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## THE ANALYSIS OF GAS CONSUMPTION IN THE REACTION OF Fe AND Cu IN $H_2^{16}O/H_2^{18}O/O_2$ GAS MIXTURES

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**Abstract**—Some general considerations in the analysis of consumption and release of gas components in reactions of a metal in  $H_2/H_2O/O_2$  gas are presented. Reactions of iron and copper at 160–300°C in  $H_2^{16}O/H_2^{18}O/O_2$  gas in the mbar pressure range were studied with mass spectrometry in a virtually closed reaction chamber. Data on oxygen and hydrogen uptake in the reaction products and fraction of oxygen coming from reaction with water lead to conclusions concerning partial and complete water dissociation in the reactions with the metals.

### INTRODUCTION

The initial reaction of Fe and Cu with gas mixtures of  $H_2O/O_2$  at  $10^{-10}$  to  $10^{-6}$  mbar pressures has been studied *in situ* with various Ultra High Vacuum (UHV) based techniques.<sup>1-3</sup> The results from these studies cannot directly be used to forecast kinetics and mechanisms of thicker reaction products formed at ambient  $H_2O/O_2$  pressures. The high difference in water activity can change the reaction mechanisms and kinetics.

Recently, a method for gas analysis has been developed in order to perform studies of oxidation, corrosion and catalysis of different materials with  $H_2/H_2^{16}O/H_2^{18}O/O_2$  gas mixtures in the mbar pressure range at moderate temperatures.<sup>4,5</sup> The experimental technique is based on the mass spectrometry of gas components in a virtually closed reaction chamber and has been used earlier in dry oxidation at relatively high temperatures.<sup>6</sup> The gas analysis offers the possibility of following the reaction kinetics *in situ* and also of calculating quantitatively certain characteristic values in the solid reaction product formed in  $H_2O/O_2$  gas mixtures at different temperatures. Such values are the H:O ratio and the fraction of O in the product that comes from reaction with water.

Results from the reaction of iron at 300°C have recently been reported in this journal<sup>5</sup> and in this paper mainly gas analysis data from reaction of Fe and Cu at 160–300°C are presented. Some general considerations of the analysis of gas consumption/gas release are presented followed by an analysis of the present data. Finally these data are interpreted in terms of partial and complete dissociation of  $H_2O$  in the presence of  $O_2$ .

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Table 1. Summary of experimental conditions and results

	Cu 25°C* (Fig. 8)	Cu 160°C (Fig. 3)	Cu 210°C (Fig. 4)	Cu 300°C (Fig. 5)	Fe 180°C (Fig. 6)	Fe 180°C (Fig. 7)	Fe 300°C (Ref. 5)
$\frac{H_{sp}}{O_{sp}}$	—	0.68	0.24	0.16	0.87	0.53	0.04
$\frac{(O_{sp})_{H_2O}}{O_{sp}}$	0.60	0.65	0.60	0.52	0.70	0.60	0.69
$\frac{H_{sp}}{(O_{sp})_{H_2O}}$	—	1.05	0.40	0.31	1.24	0.88	0.06
$P_{O_2}$ at start (mbar)	200	6.5	3.5	6.5	1	21	13
$P_{H_2O}$ at start (mbar)	28	13.5	6	18	9	26	28
Reaction time (h)	2500	61	13	8	15	20	4
Sample area (cm <sup>2</sup> )	5	100	50	35	100	50	50
Gas volume (dm <sup>3</sup> )	0.02	0.2	0.2	0.2	0.2	0.2	0.35

\*Based on SIMS measurements.

## EXPERIMENTAL METHOD

The experimental apparatus and experimental procedure were essentially the same as in the previous studies.<sup>4,5</sup>

Samples of Fe (99.7%) or Cu (99.996%), in the form of respectively, 1.5 mm and 2 mm diameter wire, were ground with 800 mesh SiC paper and wound into the shape of a spring. The samples were then ultrasonically cleaned in 99.5% ethanol and placed in the reaction chamber which was evacuated down to  $10^{-9}$  mbar. (Plates of 0.1 mm thickness were prepared in the same way and used in Secondary Ion Mass Spectrometry, SIMS analysis.) In all exposures, with the exception of Fe at 300°C, the heated zone of the reaction chamber was quartz. In Table 1 the initial O<sub>2</sub> and H<sub>2</sub>O pressures, reaction time, sample area, gas volume, metal and temperature are shown for each experiment.

SIMS was used in analysis of two reaction products formed on Cu. An Ar<sup>+</sup> beam at 4.5 kV and a current density of  $\sim 10 \mu\text{A cm}^{-2}$  were used in this analysis.

## GAS ANALYSIS

### *General considerations of the analysis of gas consumption/gas release in Me-H<sub>2</sub>-H<sub>2</sub>O-O<sub>2</sub> systems*

For the analysis of gas consumption/gas release data to be adequate for reactions with a given sample, the two following experimental conditions must be fulfilled: (i) the consumption of gas in the detection system is negligible; and (ii) any interference—consumption, release, catalytic activity—from surfaces other than the material under study is negligible.

