimens were examined by microphotography and EPMA.

The ion microanalyzer (IMA) (HITACHI IMA-S Type) was used to measure the concentration of the scales formed on the alloys oxidized in air at 1473 K for 3.6 ks (1 h). The oxidized specimens were examined without any surface treatment after the oxidation. By cycling the mass spectrometer over mass numbers from 48 to 58 (for species Ti_{48}^+ , Cr_{52}^+ and Ni_{58}^+) every 20 s, it was possible to construct a detailed depth profile for all elements of interest. The NiO and TiO_2 contents in the Cr_2O_3 scales were determined using the sintered Cr_2O_3 with various additions of NiO and TiO_2 , which were used to establish intensity ratio (M^+/Cr^+)-oxide concentration curves. Since the value of M^+/Cr^+ did not change significantly through the scale, the mean values were adopted to determine the scale composition.

For the electrical resistivity measurements, the Cr_2O_3 - $x\text{TiO}_2$ ($x=0$ –1.5 mass %) specimens were prepared in the form of rods ($20 \times 6 \times 2$ mm³) by die-pressing without a binder and sintering in alumina boats in a vacuum of 1.33×10^{-3} Pa at 1773 K for 25.2 ks (7 h). Their densities were higher than 95% of the theoretical densities. No second phase was detected by X-ray diffraction and EPMA observation. The electrical resistivity was measured in d.c. current by a 4-probe technique in the temperature range from 873 to 1473 K in air.

III. Experimental Results

As a typical example, Fig. 1 shows the mass gain-time curves at 1473 K for the Ni-20Cr alloys with various amounts of TiO_2 . The dashed lines show the expected mass gains assuming only the parabolic kinetics. For short times, e.g., for $t \leq 14.4$ ks (4 h), the oxidation rate appears to be nearly parabolic. As is seen from this figure, all alloys except the alloy with 0.7% TiO_2 showed a negative deviation from the parabolic oxidation after 14.4 ks. At 1273 and 1373 K, all alloys including the alloy with 0.7% TiO_2 showed approximately a parabolic mass gain for 36 ks (10 h) and then slightly deviated negatively from the parabolic oxidation.

Logarithms of the parabolic rate constants for the oxidation of the Ni-20Cr- $x\text{TiO}_2$ alloys at 1273, 1373 and 1473 K are plotted against the TiO_2 content of the alloy in Fig. 2. The parabolic rate constants were determined from the mass gains during the early stage where the oxidation kinetics obeyed a parabolic relationship. It is very interesting to emphasize

Fig. 1 Isothermal oxidation behavior of Ni-20Cr- $x\text{TiO}_2$ alloys in air at 1473 K.

Fig. 2 Logarithm of parabolic rate constants for the oxidation of Ni-20Cr-xTiO₂ alloys at 1273, 1373 and 1473 K.

that the oxidation rate was minimum in the Ni-20Cr alloys with 0.7%TiO₂ at 1373 and 1473 K and with 0.3%TiO₂ at 1273 K. The oxidation rate significantly increased when the TiO₂ content exceeded the one corresponding to the minimum oxidation rate. Although the dispersion of 0.7%TiO₂ was reported previously⁽¹⁾ to reduce the oxidation rate of Ni-20Cr alloy, the present investigation revealed that the oxidation rate of the Ni-20Cr-xTiO₂ alloys was minimum at 0.7%TiO₂.

Since there was a general tendency that the mass of the spalled scale was small in the alloys with low mass gain, in order to make clear the spalling behavior, it is of interest to compare the ratios given by R_{sp} = mass of the spalled scale/mass gain for the alloys with various amounts of TiO₂. The values of R_{sp} after 72 ks (20 h) oxidation in air at 1273, 1373 and 1473 K were plotted against the TiO₂ content of the alloy in Fig. 3. The value of R_{sp} = 1 does not mean that all of the scale spalled off. If all of the scale is assumed to consist of Cr₂O₃ and to spall off, the R_{sp} value

