



Title	Evaporation of Cr <sub>2</sub> O <sub>3</sub> in Atmospheres Containing H <sub>2</sub> O
Author(s)	Yamauchi, Akira; Kurokawa, Kazuya; Takahashi, Hideaki
Citation	Oxidation of Metals, 59(5/6), 517-527 <a href="https://doi.org/10.1023/A:1023671206976">https://doi.org/10.1023/A:1023671206976</a>
Issue Date	2003-06
Doc URL	<a href="http://hdl.handle.net/2115/734">http://hdl.handle.net/2115/734</a>
Rights	The original publication is available at <a href="http://www.springerlink.com">www.springerlink.com</a>
Type	article (author version)
File Information	OxidMet63-2003.pdf



[Instructions for use](#)

# Evaporation of Cr<sub>2</sub>O<sub>3</sub> in Atmospheres Containing H<sub>2</sub>O

Akira Yamauchi, <sup>a\*</sup> Kazuya Kurokawa, <sup>a</sup> and Hideaki Takahashi <sup>b</sup>

<sup>a</sup> Center for Advanced Research of Energy Conversion Materials,  
Hokkaido University, Sapporo 060-8628, Japan.

<sup>b</sup> Division of Molecular Chemistry,  
Graduate School of Engineering, Hokkaido University,  
Sapporo 060-8628, Japan.

\* E-mail: akira-y@eng.hokudai.ac.jp

## ABSTRACT

Stainless steels in atmospheres containing H<sub>2</sub>O form a Cr<sub>2</sub>O<sub>3</sub> scale in the early stage of oxidation. However, the Cr<sub>2</sub>O<sub>3</sub> scale gradually degrades with time. In order to determine the effect of H<sub>2</sub>O on the deterioration of a Cr<sub>2</sub>O<sub>3</sub> scale, evaporation behavior of Cr<sub>2</sub>O<sub>3</sub> in N<sub>2</sub>-O<sub>2</sub>-H<sub>2</sub>O atmospheres was investigated. The rate of mass loss in a N<sub>2</sub>-O<sub>2</sub>-H<sub>2</sub>O atmosphere was found to be one order of magnitude higher than the rates in N<sub>2</sub>-O<sub>2</sub> and N<sub>2</sub>-H<sub>2</sub>O atmospheres, indicating that deterioration of the Cr<sub>2</sub>O<sub>3</sub> scale is likely to occur in mixed atmospheres of oxygen and water vapor. Volatilization of Cr<sub>2</sub>O<sub>3</sub> is probably based on the following reactions:  $\frac{1}{2} \text{Cr}_2\text{O}_3(\text{s}) + \frac{3}{4} \text{O}_2(\text{g}) + \text{H}_2\text{O}(\text{g}) = \text{CrO}_2(\text{OH})_2(\text{g})$ . However, it was also speculated that the reaction,  $\text{Cr}_2\text{O}_3(\text{s}) + \frac{3}{2} \text{O}_2(\text{g}) = 2 \text{CrO}_3(\text{g})$ , affects the evaporation of Cr<sub>2</sub>O<sub>3</sub> at temperatures higher than 1323 K. The evaporation rate of Cr<sub>2</sub>O<sub>3</sub> is roughly comparable to the growth rate of the Cr<sub>2</sub>O<sub>3</sub> scale. Therefore, a Cr<sub>2</sub>O<sub>3</sub> scale can be degraded by the evaporation of Cr<sub>2</sub>O<sub>3</sub>.

Key words: High temperature oxidation, H<sub>2</sub>O-Containing atmosphere, Evaporation of Cr<sub>2</sub>O<sub>3</sub>, Deterioration of Cr<sub>2</sub>O<sub>3</sub> scale

## 1. INTRODUCTION

It is well known that oxidation of Fe-Cr alloys and stainless steels is accelerated in atmospheres

containing  $\text{H}_2\text{O}$  <sup>1-2)</sup>. In the early stage of oxidation of these alloys, an oxide scale ( $\text{Cr}_2\text{O}_3$  or Fe-Cr spinel oxide) is formed. Later, nodule-like oxides are formed locally, and then the alloy shows accelerated oxidation behavior, resulting in a large mass gain. In a hot-rolling process, such nodule-like oxides cause scale-related defects on the surface of the alloy because of the difficulty in removing them in the descaling process before hot rolling. We have investigated the initial oxidation behavior of several stainless steels at high temperatures in  $\text{H}_2\text{O}$ -containing atmospheres that modeled on heating conditions before hot-rolling processes, and our studies have clarified the effects of water vapor and content of Cr in stainless steels on the transition from an initial  $\text{Cr}_2\text{O}_3$  scale to a nodule-like oxide <sup>3-4)</sup>. However, the mechanism of the transition, that is, the cause of deterioration of a  $\text{Cr}_2\text{O}_3$  scale by water vapor, has not been clarified.

