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Evaporation of Cr₂O₃ in Atmospheres Containing H₂O

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ABSTRACT

Stainless steels in atmospheres containing H₂O form a Cr₂O₃ scale in the early stage of oxidation. However, the Cr₂O₃ scale gradually degrades with time. In order to determine the effect of H₂O on the deterioration of a Cr₂O₃ scale, evaporation behavior of Cr₂O₃ in N₂-O₂-H₂O atmospheres was investigated. The rate of mass loss in a N₂-O₂-H₂O atmosphere was found to be one order of magnitude higher than the rates in N₂-O₂ and N₂-H₂O atmospheres, indicating that deterioration of the Cr₂O₃ scale is likely to occur in mixed atmospheres of oxygen and water vapor. Volatilization of Cr₂O₃ is probably based on the following reactions: $1/2 \text{Cr}_2\text{O}_3(\text{s}) + 3/4 \text{O}_2(\text{g}) + \text{H}_2\text{O}(\text{g}) = \text{CrO}_2(\text{OH})_2(\text{g})$. However, it was also speculated that the reaction, $\text{Cr}_2\text{O}_3(\text{s}) + 3/2 \text{O}_2(\text{g}) = 2 \text{CrO}_3(\text{g})$, affects the evaporation of Cr₂O₃ at temperatures higher than 1323 K. The evaporation rate of Cr₂O₃ is roughly comparable to the growth rate of the Cr₂O₃ scale. Therefore, a Cr₂O₃ scale can be degraded by the evaporation of Cr₂O₃.

Key words: High temperature oxidation, H₂O-Containing atmosphere, Evaporation of Cr₂O₃, Deterioration of Cr₂O₃ scale

1. INTRODUCTION

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

containing H₂O¹⁻²). In the early stage of oxidation of these alloys, an oxide scale (Cr₂O₃ 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 H₂O-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 Cr₂O₃ scale to a nodule-like oxide³⁻⁴). However, the mechanism of the transition, that is, the cause of deterioration of a Cr₂O₃ scale by water vapor, has not been clarified.

Some mechanisms underlying the change from the initially formed Cr₂O₃ 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 Cr₂O₃ scale⁵⁻⁸). That is, invasion of water vapor into the substrate is caused by deterioration of the mechanical property of the Cr₂O₃ scale accompanying the generation of cracks, which is due to dissolution of hydrogen into the Cr₂O₃ scale or to an originally brittle property of it. Jianian et al.⁸) 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 Cr₂O₃ scale enabled H₂O(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 (Fe₂O₃, Fe₃O₄) and an inner scale consisting of an Fe-Cr spinel oxide. The other group of possible mechanism concerns the reaction of a Cr₂O₃ scale with H₂O(g)⁹⁻¹⁵). Asteman et al.¹⁴⁻¹⁵) 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 CrO₂(OH)₂(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 Cr₂O₃ scale changes into a nodule-like oxide, and little is known about the extent to which Cr₂O₃(s) reacts with H₂O(g). In the present study, reactions in atmospheres modeled on heating conditions before hot rolling were investigated. The evaporation behavior of Cr₂O₃ compacts in N₂-O₂-H₂O atmospheres was studied. Based on the results, the effect of water vapor on the deterioration of a Cr₂O₃ scale is discussed in this paper.

2. EXPERIMENTAL PROCEDURES

Cr₂O₃ compacts were fabricated by using a spark plasma sintering method. In this method, Cr₂O₃ powder (grain size of less than 5x10⁻⁶ 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 5x5x2(x10⁻³ m) blocks from the sintered Cr₂O₃ 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 studies³⁻⁴⁾. Reaction tests were carried out for up to 360 ks (100 hr) at 1173, 1273, 1323, 1373, and 1473 K in N₂-O₂, (N₂-O₂)-H₂O, and N₂-H₂O atmospheres. N₂-3%O₂, N₂-10%O₂, or N₂-20%O₂ mixed gas was used as a carrier gas to obtain N₂-O₂ and (N₂-O₂)-H₂O atmospheres, and the water vapor concentrations in the (N₂-O₂)-H₂O atmospheres were 6.9, 12.2, 19.7, and 45.4 vol.%. N₂ gas (purity: 99.999%) was used as a carrier gas to obtain an N₂-19.7%H₂O atmosphere. In the N₂-19.7%H₂O atmosphere, the maximum oxygen partial pressure is estimated to be about 1x10⁻⁵ atm O₂, assuming that impurity in the carrier gas, N₂, is oxygen only. Carrier gases with these H₂O concentrations were obtained by bubbling the N₂-O₂ mixed gas or the N₂ gas through distilled water maintained at 313, 323, 333, and 353 K. The flow rate was 2 × 10⁻⁴ m³/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 × 10⁻²m) 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 Cr₂O₃