When these conditions apply, a mass balance means that hydrogen and oxygen,

respectively, in gas phase (gp) and in solid reaction product (sp) are constant during the course of reaction:

$$H_{gp} + H_{sp} = \text{constant} \quad (1)$$

$$O_{gp} + O_{sp} = \text{constant} \quad (2)$$

In the general case three different reaction phenomena (A–C) have to be dealt with: (A) the formation of a solid reaction product,  $Me_xO_yH_z$ , as a result of oxidation, corrosion, hydration and hydrogenation; (B) the catalysed reaction:  $2H_2 + O_2 \rightarrow 2H_2O$ ; (C) oxygen exchange in  $O_2$  and in  $H_2O$ ; and (C') hydrogen exchange in  $H_2$  and in  $H_2O$ .

The oxygen exchange in C can be further divided into several cases: (C<sub>1</sub>) oxygen exchange between  $O_2$  and  $O_2$ ; (C<sub>2</sub>) oxygen exchange between  $H_2O$  and  $H_2O$ ; (C<sub>3</sub>) oxygen exchange between  $O_2$  and  $H_2O$ ; (C<sub>4</sub>) oxygen exchange between  $O_2$  and a metal oxide  $Me_xO_yH_z$ ; and (C<sub>5</sub>) oxygen exchange between  $H_2O$  and a metal oxide  $Me_xO_yH_z$ .

These cases and the corresponding hydrogen exchange in C' can be organised in a simple matrix:

	$O_{2gp}$	$H_{2gp}$	$H_{2gp}$	$Me_xO_yH_z$
$O_{2gp}$	C <sub>1</sub>	C <sub>3</sub>	—	C <sub>4</sub>
$H_2O_{gp}$	C <sub>3</sub>	C <sub>2</sub> C' <sub>2</sub>	C' <sub>3</sub>	C <sub>5</sub> C' <sub>5</sub>
$H_{2gp}$	—	C' <sub>3</sub>	C' <sub>1</sub>	C' <sub>4</sub>
$Me_xO_yH_z$	C <sub>4</sub>	C <sub>5</sub> C' <sub>5</sub>	C' <sub>4</sub>	—

The reactions of C<sub>1</sub>–C<sub>3</sub> and C'<sub>1</sub>–C'<sub>3</sub> are catalysed by different solid surfaces and like C<sub>4</sub>, C<sub>5</sub>, C'<sub>4</sub> and C'<sub>5</sub> are also expected to vary in rate among different metal oxides and temperatures.

#### *The use of isotopes to study the oxygen and hydrogen exchange*

Isotopes can be used to study C and C' above. Generally there is a ~30% difference in reaction rate between  $H_2$  and  $D_2$  while the corresponding isotopic effect between  $^{16,16}O_2$  and  $^{18,18}O_2$ , calculated with statistical mechanics, is estimated to be a few per cent.<sup>7</sup> Hence these oxygen isotopes can often be treated as chemically equivalent while using hydrogen isotopes in studies of kinetics of hydrogen exchange often needs some correction.

The kinetics of C<sub>1</sub> (see above for definition) can be measured by exposing the sample to  $^{16,16}O_2$  plus  $^{18,18}O_2$  with a subsequent monitoring of  $^{16,18}O_2$ . To study C<sub>2</sub> one needs to label both H and O in water. By using  $^{16,16}O_2$  together with  $H_2^{18}O$  the rate of C<sub>3</sub> can be determined by monitoring the increase of  $^{16,18}O_2$ . This is illustrated in Fig. 1 where quartz acts as a catalyst at 900°C for this oxygen exchange. The distribution of isotopes at equilibrium is calculated the same way as in di-atomic clusters in secondary ion mass spectrometry.<sup>8</sup>

In oxidation/corrosion studies (A), attention should be paid to reaction B above since it proceeds on all solid surfaces but at widely different rates. This is illustrated in

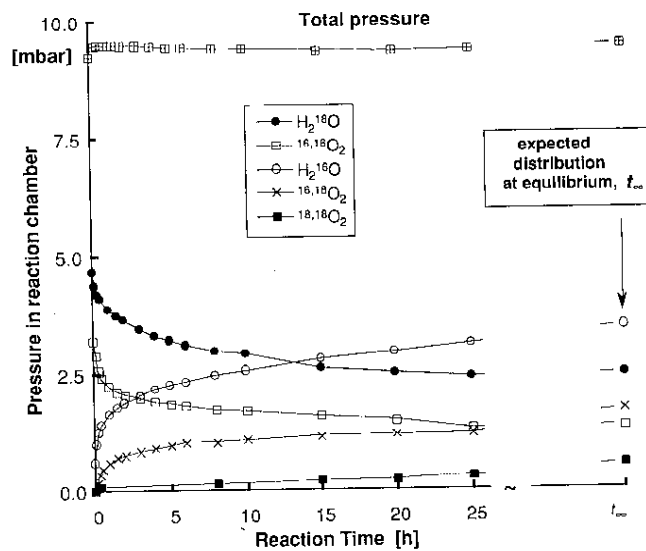


Fig. 1. Pressures of  $\text{H}_2^{16}\text{O}$ ,  $\text{H}_2^{18}\text{O}$ ,  $^{16,16}\text{O}_2$ ,  $^{16,18}\text{O}_2$  and  $^{18,18}\text{O}_2$  during exposure to  $\sim 30\text{ cm}^2$  of quartz at  $900^\circ\text{C}$  in a volume of  $0.2\text{ dm}^3$ .

Fig. 2 where this reaction has been studied at different temperatures on platinum, aluminium oxide, iron oxide, copper oxide and a chromium-rich oxide.

