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TG STUDIES ON THE REACTIONS OF HEMATITE, MAGNETITE AND WÜSTITE WITH $COCl_2$ AND $CO+Cl_2$

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ABSTRACT

The chlorination of hematite, magnetite and wüstite with $COCl_2$ and $CO+Cl_2$ were studied by thermogravimetry and X-ray diffraction. The equilibrium compositions of the gas- and solid-phases were determined by computer assisted thermodynamic calculations. During the chlorination of wüstite, as an intermediate product, $FeCl_2(s)$ was detected. A simulteneous transformation of wüstite was observed first into magnetite, and at higher temperatures, into hematite. In the case of the chlorination of magnetite with $COCl_2$, hematite and $FeCl_2(s)$ were formed as intermediate products. The reaction of wüstite with $CO+Cl_2$, started at very low temperatures and took place via the formation of $FeCl_2(s)$, $FeCl_3(s)$ and $FeOCl(s)$.

INTRODUCTION

The chlorination behaviour of hematite has been studied in details (1-5), however, much less attention has been paid to the chlorination kinetics of wüstite and magnetite (1,2). The reactions of Fe_2O_3, Fe_3O_4, FeO with Cl_2 (6) and with gaseous CCl_4 (7) were studied and published earlier. The present paper, as an extension of the early works, deals with the chlorination of hematite, magnetite and wüstite with $COCl_2$ and $CO + Cl_2$.

EXPERIMENTAL

TG measurements were carried out in a special reactor attached to a Mettler semimicro recording balance (8). Fe_2O_3 of analytical grade ($s^o=10\ m^2 \cdot g^{-1}$) was used. FeO samples (containing a small amount of α-Fe) were prepared from iron oxalate by thermal decomposition ($s^o=0.4\ m^2 \cdot g^{-1}$) and Fe_3O_4 from Fe_2O_3 by CO/CO_2 reduction ($s^o=0.3\ m^2 \cdot g^{-1}$). The crystalline structure of the samples were checked by X-ray diffraction.

RESULTS AND DISCUSSION

The equilibrium gas composition for the $Fe_2O_3+COCl_2$ system was determined by a free enthalpy minimalization program. In the temperature range 600-1200 K the equilibrium is shifted towards the volatile chloride products and $CO_2(g)$ (Fig.1). Below 1050 K the main gaseous product is $Fe_2Cl_6(g)$. Above 1100 K the concentration of $FeCl_2(g)$ is increasing at the expense of $Fe_2Cl_6(g)$.

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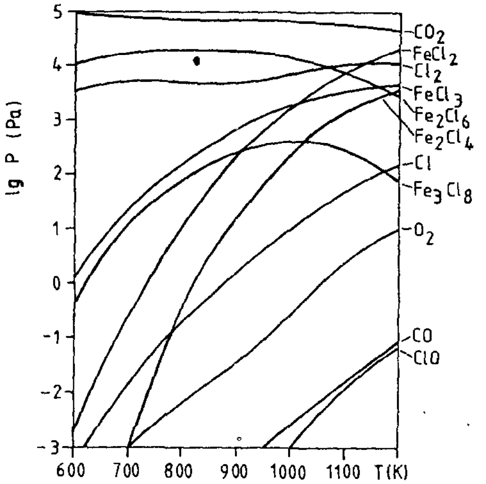


Fig.1. The equilibrium composition of the gas-phase in the case of $Fe_2O_3:COCl_2=2:3$

In order to characterize the chlorination process, anisothermal measurements were carried out using $COCl_2$ (Fig.2A) and $CO+Cl_2$ (Fig.2B). In the case of hematite only gaseous products were formed during the chlorination process thus only mass loss was observed. The volatilization began above 600 and 750 K in cases of $COCl_2$ and $CO+Cl_2$ respectively.

During the anisothermal chlorination of FeO with $COCl_2$ (Fig.2A, curve 2) two mass gain steps were observed. The first can be related to the formation of $FeCl_2$(s) with the simultaneous transformation of FeO into Fe_3O_4, while the second, to the formation of Fe_2O_3 and $FeCl_2$(s). The volatilization of $FeCl_2$(s) in form of Fe_2Cl_6(g) caused a rapid mass loss at about 750 K. This step is followed by a slower volatilization, attributed to the reaction of Fe_2O_3 formed in the previous steps. During the chlorination of magnetite (Fig.2A, curve 3), $FeCl_2$(s) and Fe_2O_3(s) are formed as intermediate products.

The chlorinated FeO samples were analyzed by X-ray diffraction. At low temperatures Fe_3O_4(s) and $FeCl_2$(s) were found, while above 680 K hematite also was detected. At 850 K the solid phase was transformed into hematite.