Fig. 1 shows mass loss of Cr₂O₃ as a function of reaction time at 1173, 1273, 1323, 1373, and 1473 K in (N₂-3%O₂)-19.7%H₂O. The slight mass loss of Cr₂O₃ 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 Cr_2O_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 Cr_2O_3 , the specimens were heated at 1473 K in N_2 -3% O_2 , $(\text{N}_2$ -3% O_2)-19.7% H_2O , and N_2 -19.7% H_2O , and the mass losses of Cr_2O_3 in the three atmospheres were compared. The results are shown in Fig. 2. The mass losses in N_2 -3% O_2 and N_2 -19.7% H_2O 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% O_2)-19.7% H_2O is quite large. This suggests that it is necessary to consider the evaporation of Cr_2O_3 based on the reaction in which both oxygen and water vapor participate.

Arrhenius plots of the evaporation rate of Cr_2O_3 in various atmospheres are shown in Fig. 3. The evaporation rate in the $(\text{N}_2$ -3% O_2)-19.7% H_2O atmosphere is one order of magnitude higher than that in the N_2 -3% O_2 and N_2 -19.7% H_2O atmospheres. A change in the slope of the line in the $(\text{N}_2$ -3% O_2)-19.7% H_2O atmosphere can be seen at a temperature around 1323 K, indicating that the evaporation mechanism of Cr_2O_3 changes at this temperature.

3.2 Effects of H_2O and O_2 concentrations

3.2.1 Effect of H_2O concentration

To determine the relationship between H_2O concentration and evaporation of Cr_2O_3 in N_2 - O_2 - H_2O atmospheres, the H_2O concentration in a carrier gas of N_2 -3% O_2 was changed.

Fig. 4 shows the time dependence of the mass loss of Cr_2O_3 at 1473 K in $(\text{N}_2$ -3% O_2)-X(=6.9,19.7,45.4)% H_2O atmospheres. As can be seen in the figure, the mass of Cr_2O_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 N_2 -10% O_2 and N_2 -20% O_2 . The rates of mass loss are shown in Fig. 5. In N_2 -3% O_2 , there is almost no dependence of rate of mass loss on H_2O concentration, while the rate of mass loss in N_2 -10% O_2 and N_2 -20% O_2 increases when the concentration of H_2O is 20% or more. The rate of mass loss also increases as the oxygen concentration increases.

3.2.2 Effect of O_2 concentration

The effect of O₂ concentration on mass loss of Cr₂O₃ was investigated in atmospheres with H₂O concentration fixed at 19.7%. Fig. 6 shows the time dependence of the mass loss at 1473 K in (N₂-X%O₂)-19.7%H₂O (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 H₂O concentrations, as shown in Fig. 7. In all atmospheres, the rate of mass loss increases linearly as oxygen partial pressure increases. When the H₂O 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% H₂O is much higher than those in atmospheres with lower H₂O concentrations and strongly depends on oxygen concentration.

4. DISCUSSION

4.1 Reactions of Cr₂O₃ with O₂ and H₂O

A Cr₂O₃ scale is formed in the initial stage of the oxidation process in H₂O-containing atmospheres at high temperatures. However, the Cr₂O₃ scale gradually degrades with oxidation time, and finally a duplex structure consisting of external and inner scales is formed³⁻⁴⁾. The external scale consists of iron oxides (Fe₂O₃, Fe₃O₄) and the inner scale consists of an Fe-Cr spinel oxide (Fe(Fe, Cr)₂O₄). In order to determine the effect of evaporation of Cr₂O₃ on deterioration of a Cr₂O₃ scale, the evaporation behavior of sintered Cr₂O₃ in various H₂O-containing atmospheres was investigated in this study. Based on the results, the reactions of Cr₂O₃ with O₂ and H₂O are discussed below.