In cases where only B and/or C (C') are operative, as exemplified in Figs 1 and 2, equations (1) and (2) are naturally reduced to a conservation of H and O in gas phase. Where A is operative, alone or simultaneously with B and/or C(C'), consumption of O and/or H takes place and the mass balance expressed by equations (1) and (2) apply.

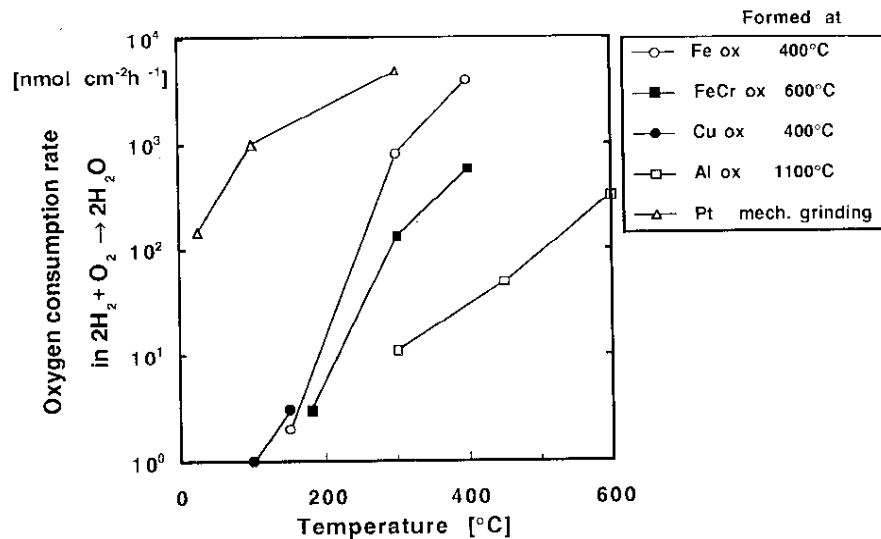


Fig. 2. Rates of  $\text{O}_2$  consumption in  $2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$  on Pt, alumina, iron oxide, copper oxide and a chromium-rich oxide measured at 5 mbar  $\text{H}_2$ , 4 mbar  $\text{O}_2$  and  $\sim 1$  mbar  $\text{H}_2\text{O}$ .

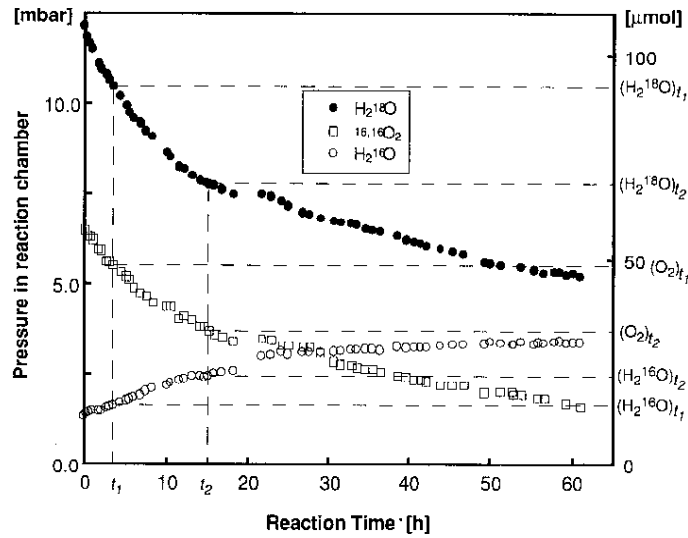


Fig. 3. Pressure and  $\mu$ moles of  $\text{H}_2^{16}\text{O}$ ,  $\text{H}_2^{18}\text{O}$  and  $^{16,16}\text{O}_2$  during reaction with Cu at  $160^\circ\text{C}$ .

#### The analysis of gas consumption in the present study

In the present study, Fe and Cu were exposed to oxygen-labelled water,  $\text{H}_2^{18}\text{O}$ , and normal molecular oxygen, which contains predominantly  $^{16,16}\text{O}_2$  and negligible amounts of  $^{17}\text{O}$  and  $^{18}\text{O}$ . The gas components monitored were therefore  $\text{H}_2$ ,  $\text{H}_2^{16}\text{O}$ ,  $\text{H}_2^{18}\text{O}$ ,  $^{16,16}\text{O}_2$ ,  $^{16,18}\text{O}_2$  and  $^{18,18}\text{O}_2$ , but there were no significant signals in the mass spectrometer from masses 34 and 36 corresponding to  $^{16,18}\text{O}_2$  and  $^{18,18}\text{O}_2$ . This means that the oxygen exchange according to  $\text{C}_3$  and  $\text{C}_4$  was negligible during the course of the oxidation/corrosion. The concentration of  $\text{H}_2$  in the gas phase was also too low to be detected ( $<0.5$  mbar). Hence these gas components are omitted in the analysis below and also not shown in most of the figures.