Some mechanisms underlying the change from the initially formed  $\text{Cr}_2\text{O}_3$  scale to a nodule-like oxide have been proposed. They can be classified into two main groups. One group concerns the deterioration of the mechanical property of a  $\text{Cr}_2\text{O}_3$  scale <sup>5-8)</sup>. That is, invasion of water vapor into the substrate is caused by deterioration of the mechanical property of the  $\text{Cr}_2\text{O}_3$  scale accompanying the generation of cracks, which is due to dissolution of hydrogen into the  $\text{Cr}_2\text{O}_3$  scale or to an originally brittle property of it. Jianian et al. <sup>8)</sup> investigated the mechanism of breakaway oxidation in Fe-Cr alloys at 1173 K in wet oxygen, and they suggested that microchannels or microcracks in the initially formed  $\text{Cr}_2\text{O}_3$  scale enabled  $\text{H}_2\text{O}(\text{g})$  to pass through the scale, resulting in the formation of nodule-like oxides and then the development of an external scale consisting of iron oxides ( $\text{Fe}_2\text{O}_3$ ,  $\text{Fe}_3\text{O}_4$ ) and an inner scale consisting of an Fe-Cr spinel oxide. The other group of possible mechanism concerns the reaction of a  $\text{Cr}_2\text{O}_3$  scale with  $\text{H}_2\text{O}(\text{g})$  <sup>9-15)</sup>. Asteman et al. <sup>14-15)</sup> reported that evaporation of chromia occurred during oxidation of Type 304L at 873 K in humid oxygen. They showed that the evaporation of chromia, probably in the form of  $\text{CrO}_2(\text{OH})_2(\text{g})$ , resulted in the conversion of a Cr-rich oxide scale into a nonprotective iron-rich oxide scale.

As mentioned above, it is not still clear how an initially formed  $\text{Cr}_2\text{O}_3$  scale changes into a nodule-like oxide, and little is known about the extent to which  $\text{Cr}_2\text{O}_3(\text{s})$  reacts with  $\text{H}_2\text{O}(\text{g})$ . In the present study, reactions in atmospheres modeled on heating conditions before hot rolling were investigated. The evaporation behavior of  $\text{Cr}_2\text{O}_3$  compacts in  $\text{N}_2\text{-O}_2\text{-H}_2\text{O}$  atmospheres was studied. Based on the results, the effect of water vapor on the deterioration of a  $\text{Cr}_2\text{O}_3$  scale is discussed in this paper.

## 2. EXPERIMENTAL PROCEDURES

Cr<sub>2</sub>O<sub>3</sub> compacts were fabricated by using a spark plasma sintering method. In this method, Cr<sub>2</sub>O<sub>3</sub> powder (grain size of less than  $5 \times 10^{-6}$  m) was sintered at 1673 K. A high heating rate (10 K/s) and a compressive stress of 40 MPa in a graphite die were used for the sintering. The relative density of the sintered body was estimated to be about 95%, indicating a dense body. Specimens for the reaction tests were cut into  $5 \times 5 \times 2 (\times 10^{-3})$  m blocks from the sintered Cr<sub>2</sub>O<sub>3</sub> compact, and then the surfaces were polished up to a micrometer diamond finish. Prior to the reaction test, the specimens were ultrasonically cleaned in ethanol, and the mass and the surface area were measured.

The experimental apparatus used in this study was the same as that used in previous studies<sup>3-4)</sup>. Reaction tests were carried out for up to 360 ks (100 hr) at 1173, 1273, 1323, 1373, and 1473 K in N<sub>2</sub>-O<sub>2</sub>, (N<sub>2</sub>-O<sub>2</sub>)-H<sub>2</sub>O, and N<sub>2</sub>-H<sub>2</sub>O atmospheres. N<sub>2</sub>-3%O<sub>2</sub>, N<sub>2</sub>-10%O<sub>2</sub>, or N<sub>2</sub>-20%O<sub>2</sub> mixed gas was used as a carrier gas to obtain N<sub>2</sub>-O<sub>2</sub> and (N<sub>2</sub>-O<sub>2</sub>)-H<sub>2</sub>O atmospheres, and the water vapor concentrations in the (N<sub>2</sub>-O<sub>2</sub>)-H<sub>2</sub>O atmospheres were 6.9, 12.2, 19.7, and 45.4 vol.%. N<sub>2</sub> gas (purity: 99.999%) was used as a carrier gas to obtain an N<sub>2</sub>-19.7%H<sub>2</sub>O atmosphere. In the N<sub>2</sub>-19.7%H<sub>2</sub>O atmosphere, the maximum oxygen partial pressure is estimated to be about  $1 \times 10^{-5}$  atm O<sub>2</sub>, assuming that impurity in the carrier gas, N<sub>2</sub>, is oxygen only. Carrier gases with these H<sub>2</sub>O concentrations were obtained by bubbling the N<sub>2</sub>-O<sub>2</sub> mixed gas or the N<sub>2</sub> gas through distilled water maintained at 313, 323, 333, and 353 K. The flow rate was  $2 \times 10^{-4}$  m<sup>3</sup>/min at room temperature.

For the reaction test, the specimen was quickly inserted into the hot zone of a reaction tube (internal diameter:  $2.5 \times 10^{-2}$  m) in an electric furnace maintained at a desired temperature and atmosphere. The specimen was heated for a desired time and then quickly removed from the hot zone and cooled in air. The reaction kinetics (evaporation behavior) was determined by measuring the difference in masses before and after heating.