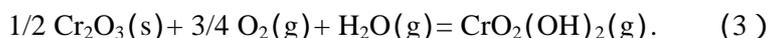
Stearns¹¹⁾ reported that the evaporation of Cr₂O₃ in O₂ atmospheres is caused by the following reaction:



However, it is well known that the evaporation rates of Cr₂O₃ at temperatures below 1273 K are negligibly small¹⁶⁾. The measurement of mass loss of Cr₂O₃ in an N₂-3%O₂ atmosphere in the present study also indicated that a measurable amount of Cr₂O₃ evaporated at temperatures higher than 1373 K. However, the evaporation rate in this atmosphere was one order of magnitude lower than that in the N₂-O₂-H₂O atmospheres. In addition, the evaporation behavior of Cr₂O₃ in the N₂-H₂O atmosphere was identical to that in N₂-3%O₂. 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 Cr₂O₃ is accelerated in the presence of both of oxygen and water vapor. Therefore, the evaporation of Cr₂O₃, which occurs by following reaction, would be predominant, as Ebbinghaus¹³⁾ calculated the partial pressures of various gaseous species from thermodynamic data for mixed atmospheres of O₂ and H₂O.



Now let us consider that the carrier gas, N₂, in N₂-19.7% H₂O contains minute amounts of oxygen. Assuming a gas composition of (N₂-0.001% O₂) -19.7% H₂O, equilibrium partial pressures of CrO₂(OH)₂ at 1373 and 1473 K are roughly in the order of 10⁻⁷ atm from calculations using the thermodynamic data provided by Ebbinghaus¹³⁾. In a similar calculation, the equilibrium partial pressures of CrO₃ at 1373 and 1473 K are estimated to be identical to that of CrO₂(OH)₂ in (N₂-0.001% O₂) -19.7% H₂O. These results may explain the observed mass loss without assuming the formation of CrOOH.

Similarly the equilibrium partial pressures of CrO₂(OH)₂ in N₂-2.4% O₂-19.7% H₂O were calculated. The calculated pressure is three order of magnitude higher than that of CrO₂(OH)₂ in N₂-19.7% H₂O. This result is in good agreement with the effect of O₂ concentration on the evaporation of Cr₂O₃ in the formation of Cr oxyhydroxide.

As another mechanism, Glemser and Müller¹⁷⁾, Johnson and Panas¹⁸⁻¹⁹⁾ proposed the evaporation based on the following reaction:



As shown in Fig. 3, the mechanism of evaporation of Cr₂O₃ in the N₂-O₂-H₂O atmosphere changes at 1323 K. The evaporation of Cr₂O₃ at temperatures lower than 1323 K may be governed by reaction (3), while, according to reaction (4), the formation of CrO₃(g) at higher temperatures may also strongly affect the evaporation of Cr₂O₃.

4.2 Deterioration of Cr₂O₃ scale

The effect of evaporation of Cr₂O₃ on deterioration of Cr₂O₃ scales on stainless steels in atmospheres containing H₂O is discussed below. Fig. 8 shows the estimated reductions in thickness of sintered Cr₂O₃ at temperatures of 1173, 1323, and 1473 K in N₂-2.4% O₂-19.7% H₂O. The reduction in thickness was calculated from the evaporation rate of sintered Cr₂O₃. For example, the estimated reduction in thickness of Cr₂O₃ at 1473 K is about 10⁻¹¹ m/s. On the other hand, the growth rate of a Cr₂O₃ scale on Type 430 at 1473 K in N₂-3% O₂ is about 10⁻¹⁰ m/s³⁻⁴⁾, which was estimated under an assumption that the growth of a

Cr₂O₃ scale obeys a linear rate law. The slight difference in these rates suggests that the evaporation of Cr₂O₃ can not be neglected for the stable growth of a Cr₂O₃ scale. This is in agreement with the result of Asteman's study¹⁴⁻¹⁵⁾ showing that H₂O reduced the ability of stainless steel to maintain a protective Cr₂O₃ scale due to volatile species. Consequently, it can be concluded that evaporation of Cr₂O₃ has a strong effect on the deterioration of a Cr₂O₃ scale formed in the early stage of oxidation of stainless steels in N₂-O₂-H₂O atmospheres.