Fig. 3 Variation of the R_{sp} values with TiO₂ content of the alloy after oxidation of Ni-20Cr-xTiO₂ alloys at 1273, 1373 and 1473 K for 72 ks in air.

will become 3.17. Spalling of the scale was hardly observed upon cooling after the oxidation at 1273 K except for the alloy with 2.0% TiO₂. In contrast, the dependence of the spalling on the TiO₂ content of the alloy was apparent at 1373 and 1473 K. This figure shows that about 85% of the scale spalled off upon cooling in the case of the Ni-20Cr-2.0%TiO₂

Fig. 4 IMA results of the scale formed on Ni-20Cr-xTiO₂ alloys oxidized in air for 3.6 ks at 1473 K.

alloy at 1473 K. The size of the spalled scale was much finer in the Ni-20Cr- x TiO₂ alloys except the Ni-20Cr-6.0TiO₂ alloy than in the Ni-20Cr- x Ti alloys reported previously⁽²⁾. The scale formed on the Ni-20Cr-6.0TiO₂ alloy spalled off as a sheet at a touch with relatively slight force as was observed on the Ni-20Cr alloys with 1%Ti or more.

Figure 4 shows the IMA results of the scale formed on the Ni-20Cr- x TiO₂ alloys after 3.6 ks (1 h) oxidation at 1473 K. The TiO₂ content of the scale markedly increased with increasing TiO₂ content of the alloy, while the NiO content of the scale decreased up to 0.7%TiO₂ and increased beyond 0.7%TiO₂.

Figure 5 shows the relation between the resistivity and the reciprocal absolute temperature for the sintered Cr₂O₃- x TiO₂ ($x=0-1.5$ mass%). The indicated relation is typical for a semiconductor, i.e. the resistivity decreases as the temperature increases. Fair agreement is obtained with the results of other authors on the sample of pure Cr₂O₃⁽³⁾⁽⁴⁾. All plots

Fig. 5 Variation of electrical resistivity of sintered Cr₂O₃- x TiO₂ with temperature.

Fig. 6 Variation of electrical resistivity of sintered Cr₂O₃- x TiO₂ with TiO₂ content.

show two different slope lines. The data were quite reproducible at all temperatures. It is very interesting to note that the slopes for pure Cr₂O₃ and Cr₂O₃-0.1TiO₂ were approximately the same and much smaller than those for Cr₂O₃ with higher amounts of TiO₂.

The effect of TiO₂ dopant concentration on the resistivity is shown in Fig. 6. It should be emphasized at this point that the resistivity of the sintered Cr₂O₃- x TiO₂ was maximum at 0.1-0.2 mass%TiO₂ at all temperatures, over which concentration the resistivity gradually decreased. The relation between the oxidation behavior of the Ni-20Cr- x TiO₂ alloys and the resistivity of Cr₂O₃- x TiO₂ will be discussed later.

IV. Discussion

One of the interesting results obtained in this study was the fact that the oxidation rate was minimum in the Ni-20Cr alloys with 0.3-0.7 mass%TiO₂, beyond which the oxidation rate of the Ni-20Cr alloy markedly increased with increasing TiO₂ content of the alloy. In our previous study on the oxidation behavior

of the Ni-20Cr-xTi alloys⁽²⁾, the mass gain gradually increased with increasing Ti content of the alloy. The increment in the oxidation rate of the Ni-20Cr alloy by the addition of Ti was explained by the alteration in the defect structure of the scale due to the introduction of Ti into the Cr₂O₃ scale. The introduction of Ti into Cr₂O₃ creates Cr vacancies by substituting Ti⁴⁺ for Cr³⁺. Increasing the Cr vacancy concentration will enhance the diffusivity of the cations in the oxidation process and consequently increase the oxidation rate of the Ni-20Cr alloy. However, on the basis of this explanation, the oxidation rate of the Ni-20Cr-xTiO₂ alloys should gradually increase with increasing TiO₂ content of the alloy, if the TiO₂ content of the Cr₂O₃ scale is within its solubility limit. That is to say, the minimum oxidation rate observed at 0.3–0.7 mass%TiO₂ of the Ni-20Cr alloys can not be explained by this explanation.