### 3. RESULTS

#### 3.1 Evaporation behavior of Cr<sub>2</sub>O<sub>3</sub>

Fig. 1 shows mass loss of Cr<sub>2</sub>O<sub>3</sub> as a function of reaction time at 1173, 1273, 1323, 1373, and 1473 K in (N<sub>2</sub>-3%O<sub>2</sub>)-19.7%H<sub>2</sub>O. The slight mass loss of Cr<sub>2</sub>O<sub>3</sub> in the early stage of the reaction may be due to the roughness of the surface of specimen. After the early stage, a steady mass loss is observed at all

temperatures, probably due to smoothing of the surface of the specimen. The mass of  $\text{Cr}_2\text{O}_3$  linearly decreases with reaction time at all temperatures. The slope of the line becomes larger with increase in temperature.

In order to determine the cause of the mass loss of  $\text{Cr}_2\text{O}_3$ , the specimens were heated at 1473 K in  $\text{N}_2$ -3% $\text{O}_2$ ,  $(\text{N}_2$ -3% $\text{O}_2$ )-19.7% $\text{H}_2\text{O}$ , and  $\text{N}_2$ -19.7% $\text{H}_2\text{O}$ , and the mass losses of  $\text{Cr}_2\text{O}_3$  in the three atmospheres were compared. The results are shown in Fig. 2. The mass losses in  $\text{N}_2$ -3% $\text{O}_2$  and  $\text{N}_2$ -19.7% $\text{H}_2\text{O}$  are almost identical, and the values are small. This result shows that the partial pressure of the evaporating species is almost equal in the both environments. On the other hand, the mass loss in  $(\text{N}_2$ -3% $\text{O}_2$ )-19.7% $\text{H}_2\text{O}$  is quite large. This suggests that it is necessary to consider the evaporation of  $\text{Cr}_2\text{O}_3$  based on the reaction in which both oxygen and water vapor participate.

Arrhenius plots of the evaporation rate of  $\text{Cr}_2\text{O}_3$  in various atmospheres are shown in Fig. 3. The evaporation rate in the  $(\text{N}_2$ -3% $\text{O}_2$ )-19.7% $\text{H}_2\text{O}$  atmosphere is one order of magnitude higher than that in the  $\text{N}_2$ -3% $\text{O}_2$  and  $\text{N}_2$ -19.7% $\text{H}_2\text{O}$  atmospheres. A change in the slope of the line in the  $(\text{N}_2$ -3% $\text{O}_2$ )-19.7% $\text{H}_2\text{O}$  atmosphere can be seen at a temperature around 1323 K, indicating that the evaporation mechanism of  $\text{Cr}_2\text{O}_3$  changes at this temperature.

### 3.2 Effects of $\text{H}_2\text{O}$ and $\text{O}_2$ concentrations

#### 3.2.1 Effect of $\text{H}_2\text{O}$ concentration

To determine the relationship between  $\text{H}_2\text{O}$  concentration and evaporation of  $\text{Cr}_2\text{O}_3$  in  $\text{N}_2$ - $\text{O}_2$ - $\text{H}_2\text{O}$  atmospheres, the  $\text{H}_2\text{O}$  concentration in a carrier gas of  $\text{N}_2$ -3% $\text{O}_2$  was changed.

Fig. 4 shows the time dependence of the mass loss of  $\text{Cr}_2\text{O}_3$  at 1473 K in  $(\text{N}_2$ -3% $\text{O}_2$ )-X(=6.9,19.7,45.4)%  $\text{H}_2\text{O}$  atmospheres. As can be seen in the figure, the mass of  $\text{Cr}_2\text{O}_3$  decreases linearly with time in all atmospheres, and the slopes of the lines are almost identical. In the same way, the mass losses were measured for carrier gases of  $\text{N}_2$ -10% $\text{O}_2$  and  $\text{N}_2$ -20% $\text{O}_2$ . The rates of mass loss are shown in Fig. 5. In  $\text{N}_2$ -3% $\text{O}_2$ , there is almost no dependence of rate of mass loss on  $\text{H}_2\text{O}$  concentration, while the rate of mass loss in  $\text{N}_2$ -10% $\text{O}_2$  and  $\text{N}_2$ -20% $\text{O}_2$  increases when the concentration of  $\text{H}_2\text{O}$  is 20% or more. The rate of mass loss also increases as the oxygen concentration increases.

#### 3.2.2 Effect of $\text{O}_2$ concentration

The effect of O<sub>2</sub> concentration on mass loss of Cr<sub>2</sub>O<sub>3</sub> was investigated in atmospheres with H<sub>2</sub>O concentration fixed at 19.7%. Fig. 6 shows the time dependence of the mass loss at 1473 K in (N<sub>2</sub>-X%O<sub>2</sub>)-19.7%H<sub>2</sub>O (X=3,10,20) atmospheres. The mass loss decreases linearly with time in all atmospheres. The rate of mass loss becomes higher as the oxygen concentration increases. Such a tendency is also seen for various H<sub>2</sub>O concentrations, as shown in Fig. 7. In all atmospheres, the rate of mass loss increases linearly as oxygen partial pressure increases. When the H<sub>2</sub>O concentrations are 6.9% and 19.7%, the rates of mass loss are almost the same. However, the evaporation rate in the atmosphere with 45.4% H<sub>2</sub>O is much higher than those in atmospheres with lower H<sub>2</sub>O concentrations and strongly depends on oxygen concentration.