5. CONCLUSIONS

1. A large amount of Cr₂O₃ evaporation occurs in mixed atmospheres of O₂ and H₂O.
2. Cr₂O₃ evaporates linearly with time in N₂-O₂-H₂O atmospheres, and the evaporation rate of Cr₂O₃ depends on O₂ and H₂O vapor concentrations.
3. The mechanism of the evaporation of Cr₂O₃ changes at 1323 K.
4. The evaporation of Cr₂O₃ in O₂-H₂O atmospheres results in deterioration of a Cr₂O₃ scale.

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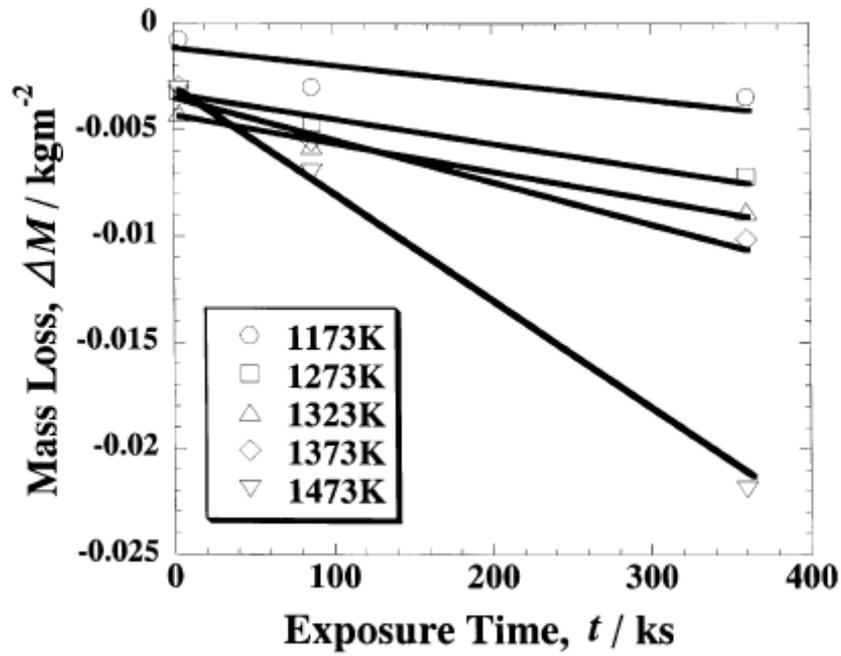


Fig. 1. Mass loss kinetics of Cr₂O₃ in N₂-2.4%O₂-19.7%H₂O atmospheres.

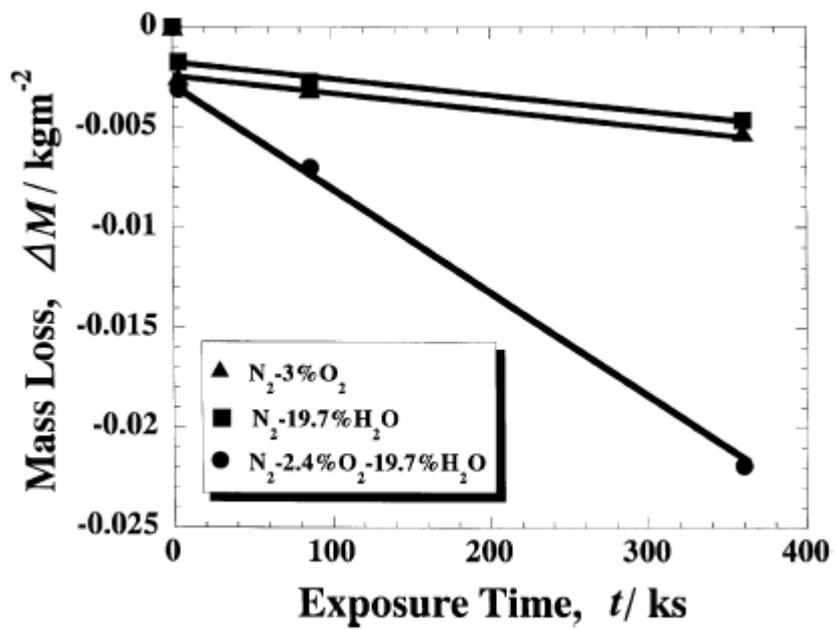


Fig. 2. Mass loss kinetics of Cr₂O₃ at 1473 K in N₂-3%O₂, N₂-19.7%H₂O, and N₂-2.4%O₂-19.7%H₂O atmospheres.