Electrical resistivity measurements of sintered Cr₂O₃-xTiO₂ revealed that the resistivity did not gradually decrease with increasing TiO₂ content but had a maximum at 0.1–0.2 mass% TiO₂ at all temperatures, as shown in Fig. 6.

Fig. 7 IMA results of the scale formed on Ni-20Cr-xTi and Ni-20Cr-xTiO₂ alloys oxidized in air for 3.6 ks at 1473 K.

In order to correlate the results of the oxidation rate with the resistivity results, it is very interesting to use IMA results of the scale formed on the Ni-20Cr-xTiO₂ alloys. Figure 7 shows a plot of the TiO₂ content of the Cr₂O₃ scale formed after 3.6 ks (1 h) oxidation in air at 1473 K as a function of the TiO₂ content of the alloy. The previous results⁽²⁾ for the Ni-20Cr-xTi alloys are also shown in this figure as a dotted line. Although these two results are not directly comparable, as can be seen from this figure, the TiO₂ contents of the scale formed on the Ni-20Cr-xTi alloys are larger than those on the Ni-20Cr-xTiO₂ alloys. The difference is understandable because Ti has a strong affinity for oxygen and can diffuse in the alloy to react with oxygen. The shadowed regions on the ordinate and the abscissa are the TiO₂ content of the scale showing a maximum resistivity and the TiO₂ content of the alloy showing a minimum oxidation rate, respectively. Fair agreement was obtained between these two TiO₂ contents. Accordingly, it can be considered that the scale with the maximum electrical resistivity was formed on the alloy with a maximum oxidation resistance.

By using IMA results of the scale formed on the Ni-20Cr-xTiO₂ alloys, it seems to be possible to correlate the electrical resistivity of the Cr₂O₃-xTiO₂ with the oxidation behavior of the Ni-20Cr-xTiO₂ alloys. It should be emphasized at this point that Cr₂O₃ doped with TiO₂ has a maximum in electrical resistivity. Analogous maxima in the electrical resistivity are reported in Cr₂O₃ doped with Al₂O₃⁽³⁾ and Fe₂O₃⁽⁴⁾. Footner *et al.*⁽⁴⁾ explained the maximum due to the transition from a cation deficient p-type to an anion deficient semiconductor. Analogous transition from p to n-type may occur at the TiO₂ content where the electrical resistivity was maximum. According to this model, since the scale composition where the transition occurs is considered to approach the stoichiometry, the vacancy concentration may be minimum at the composition. If this model is valid, the scale with this composition will have very low ionic diffusion rates, and therefore the Ni-20Cr alloys with 0.3–0.7 mass%TiO₂ will give the lowest oxidation rate.

As can be seen from Fig. 7, the dotted line

for the Ni-20Cr- x Ti alloys does not cross the shadowed region beyond 0.1 mass%Ti of the alloy. Consequently the mass gain for the Ni-20Cr- x Ti alloys might gradually increase. According to this model, the Ti addition less than 0.1 mass% may improve the oxidation resistance of the Ni-20Cr alloy. However, since Fischer and Lorenz⁽⁵⁾ reported that, when doped with TiO₂, Cr₂O₃ became a n-type semiconductor in argon but not in air and furthermore since the defect structure of undoped Cr₂O₃ is complex and is not yet clear, as Kofstad pointed out⁽⁶⁾, further detailed studies are required before concluding the mechanism by which the Ni-20Cr alloys with 0.3–0.7%TiO₂ showed a minimum oxidation rate.

Another important feature observed in the IMA results (Fig. 3) was the fact that the NiO content of the scale was also minimum on the alloy with 0.7%TiO₂, which showed a minimum oxidation rate. It is reported^{(4)(7)–(11)} that the Fe₂O₃ and NiO contents of the scale formed during the early stage of oxidation may play an important role in the following oxidation process. That is to say, Cr₂O₃ scales with lower content of Fe₂O₃ and NiO have a lower dissociation oxygen pressure of the scale, under which the dissolution of Fe and Ni into Cr₂O₃ is suppressed during the following oxidation process, and consequently the oxidation is suppressed. However, further research is required before concluding whether or not this explanation is valid.