As an example the amounts ( $\mu\text{mol}$ ) of  $\text{H}_2^{16}\text{O}$ ,  $\text{H}_2^{18}\text{O}$  and  $^{16,16}\text{O}_2$  are indicated at times  $t_1$  and  $t_2$  in Fig. 3. Based on the mass balance expressed in equations (1) and (2) the oxygen and hydrogen uptake in the solid reaction product  $\text{Me}_x\text{O}_y\text{H}_z$  during the time interval  $t_1$  to  $t_2$  can be calculated:

$$^{18}\text{O uptake in } \text{Me}_x\text{O}_y\text{H}_z = ^{18}\text{O}_{\text{sp}} = (\text{H}_2^{18}\text{O})_{t_1} - (\text{H}_2^{18}\text{O})_{t_2}, \quad (3)$$

$$^{16}\text{O uptake in } \text{Me}_x\text{O}_y\text{H}_z = ^{16}\text{O}_{\text{sp}} = 2(^{16}\text{O}_2)_{t_1} - 2(^{16}\text{O}_2)_{t_2} + (\text{H}_2^{16}\text{O})_{t_1} - (\text{H}_2^{16}\text{O})_{t_2}. \quad (4)$$

Consequently, the total oxygen uptake in solid reaction product is:

$$\text{O}_{\text{sp}} = ^{18}\text{O}_{\text{sp}} + ^{16}\text{O}_{\text{sp}}, \quad (5)$$

$$\text{H uptake in } \text{Me}_x\text{O}_y\text{H}_z = \text{H}_{\text{sp}} = 2(\text{H}_2^{18}\text{O})_{t_1} - 2(\text{H}_2^{18}\text{O})_{t_2} + 2(\text{H}_2^{16}\text{O})_{t_1} - 2(\text{H}_2^{16}\text{O})_{t_2}. \quad (6)$$

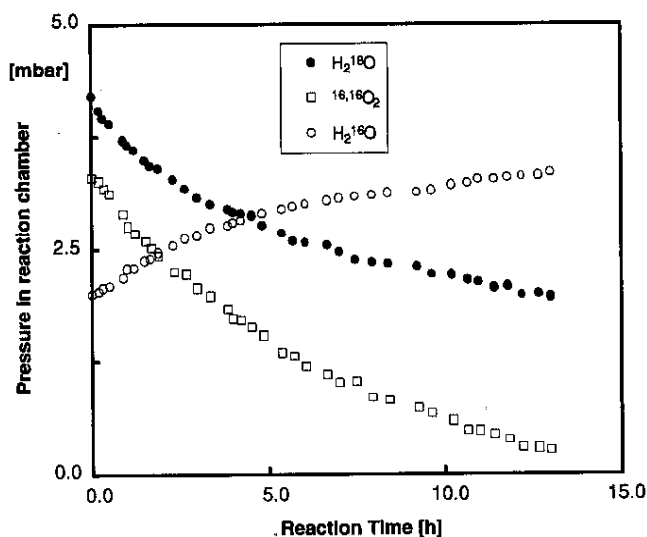


Fig. 4. Pressure of  $\text{H}_2^{16}\text{O}$ ,  $\text{H}_2^{18}\text{O}$  and  $^{16,16}\text{O}_2$  during reaction with Cu at  $210^\circ\text{C}$ .

The ratio of hydrogen to oxygen uptake in the solid reaction product is then from equations (5) and (6):

$$\frac{H_{\text{sp}}}{O_{\text{sp}}} \quad (7)$$

Oxygen uptake in solid reaction product from reaction with water is:

$$(O_{\text{sp}})_{\text{H}_2\text{O}} = {}^{18}\text{O}_{\text{sp}} + \frac{(\text{H}_2^{16}\text{O})}{(\text{H}_2^{18}\text{O})} \times {}^{18}\text{O}_{\text{sp}}, \quad (8)$$

where  $(\text{H}_2^{16}\text{O})$  and  $(\text{H}_2^{18}\text{O})$  are mean values in time interval  $t_1 - t_2$ . In equation (8), advantage can be made of the use of  $^{18}\text{O}$  labelled water.

The fraction of oxygen uptake in solid reaction product from reaction with water is then from equations (5) and (8):

$$\frac{(O_{\text{sp}})_{\text{H}_2\text{O}}}{O_{\text{sp}}} \quad (9)$$

Finally the ratio between hydrogen and oxygen in solid reaction product is defined where oxygen comes from reaction with water:

$$\frac{H_{\text{sp}}}{(O_{\text{sp}})_{\text{H}_2\text{O}}} \quad (10)$$

The above calculations have been applied to the data shown in Figs 3–7 in this paper and the results are summarised in Table 1.

#### EXPERIMENTAL RESULTS AND DISCUSSION

Figures 3–7 show the measured pressures of  $\text{H}_2^{16}\text{O}$ ,  $\text{H}_2^{18}\text{O}$  and  $^{16,16}\text{O}_2$  during reaction with Fe and Cu. The analysis of these data has been described above. The

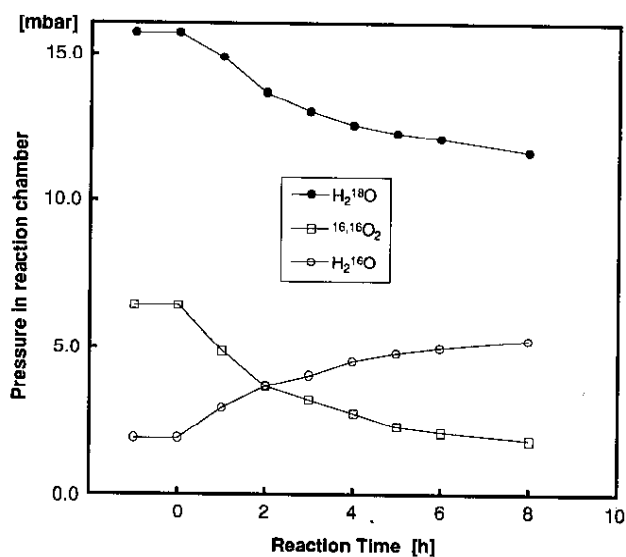


Fig. 5. Pressure of  $H_2^{16}O$ ,  $H_2^{18}O$  and  $^{16,16}O_2$  during reaction with Cu at 300°C.