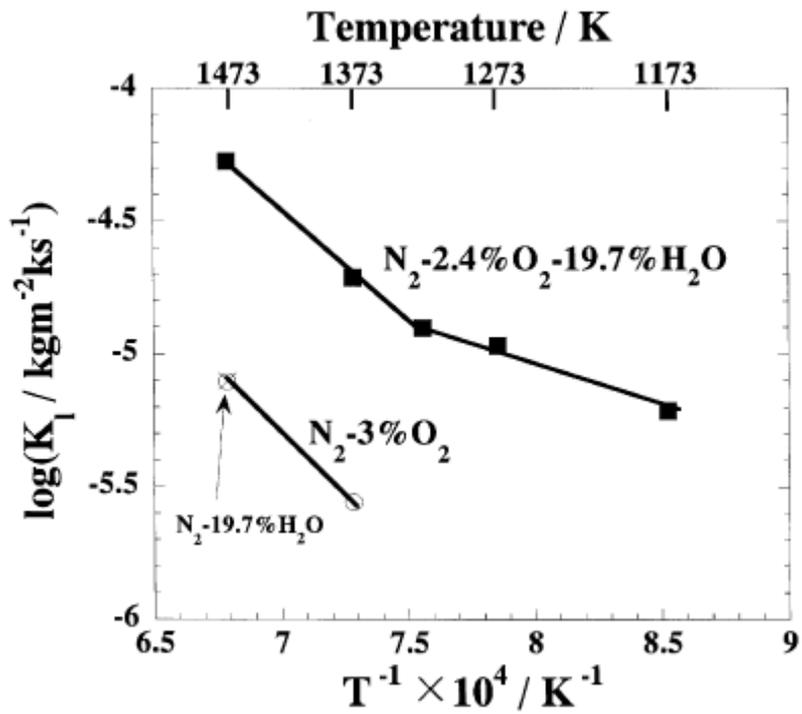


Fig. 3. Arrhenius plots of the evaporation rates of Cr_2O_3 in $\text{N}_2-3\%O_2$, $\text{N}_2-19.7\%H_2O$ and $\text{N}_2-2.4\%O_2-19.7\%H_2O$ atmospheres.