## 4. DISCUSSION

### 4.1 Reactions of Cr<sub>2</sub>O<sub>3</sub> with O<sub>2</sub> and H<sub>2</sub>O

A Cr<sub>2</sub>O<sub>3</sub> scale is formed in the initial stage of the oxidation process in H<sub>2</sub>O-containing atmospheres at high temperatures. However, the Cr<sub>2</sub>O<sub>3</sub> scale gradually degrades with oxidation time, and finally a duplex structure consisting of external and inner scales is formed<sup>3-4)</sup>. The external scale consists of iron oxides (Fe<sub>2</sub>O<sub>3</sub>, Fe<sub>3</sub>O<sub>4</sub>) and the inner scale consists of an Fe-Cr spinel oxide (Fe(Fe, Cr)<sub>2</sub>O<sub>4</sub>). In order to determine the effect of evaporation of Cr<sub>2</sub>O<sub>3</sub> on deterioration of a Cr<sub>2</sub>O<sub>3</sub> scale, the evaporation behavior of sintered Cr<sub>2</sub>O<sub>3</sub> in various H<sub>2</sub>O-containing atmospheres was investigated in this study. Based on the results, the reactions of Cr<sub>2</sub>O<sub>3</sub> with O<sub>2</sub> and H<sub>2</sub>O are discussed below.

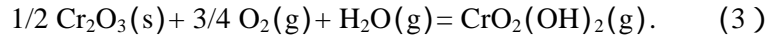
Stearns<sup>11)</sup> reported that the evaporation of Cr<sub>2</sub>O<sub>3</sub> in O<sub>2</sub> atmospheres is caused by the following reaction:



However, it is well known that the evaporation rates of Cr<sub>2</sub>O<sub>3</sub> at temperatures below 1273 K are negligibly small<sup>16)</sup>. The measurement of mass loss of Cr<sub>2</sub>O<sub>3</sub> in an N<sub>2</sub>-3%O<sub>2</sub> atmosphere in the present study also indicated that a measurable amount of Cr<sub>2</sub>O<sub>3</sub> evaporated at temperatures higher than 1373 K. However, the evaporation rate in this atmosphere was one order of magnitude lower than that in the N<sub>2</sub>-O<sub>2</sub>-H<sub>2</sub>O atmospheres. In addition, the evaporation behavior of Cr<sub>2</sub>O<sub>3</sub> in the N<sub>2</sub>-H<sub>2</sub>O atmosphere was identical to that in N<sub>2</sub>-3%O<sub>2</sub>. Therefore, the evaporation as CrOOH, which is produced by the following reaction, can also be neglected at temperatures lower than 1373 K.



Based on the above discussion, the evaporation of  $\text{Cr}_2\text{O}_3$  is accelerated in the presence of both of oxygen and water vapor. Therefore, the evaporation of  $\text{Cr}_2\text{O}_3$ , which occurs by following reaction, would be predominant, as Ebbinghaus<sup>13)</sup> calculated the partial pressures of various gaseous species from thermodynamic data for mixed atmospheres of  $\text{O}_2$  and  $\text{H}_2\text{O}$ .



Now let us consider that the carrier gas,  $\text{N}_2$ , in  $\text{N}_2$ -19.7% $\text{H}_2\text{O}$  contains minute amounts of oxygen. Assuming a gas composition of ( $\text{N}_2$ -0.001% $\text{O}_2$ )-19.7% $\text{H}_2\text{O}$ , equilibrium partial pressures of  $\text{CrO}_2(\text{OH})_2$  at 1373 and 1473 K are roughly in the order of  $10^{-7}$  atm from calculations using the thermodynamic data provided by Ebbinghaus<sup>13)</sup>. In a similar calculation, the equilibrium partial pressures of  $\text{CrO}_3$  at 1373 and 1473 K are estimated to be identical to that of  $\text{CrO}_2(\text{OH})_2$  in ( $\text{N}_2$ -0.001% $\text{O}_2$ )-19.7% $\text{H}_2\text{O}$ . These results may explain the observed mass loss without assuming the formation of  $\text{CrOOH}$ .

Similarly the equilibrium partial pressures of  $\text{CrO}_2(\text{OH})_2$  in  $\text{N}_2$ -2.4% $\text{O}_2$ -19.7% $\text{H}_2\text{O}$  were calculated. The calculated pressure is three order of magnitude higher than that of  $\text{CrO}_2(\text{OH})_2$  in  $\text{N}_2$ -19.7% $\text{H}_2\text{O}$ . This result is in good agreement with the effect of  $\text{O}_2$  concentration on the evaporation of  $\text{Cr}_2\text{O}_3$  in the formation of Cr oxyhydroxide.

As another mechanism, Glemser and Müller<sup>17)</sup>, Johnson and Panas<sup>18-19)</sup> proposed the evaporation based on the following reaction:



As shown in Fig. 3, the mechanism of evaporation of  $\text{Cr}_2\text{O}_3$  in the  $\text{N}_2$ - $\text{O}_2$ - $\text{H}_2\text{O}$  atmosphere changes at 1323 K. The evaporation of  $\text{Cr}_2\text{O}_3$  at temperatures lower than 1323 K may be governed by reaction (3), while, according to reaction (4), the formation of  $\text{CrO}_3(\text{g})$  at higher temperatures may also strongly affect the evaporation of  $\text{Cr}_2\text{O}_3$ .