numerical results from this analysis are summarised in Table 1 where also results from Fe at 300°C are collected from Ref. 5. Cu has also been exposed at room temperature to air of ~200 mbar normal molecular oxygen, ~30 mbar  $H_2^{18}O$  and <1 mbar  $H_2^{16}O$ . The reaction product was subsequently analysed with SIMS. The  $Cu_2-O-H$  part of the positive spectrum is shown in Fig. 8, from which  $(O_{sp})_{H_2O}/O_{sp}$  is calculated and shown in Table 1.

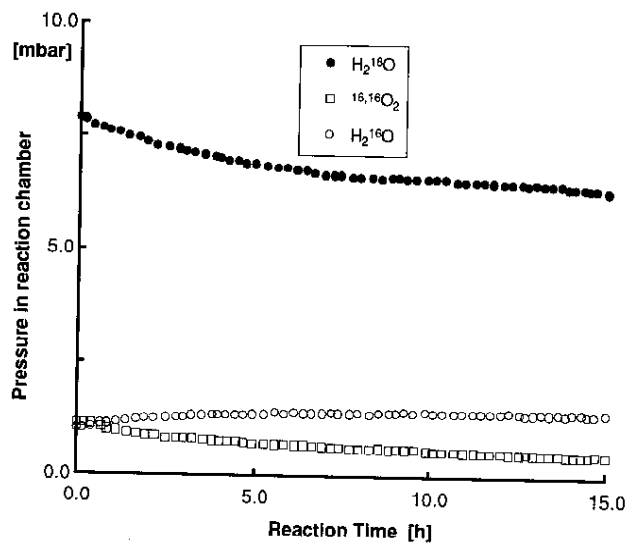


Fig. 6. Pressure of  $H_2^{16}O$ ,  $H_2^{18}O$  and  $^{16,16}O_2$  during reaction with Fe at 180°C.

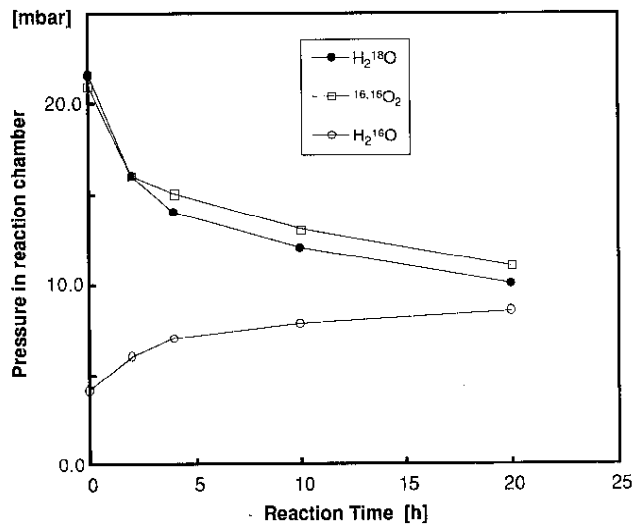


Fig. 7. Pressure of H<sub>2</sub><sup>16</sup>O, H<sub>2</sub><sup>18</sup>O and <sup>16,16</sup>O<sub>2</sub> during reaction with Fe at 180°C.

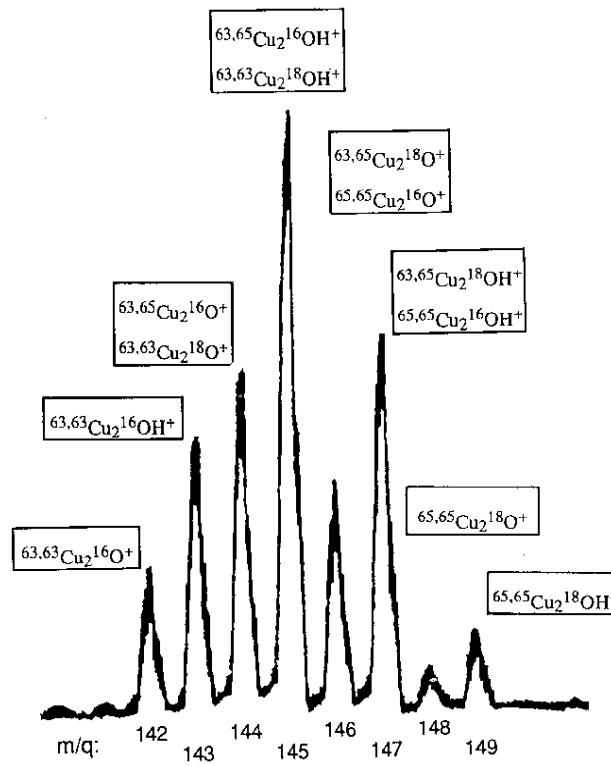


Fig. 8. SIMS spectrum of positive Cu<sub>2</sub>-O-H ions in sputtering of the product formed in air of ~200 mbar "normal" molecular oxygen, ~30 mbar H<sub>2</sub><sup>18</sup>O and <1 mbar H<sub>2</sub><sup>16</sup>O. Relative distribution of Cu<sub>2</sub><sup>+</sup>: <sup>63,63</sup>Cu<sub>2</sub><sup>+</sup> = 47.8%, <sup>63,65</sup>Cu<sub>2</sub><sup>+</sup> = 42.7% and <sup>65,65</sup>Cu<sub>2</sub><sup>+</sup> = 9.5%. The relevant ions indicated at respective mass (m/q).