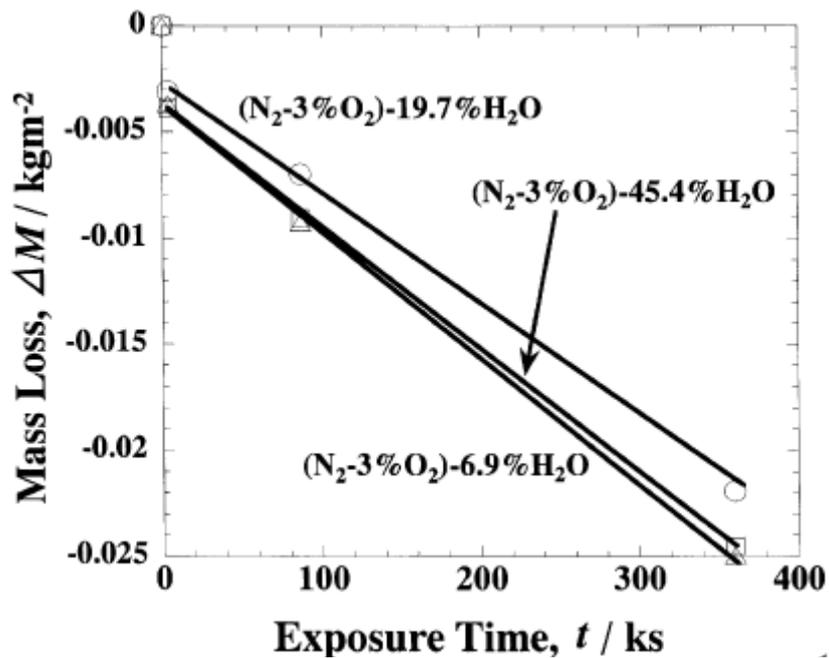


Fig. 4. Mass loss kinetics of Cr_2O_3 at 1473 K in $(\text{N}_2-3\%O_2)-X\%H_2O$ ($X=6.9, 19.7, 45.4\%$) atmospheres.

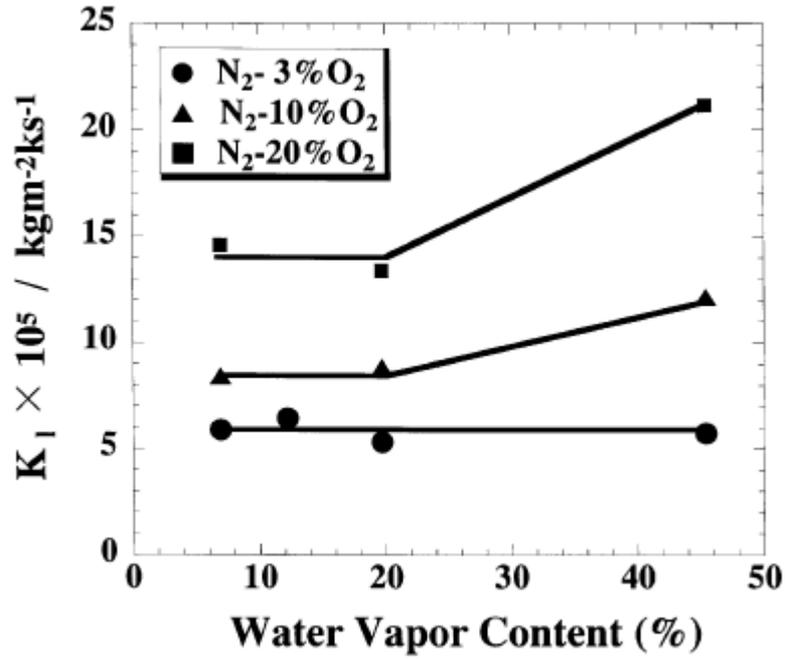


Fig. 5. Evaporation rate of Cr₂O₃ as a function of H₂O concentration at 1473 K in N₂-O₂-H₂O atmospheres.

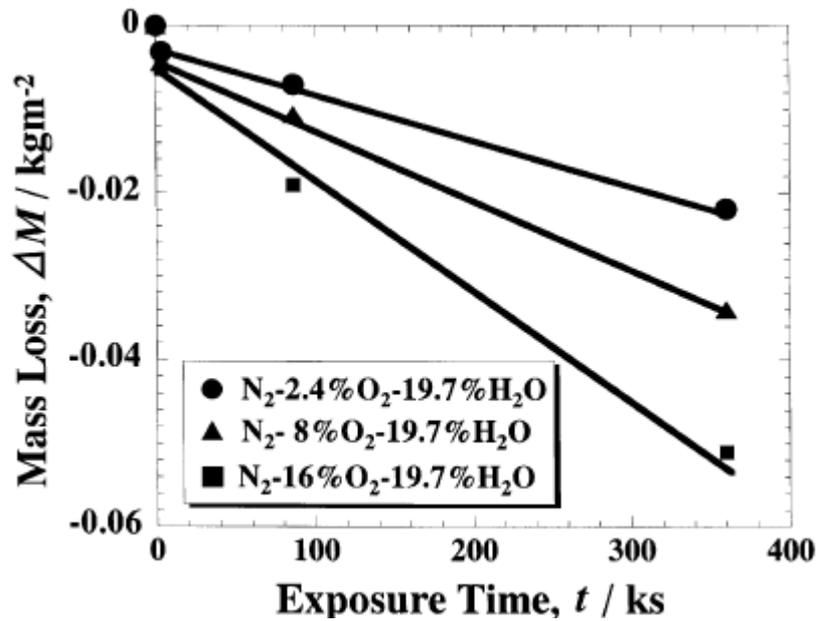


Fig. 6. Mass loss kinetics of Cr₂O₃ at 1473 K in (N₂-X%O₂)-19.7% H₂O (X=3, 10, 20%) atmospheres.