A couple of interesting results were observed in the spalling behavior of the scale. As can be seen from Fig. 3, the value of R_{sp} was apparently dependent on the TiO₂ content of the alloy. In the case of the Ni-20Cr- x TiO₂ alloys, there seemed to be a general tendency that the value of R_{sp} was smaller in the alloys with smaller oxidation rate. Although this tendency seems to suggest that the oxidation rate affects the spalling behavior of the scale, conversely the spalling behavior of the scale can affect the oxidation rate of the alloy. It is not clear at this point why only the alloy with 0.7%TiO₂ showed a positive deviation from the parabolic kinetics at 1473 K in spite of the fact that both the oxidation rate and the value of R_{sp} were

the smallest in this alloy. Further systematic investigation is required concerning the spalling behavior of the scale because this behavior is very complex and has many problems to be resolved.

V. Conclusion

The isothermal oxidation behavior of the Ni-20Cr alloys with various amounts of TiO₂ was investigated in air at 1273, 1373 and 1473 K. In order to clarify the effect of Ti and TiO₂ addition on the oxidation behavior, the electrical resistivity of sintered Cr₂O₃- x TiO₂ was measured in the temperature range from 873 to 1473 K in air. The results obtained were as follows;

(1) The oxidation rate was minimum on the alloys with 0.7 mass%TiO₂ at 1373 and 1473 K and with 0.3 mass%TiO₂ at 1273 K. The oxidation rate markedly increased, when the TiO₂ content exceeded the one corresponding to the minimum oxidation rate. Spalling behavior of the scale was also significantly dependent on the TiO₂ content of the alloy.

(2) IMA results revealed that the composition of the scale formed during the early stage of oxidation was strongly dependent on the TiO₂ content of the alloy. The TiO₂ content of the scale gradually increased with increasing TiO₂ content of the alloy, while the NiO content was minimum on the alloy with 0.7%TiO₂, beyond which the NiO content increased again.

(3) The electrical resistivity of the sintered Cr₂O₃- x TiO₂ ($x=0$ –1.5 mass%) in the temperature range from 873 to 1473 K was markedly dependent on the TiO₂ content. The electrical resistivity of the sintered Cr₂O₃- x TiO₂ was maximum at 0.1–0.2 mass%TiO₂ at all temperatures, over which concentration the resistivity gradually decreased. It was found that the TiO₂ content of the scale formed on the alloy with a maximum oxidation resistance corresponded with the TiO₂ content of the sintered Cr₂O₃- x TiO₂ with a maximum electrical resistivity.

REFERENCES

- (1) H. Nagai and M. Okabayashi: Trans. JIM, 22

- (1981), 101.
- (2) H. Nagai and M. Okabayashi: *ibid.*, **22** (1981), 691.
- (3) J. R. Hensler and E. C. Henry: *J. Amer. Ceram. Soc.*, **36** (1953), 76.
- (4) P. K. Footner, D. R. Holmes and D. Mortimer: *Nature*, **216** (1967), 54.
- (5) W. A. Fischer und G. Lorenz: *Phys. Chem.*, **18** (1958), 308.
- (6) P. Kofstad: *Non-Stoichiometry, Diffusion and Electrical Conductivity in Binary Metal Oxides*, Wiley, N. Y., p. 203.
- (7) H. Nagai, T. Murai, M. Okabayashi and H. Mitani: *J. Japan Inst. Metals*, **43** (1979), 479 (in Japanese).
- (8) H. Nagai, T. Murai and H. Mitani: *Trans. JIM*, **20** (1979), 442.
- (9) H. Nagai, M. Okabayashi and H. Mitani: *ibid.*, **21** (1980), 341.
- (10) H. Nagai, T. Murai and H. Mitani: *ibid.*, **21** (1980), 563.
- (11) H. Nagai, Y. Takebayashi and H. Mitani: *Met. Trans.*, **12A** (1981), 435.
-