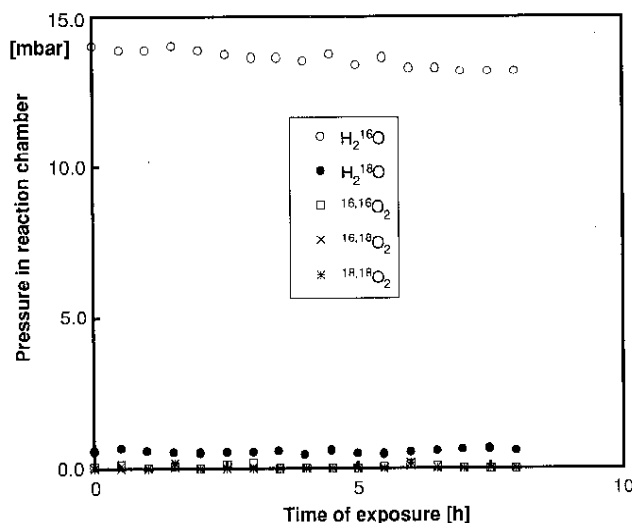


Fig. 9. Pressure of  $\text{H}_2^{16}\text{O}$ ,  $\text{H}_2^{18}\text{O}$ ,  $^{16,16}\text{O}_2$ ,  $^{16,18}\text{O}_2$  and  $^{18,18}\text{O}_2$  during exposure at  $300^\circ\text{C}$  of Fe oxide with  $91 \pm 2\%$   $^{18}\text{O}$ .

#### Oxygen exchange between $\text{O}_2/\text{H}_2\text{O}$ and the Fe and Cu oxides

Before the principal reaction paths in the oxidation/corrosion of Fe and Cu are discussed the possibility of oxygen exchange according to reaction (C) should be further considered. Since  $^{16,18}\text{O}_2$  and  $^{18,18}\text{O}_2$  could not be detected in any of the experiments with Fe and Cu it has been concluded that neither oxygen exchange between  $\text{H}_2\text{O}$  and  $\text{O}_2$  ( $C_3$ ) nor oxygen exchange between  $\text{O}_2$  and the solid reaction products ( $C_4$ ) are operative in the reaction of Fe and Cu with  $\text{H}_2\text{O}/\text{O}_2$  gas mixtures at the temperatures applied here. (From the conclusion that  $C_3 \approx 0$ , at least one of  $C_1$  and  $C_2$  is likely to be zero). For a discussion of reaction paths in the oxidation of the metals no further knowledge of  $C_1$  and  $C_2$  is needed. On the other hand, knowledge about  $C_5$  is needed.

In the case of Fe a separate experiment was conducted to determine the kinetics associated with  $C_5$ . A relatively thick Fe oxide was produced in controlled  $\text{H}_2^{16}\text{O}/\text{H}_2^{18}\text{O}$  gas at  $400^\circ\text{C}$ . This resulted in an oxide with  $91 \pm 2\%$  of  $^{18}\text{O}$ . The  $^{18}\text{O}$  content was also analysed with SIMS in four different laboratories where the  $^{18}\text{O}$  content from gas consumption was confirmed.<sup>9</sup> This oxide was exposed at  $300^\circ\text{C}$  to  $\text{H}_2^{16}\text{O}$ . In Fig. 9 no increase is found in  $\text{H}_2^{18}\text{O}$  upon this exposure. Hence it is believed that the oxygen exchange rate between  $\text{H}_2\text{O}$  and the Fe oxides is also negligible compared with the reaction rate of Fe with water at the temperatures studied here ( $\leq 300^\circ\text{C}$ ). The highly  $^{18}\text{O}$  enriched iron oxide was also stored in air at room temperature for 14 months without any significant oxygen exchange ( $< 3\%$ ).<sup>9</sup> The iron oxide shown in Fig. 6 has also been exposed for more than a year at room temperature in air almost without any change in  $^{18}\text{O}$  content as analysed with SIMS. The measured  $52\%$   $^{18}\text{O}$  should be compared with  $60\%$  as calculated from Fig. 6.