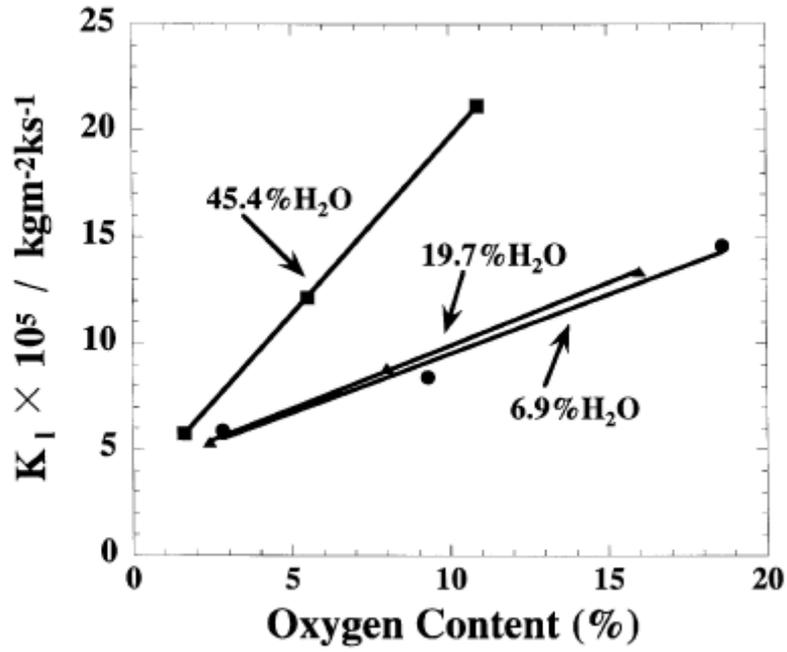


Fig. 7. Evaporation rate of Cr_2O_3 as a function of O_2 concentration at 1473 K in $\text{N}_2\text{-O}_2\text{-H}_2\text{O}$ atmospheres.

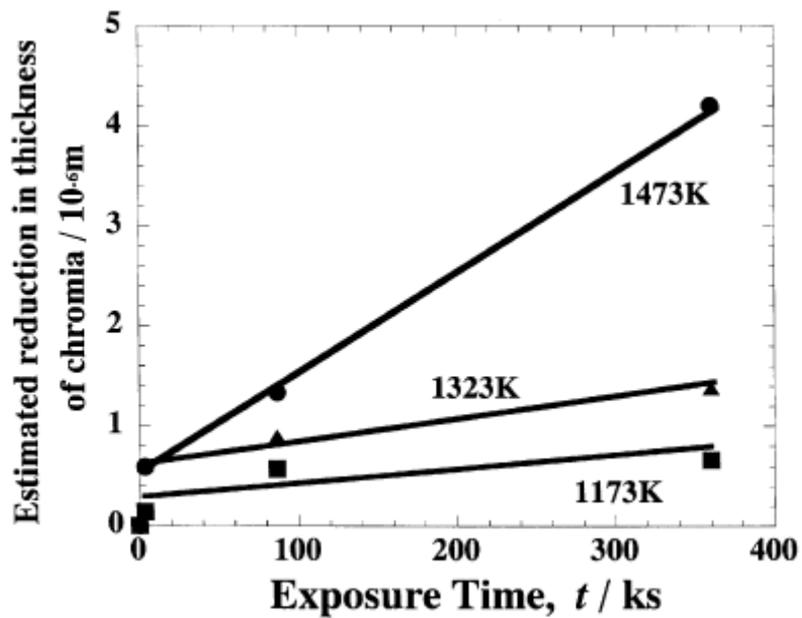


Fig. 8. Change in the estimated thickness of Cr_2O_3 with time at various temperatures in $\text{N}_2\text{-2.4\%O}_2\text{-19.7\%H}_2\text{O}$ atmospheres.