#### 4.2 Deterioration of $\text{Cr}_2\text{O}_3$ scale

The effect of evaporation of  $\text{Cr}_2\text{O}_3$  on deterioration of  $\text{Cr}_2\text{O}_3$  scales on stainless steels in atmospheres containing  $\text{H}_2\text{O}$  is discussed below. Fig. 8 shows the estimated reductions in thickness of sintered  $\text{Cr}_2\text{O}_3$  at temperatures of 1173, 1323, and 1473 K in  $\text{N}_2$ -2.4% $\text{O}_2$ -19.7% $\text{H}_2\text{O}$ . The reduction in thickness was calculated from the evaporation rate of sintered  $\text{Cr}_2\text{O}_3$ . For example, the estimated reduction in thickness of  $\text{Cr}_2\text{O}_3$  at 1473 K is about  $10^{-11}$  m/s. On the other hand, the growth rate of a  $\text{Cr}_2\text{O}_3$  scale on Type 430 at 1473 K in  $\text{N}_2$ -3% $\text{O}_2$  is about  $10^{-10}$  m/s<sup>3-4)</sup>, which was estimated under an assumption that the growth of a

Cr<sub>2</sub>O<sub>3</sub> scale obeys a linear rate law. The slight difference in these rates suggests that the evaporation of Cr<sub>2</sub>O<sub>3</sub> can not be neglected for the stable growth of a Cr<sub>2</sub>O<sub>3</sub> scale. This is in agreement with the result of Asteman's study <sup>14-15)</sup> showing that H<sub>2</sub>O reduced the ability of stainless steel to maintain a protective Cr<sub>2</sub>O<sub>3</sub> scale due to volatile species. Consequently, it can be concluded that evaporation of Cr<sub>2</sub>O<sub>3</sub> has a strong effect on the deterioration of a Cr<sub>2</sub>O<sub>3</sub> scale formed in the early stage of oxidation of stainless steels in N<sub>2</sub>-O<sub>2</sub>-H<sub>2</sub>O atmospheres.

## 5. CONCLUSIONS

1. A large amount of Cr<sub>2</sub>O<sub>3</sub> evaporation occurs in mixed atmospheres of O<sub>2</sub> and H<sub>2</sub>O.
2. Cr<sub>2</sub>O<sub>3</sub> evaporates linearly with time in N<sub>2</sub>-O<sub>2</sub>-H<sub>2</sub>O atmospheres, and the evaporation rate of Cr<sub>2</sub>O<sub>3</sub> depends on O<sub>2</sub> and H<sub>2</sub>O vapor concentrations.
3. The mechanism of the evaporation of Cr<sub>2</sub>O<sub>3</sub> changes at 1323 K.
4. The evaporation of Cr<sub>2</sub>O<sub>3</sub> in O<sub>2</sub>-H<sub>2</sub>O atmospheres results in deterioration of a Cr<sub>2</sub>O<sub>3</sub> scale.

## Acknowledgement

We would like to express my sincere thanks for the financial support from the Iron and Steel Institute of Japan.

## REFERENCES

- 1) C. T. Fujii and R. A. Meussner, J. Electrochem. Soc., 111, 1215(1964).
- 2) K. Kusabiraki, T. Sugihara, and T. Ooka, TESTU-TO-HAGANE, 77, 123(1991).
- 3) A. Yamauchi, K. Kurokawa, H. Takahashi, and Y. Takada, J. Japan Inst. Metals, 64, 359(2000).
- 4) A. Yamauchi, K. Kurokawa, H. Takahashi, and Y. Takada, Materials at High Temperatures, 18, 111(2001).
- 5) I. Kvernes, M. Oliveira, and P. Kofstad, Corros. Sci., 17, 237(1977).



- 6) Per Kofstad, *Oxid. Met.*, 24, 265(1985).
- 7) Per Kofstad, *High-Temperature Corrosion*, Elsevier Applied Science, Chap.11, 382, (1988)
- 8) S. Jianian, Z. Longjiang and L. Tiefan, *Oxid. Met.*, 48, 347(1997).
- 9) C. S. Tedmond, Jr., *J. Electrochem. Soc.*, 113, 766(1966).
- 10) H. C. Graham, and H. H. Davis, *J. Amer. Ceram. Soc.*, 54, 89(1971).
- 11) C. A. Stearns, F. J. Kohl, and G. C. Fryburg, *J. Electrochem. Soc.*, 121, 945(1974).
- 12) Y-W Kim, and G. R. Belton, *Met. Trans.* , 5, 1811(1974).
- 13) B. B. Ebbinghaus, *Combustion Flame*, 93, 119(1993).
- 14) H. Asteman, J. E. Svensson, L. G. Johansson, and M. Norell, *Oxid. Met.*, 52,95(1999).
- 15) H. Asteman, J. E. Svensson, M. Norell, and L. G. Johansson, *Oxid. Met.*, 54,11(2000).
- 16) D. Caplan and M. Cohen, *J. Electrochem. Soc.* , 108, 438(1961).
- 17) O. Glemser and A. Müller, *Z. anorg. allgem. Chem.*, 334, 151 (1964).
- 18) J. R. T. Johnson and I. Panas, *Inorg. Chem.*, 39, 3181 (2000).
- 19) J. R. T. Johnson and I. Panas, *Inorg. Chem.*, 39, 3192(2000).