To judge if  $C_5$  is operative in the case of Cu the oxide grown in Fig. 5 was exposed to  $\text{H}_2^{18}\text{O}$  enriched water ( $> 80\%$ ). Since the oxide contains  $\sim 40\%$   $^{18}\text{O}$  ( $60\%$   $^{16}\text{O}$ ) the pressure of  $\text{H}_2^{18}\text{O}$  should decrease if an oxygen exchange between  $\text{H}_2\text{O}$  and the Cu oxide was operative. As seen in Fig. 10, the rate of oxygen exchange between  $\text{H}_2\text{O}$

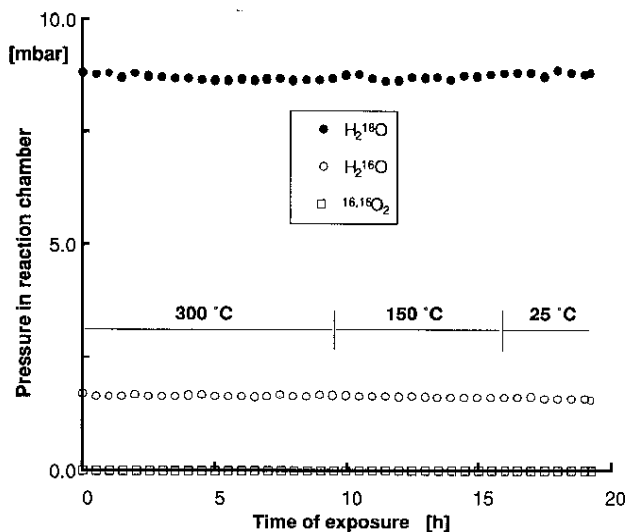


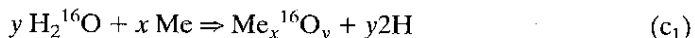
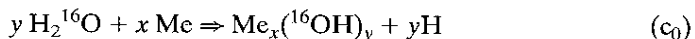
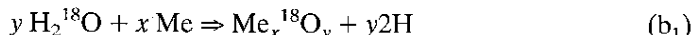
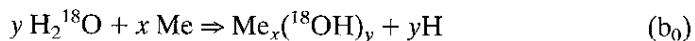
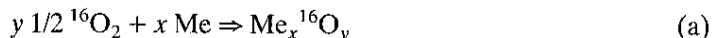
Fig. 10. Pressure of  $\text{H}_2^{16}\text{O}$ ,  $\text{H}_2^{18}\text{O}$  and  $^{16,16}\text{O}_2$  during exposure at different temperatures of the Cu oxide formed as shown in Fig. 5, 40%  $^{18}\text{O}$  in the oxide.

and the Cu oxide is not significant. Therefore it is negligible compared with the oxidation/corrosion rate of Cu at the applied temperatures. Figure 10 also demonstrates that the oxide does not incorporate water upon cooling from 300 to 25°C.

In a separate experiment Cu was exposed to 20 mbar  $\text{H}_2^{18}\text{O}$ , 3 mbar  $\text{H}_2^{16}\text{O}$  and 5 mbar  $^{16}\text{O}_2$  for 24 h at 150°C. Due to the small ( $\sim 2 \text{ cm}^2$ ) sample area used, the gas pressure did not significantly change due to the gas consumption/gas release. In Fig. 11 the SIMS analysis of  $\text{Cu}_2\text{O}$  and  $\text{Cu}_2\text{OH}$  ions are shown. A highly  $^{18}\text{O}$ -enriched  $\text{Cu}_x\text{O}_y\text{H}_z$  oxide was formed which remained  $^{18}\text{O}$ -enriched upon heating to 300°C in UHV. This treatment resulted in disappearance of the  $\text{Cu}_2\text{OH}$  species as clearly seen in the figure. During heating in UHV, extremely low activities of  $\text{O}_2$  and  $\text{H}_2\text{O}$  are present which result in a conversion of the oxide to probably  $\text{Cu}_2\text{O}$ .

#### *The principal reactions in the oxidation of Fe and Cu in $\text{O}_2/\text{H}_2\text{O}$*

Based on the above discussion and results, the following principal reactions are considered to operate in the oxidation of Fe and Cu in  $\text{H}_2^{16}\text{O}/\text{H}_2^{18}\text{O}/^{16,16}\text{O}_2$  gas mixtures at 160–300°C:



The reactions of (b<sub>1</sub>) and (c<sub>1</sub>) express a complete dissociation of water. This

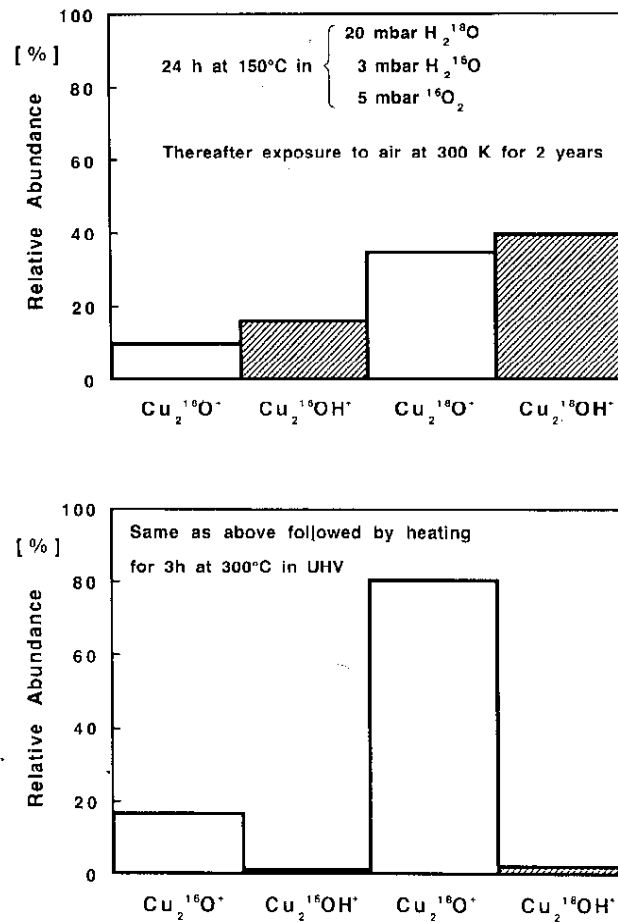


Fig. 11. Relative distribution of  $\text{Cu}_2^{16}\text{O}^+$ ,  $\text{Cu}_2^{16}\text{OH}^+$ ,  $\text{Cu}_2^{18}\text{O}^+$ , and  $\text{Cu}_2^{18}\text{OH}^+$  ions in SIMS analysis.