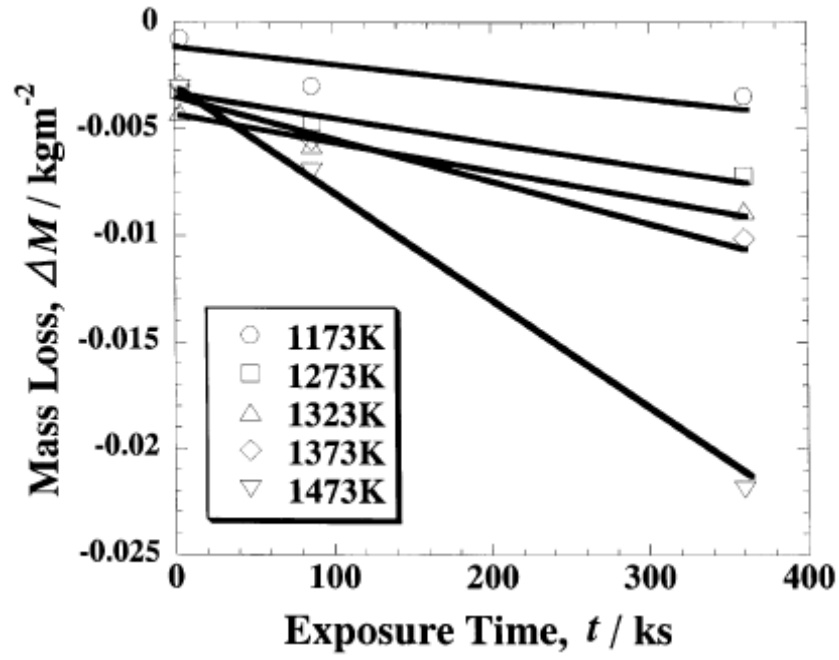


Fig. 1. Mass loss kinetics of  $\text{Cr}_2\text{O}_3$  in  $\text{N}_2$ -2.4% $\text{O}_2$ -19.7% $\text{H}_2\text{O}$  atmospheres.

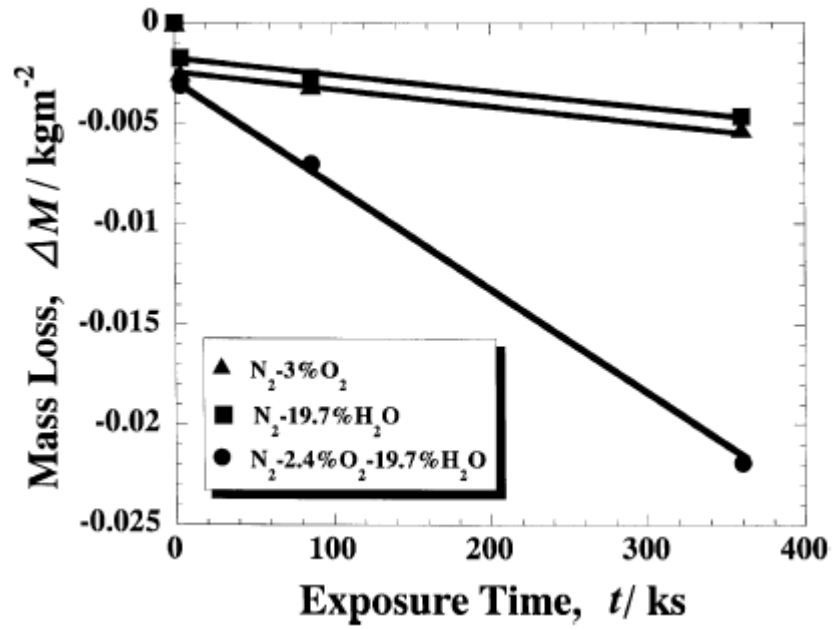


Fig. 2. Mass loss kinetics of  $\text{Cr}_2\text{O}_3$  at 1473 K in  $\text{N}_2$ -3% $\text{O}_2$ ,  $\text{N}_2$ -19.7% $\text{H}_2\text{O}$ , and  $\text{N}_2$ -2.4% $\text{O}_2$ -19.7% $\text{H}_2\text{O}$  atmospheres.

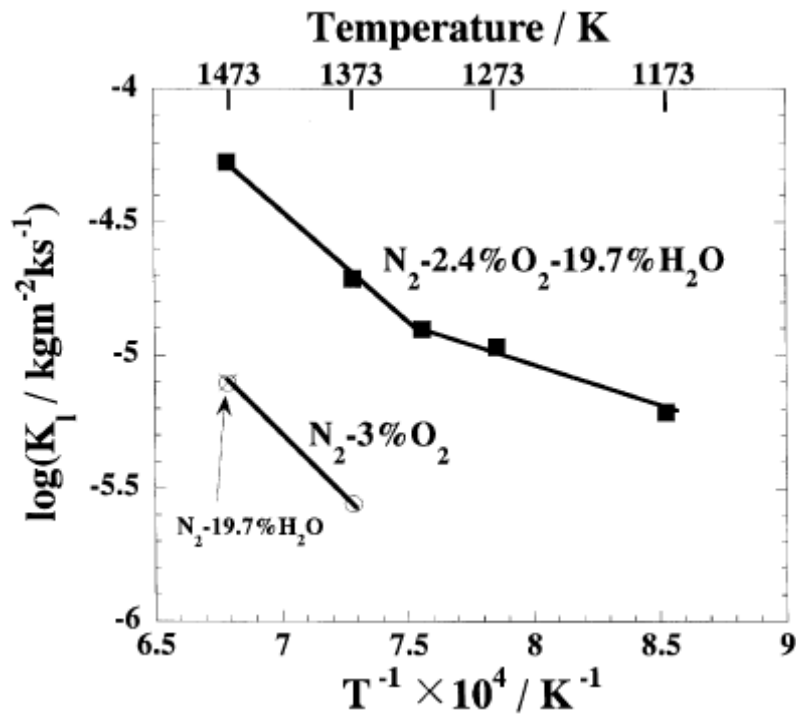


Fig. 3. Arrhenius plots of the evaporation rates of  $\text{Cr}_2\text{O}_3$  in  $\text{N}_2$ -3% $\text{O}_2$ ,  $\text{N}_2$ -19.7% $\text{H}_2\text{O}$  and  $\text{N}_2$ -2.4% $\text{O}_2$ -19.7% $\text{H}_2\text{O}$  atmospheres.

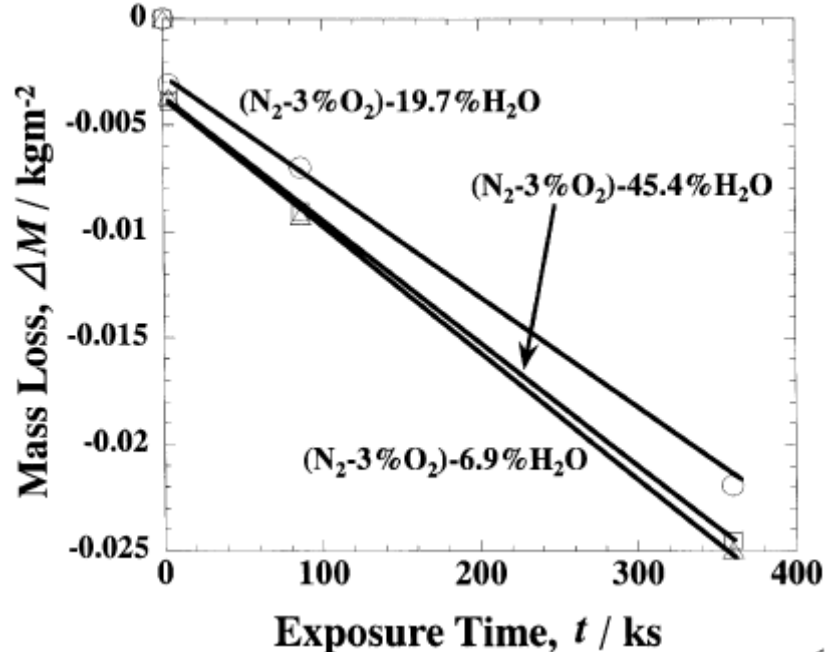


Fig. 4. Mass loss kinetics of  $\text{Cr}_2\text{O}_3$  at 1473 K in  $(\text{N}_2$ -3% $\text{O}_2$ )-X% $\text{H}_2\text{O}$  (X=6.9, 19.7, 45.4%) atmospheres.

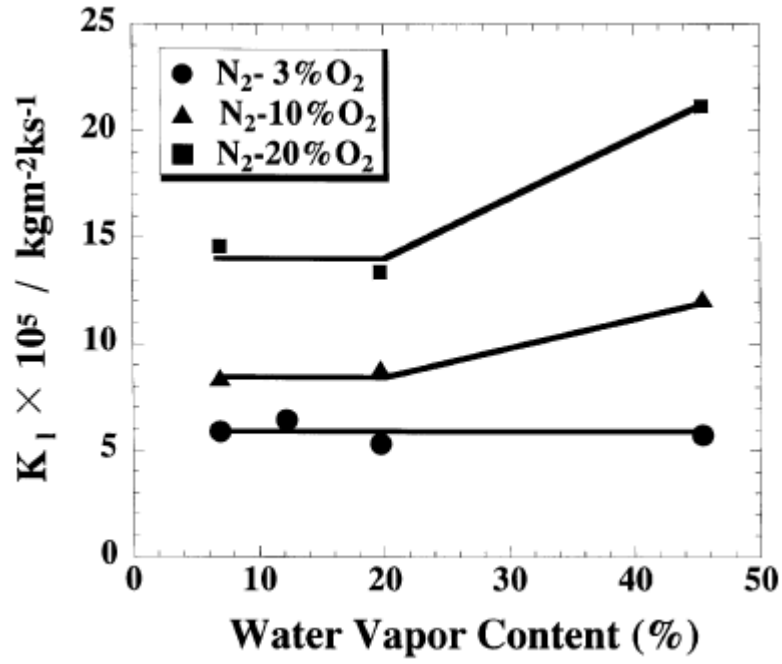


Fig. 5. Evaporation rate of Cr<sub>2</sub>O<sub>3</sub> as a function of H<sub>2</sub>O concentration at 1473 K in N<sub>2</sub>-O<sub>2</sub>-H<sub>2</sub>O atmospheres.