complete water dissociation seems to operate in the exposure of Fe at 300°C since the hydrogen content in the reaction product is low,  $H_{\text{sp}}/O_{\text{sp}} = 0.04$ , but at the same time a considerable fraction of oxygen in the product comes from water,  $(O_{\text{sp}})_{\text{H}_2\text{O}}/O_{\text{sp}} = 0.69$  (see Table 1).

At the lower temperatures both Fe and Cu form solid products with substantial hydrogen contents. This can be explained by the partial water dissociation in reactions (b<sub>0</sub>) and (c<sub>0</sub>). We can see in Table 1 that the ratio of hydrogen to oxygen which comes from reaction with water,  $H_{\text{sp}}/(O_{\text{sp}})_{\text{H}_2\text{O}}$ , is close to one in the case of Fe at 180°C and Cu at 160°C. This ratio is expected when mainly a partial water dissociation is operative in combination with (b<sub>2</sub>) and (c<sub>2</sub>). The absence of  $\text{H}_2\text{O}$  uptake in Fig. 10 further indicates that H in the Cu oxide is not in the form of undissociated  $\text{H}_2\text{O}$ . Also in the monolayer reaction products on polycrystalline Fe and Cu formed in  $\text{H}_2\text{O}/\text{O}_2$  gas at  $10^{-10}$  to  $10^{-6}$  mbar pressures at room temperature we have found high hydrogen contents in SIMS measurements.<sup>10</sup>

The reactions (b<sub>2</sub>) and (c<sub>2</sub>) are coupled to (b<sub>0</sub>), (b<sub>1</sub>) and (c<sub>0</sub>), (c<sub>1</sub>) respectively, by combination of oxygen and hydrogen to water. (A combination of  $\text{O}_2$  with hydrogen

can also result in  $\text{Me}_x(^{16}\text{OH})_y$ , as for iron near 300 K).<sup>2</sup> When comparing the rates of ( $b_2$ ), measured as rate of increase of  $\text{H}_2^{16}\text{O}$  in Figs 3–7, with rates of  $2\text{H}_2 + \text{O}_2 \rightarrow \text{H}_2\text{O}$  in Fig. 2 (reaction B), we find these rates to be in the same magnitude. This is consistent with the observation that no  $\text{H}_2$  is found during the reactions in this study.

### SUMMARY AND CONCLUSIONS

Some general considerations of gas analysis in reactions of a metal with  $\text{H}_2/\text{H}_2\text{O}/\text{O}_2$  gas mixtures in a virtually closed system are presented. The use of oxygen isotopes is shown to be powerful to identify and quantify various reaction phenomena. Data from reaction of Fe and Cu at 160–300°C in  $\text{H}_2^{16}\text{O}/\text{H}_2^{18}\text{O}/\text{O}_2$  gas mixtures in the mbar pressure range have been analysed. Conclusions concerning molecular hydrogen in gas, hydrogen uptake in solid reaction product, fraction of oxygen in solid reaction product that comes from reaction with water and oxygen exchange between gas and reaction product are extracted from the experimental data:

- (1) No  $\text{H}_2$  was detected in the reactions.
- (2) The solid reaction products on iron and copper catalyse the reaction:  $2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$  at a rate comparable with the reaction rate of  $\text{H}_2\text{O}$  with the metals. This can explain the observation in conclusion (1).
- (3) In reaction of Fe at 300°C a complete water dissociation takes place since the product is essentially free from hydrogen but at the same time it contains a considerable fraction of oxygen from reaction with water.
- (4) There is a substantial hydrogen concentration in the reaction product formed on both Fe and Cu below approximately 300°C. This concentration increases with lowered temperature.
- (5) The hydrogen in (4) is not in the form of undissociated water but rather as hydroxide which results from partial dissociation of water in the presence of molecular oxygen.
- (6) As a consequence of (4) and (5) no simple metal oxides,  $\text{Me}_x\text{O}_y$ , are formed when Fe and Cu are reacting with a  $\text{H}_2\text{O}/\text{O}_2$  gas mixture below approximately 300°C.
- (7) In all the studied reactions the fraction of oxygen in the solid reaction product that comes from reaction with water exceeds 50%.
- (8) The reaction products on the metals did not catalyse oxygen exchange between  $\text{H}_2\text{O}$  and  $\text{O}_2$  gas at a measurable rate.
- (9) The rate of oxygen exchange between  $\text{O}_2$  gas and oxygen in the reaction product is negligible compared with the rate of  $\text{O}_2$  consumption in the metal oxidation.
- (10) The rate of oxygen exchange between  $\text{H}_2\text{O}$  gas and oxygen in the reaction product is negligible compared with the rate of  $\text{H}_2\text{O}$  consumption in the metal oxidation.

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