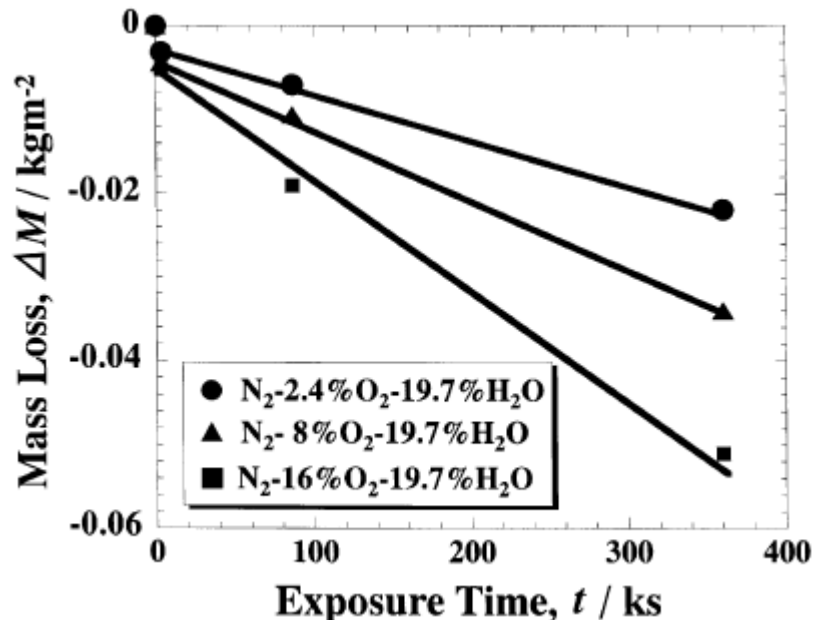


Fig. 6. Mass loss kinetics of Cr<sub>2</sub>O<sub>3</sub> at 1473 K in (N<sub>2</sub>-X%O<sub>2</sub>)-19.7%H<sub>2</sub>O (X=3, 10, 20%) atmospheres.

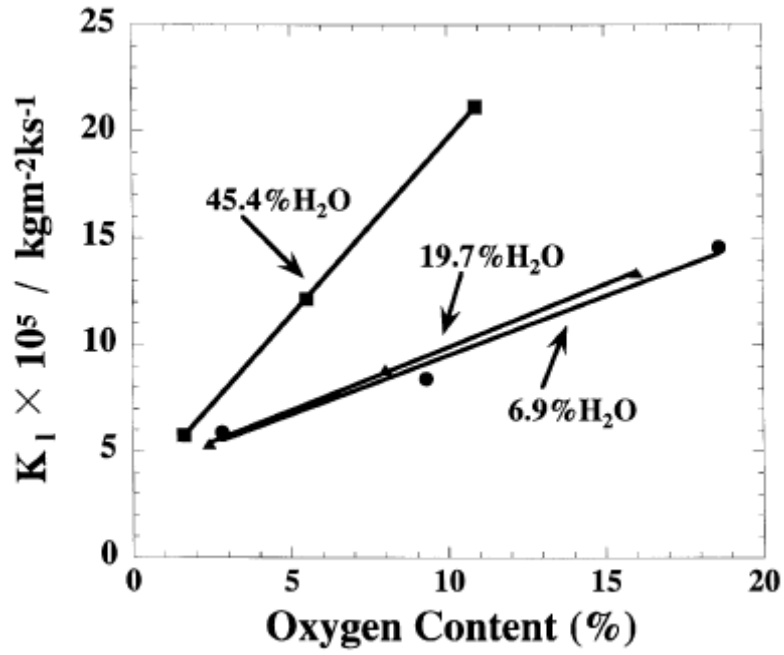


Fig. 7. Evaporation rate of  $\text{Cr}_2\text{O}_3$  as a function of  $\text{O}_2$  concentration at 1473 K in  $\text{N}_2\text{-O}_2\text{-H}_2\text{O}$  atmospheres.

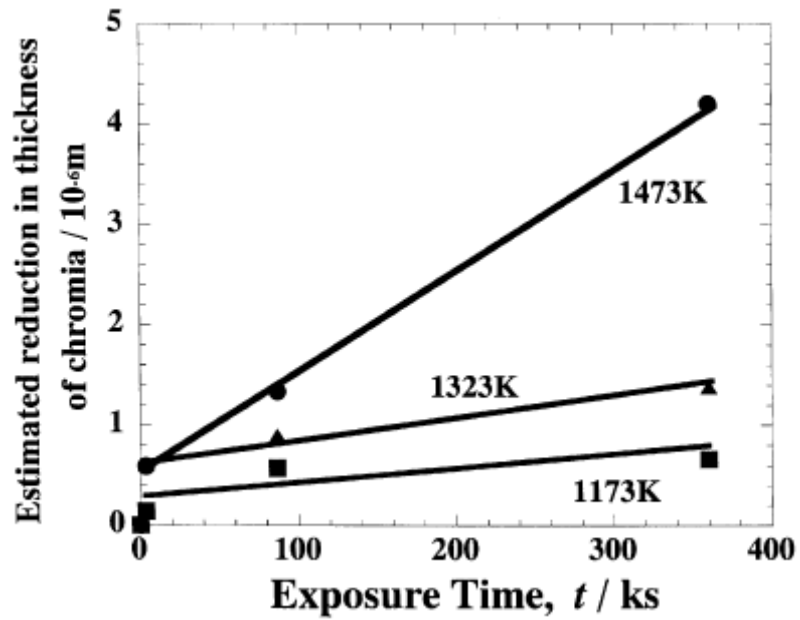


Fig. 8. Change in the estimated thickness of  $\text{Cr}_2\text{O}_3$  with time at various temperatures in  $\text{N}_2\text{-2.4\%O}_2\text{-19.7\%H}_2\text{O}$  atmospheres.