The following overall chemical equations are proposed for describing the above processes:

$$4\,FeO(s) + COCl_2(g) = FeCl_2(s) + Fe_3O_4(s) + CO(g) \qquad (1)$$

$$Fe_3O_4(s) + COCl_2(g) = FeCl_2(s) + Fe_2O_3(s) + CO_2(g) \qquad (2)$$

$$2\,FeCl_2(s) + COCl_2(g) = Fe_2Cl_6(g) + CO(g) \qquad (3)$$

$$Fe_2O_3(s) + 3\,COCl_2(g) = Fe_2Cl_6(g) + 3\,CO_2(g) \qquad (4)$$

The isothermal TG curves of FeO (Fig.3A) and Fe_3O_4 (Fig.3B) are in accordance with these simplified equations. At low teamperatures only mass gain can be observed due to the formation of $FeCl_2$(s). Increasing the temperature results in the volatilization of $FeCl_2$(s) in form of Fe_2Cl_6(g). After an initial mass gain step two volatilization region can be distinguished in the isothermal curves above 750 K, attributed predominantly to the volatilization of $FeCl_2$(s) and to the chlorination of the previously formed Fe_2O_3.

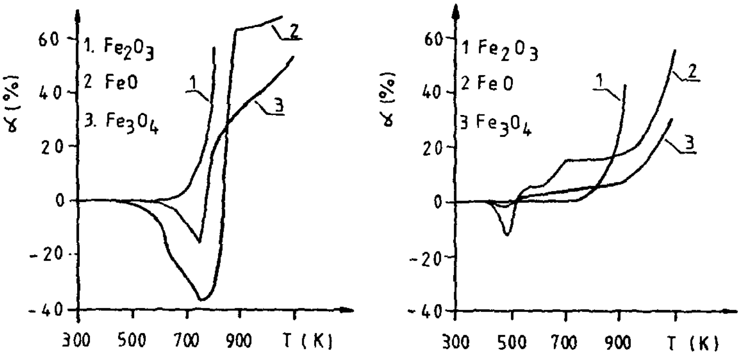


Fig.2. Anisothermal TG curves. Heating rate: 10 K·min^{-1}, α: mass loss (%) (A)-Chlorination with $COCl_2$ (P_{COCl_2}=10.1 kPa); (B)-Chlorination with $CO+Cl_2$ ($P_{CO}=P_{Cl_2}$=10.1 kPa)

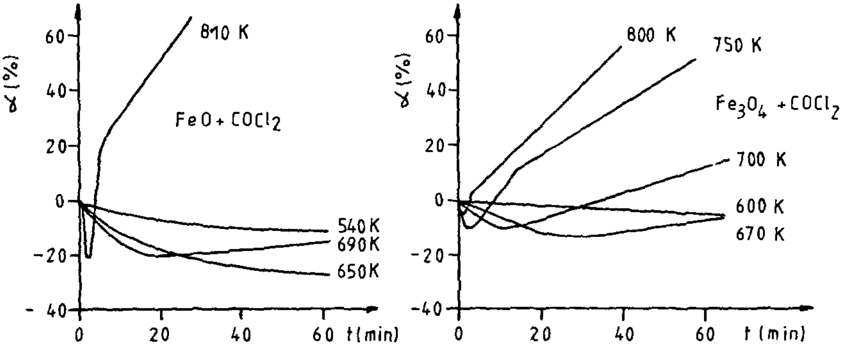
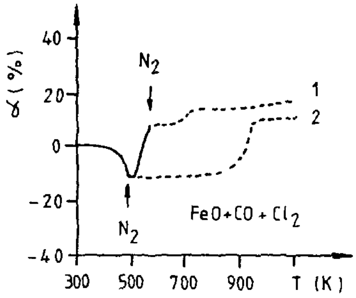


Fig.3. Isothermal chlorination measurements at P_{COCl_2}=10.1 kPa (A)-FeO; (B)-Fe_3O_4



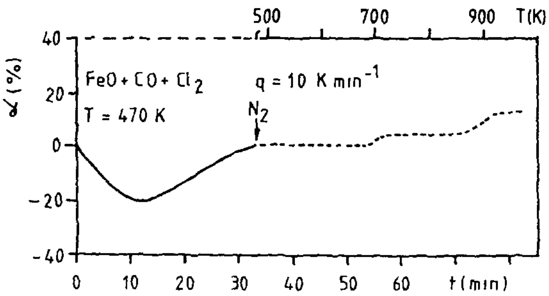


Fig.4. (A) Anisothermal clorination of FeO; changing the ($CO+Cl_2$) flow to N_2 at T=550 K (curve 1) and T=470 (curve 2); heating rate 10 K·min^{-1}

Fig.4. (B) Isothermal chlorination of FeO at T=470 K, followed by anisothermal heating in N_2.

In the case of $FeO+CO+Cl_2$ system (Fig.2B, curve 2), the reaction starts at about 475 K with a considerable mass gain with the formation of $FeCl_2(s)$, $FeCl_3(s)$ and $FeOCl(s)$. This stage is followed by two mass loss steps, attributed to the gasification of $FeCl_2(s)$ and $FeCl_3(s)$ in form of $Fe_2Cl_6(g)$, and to the disproportion of $FeOCl(s)$ into $Fe_2Cl_6(g)$ and $Fe_2O_3(s)$. The above intermedier products were detected by X-ray diffraction measurements of the chlorinated FeO samples. Similar but significantly smaller mass changes can be observed during the anisothermal chlorination of Fe_3O_4 (Fig.2B, curve 3).

The solid iron chloride products formed during the chlorination of FeO were studied also in inert atmosphere. In Fig. 4A anisothermal TG measurements are shown, where the active gas flow was changed to N_2 at a given temperature. The second mass loss step can also be observed in N_2, when the $CO+Cl_2$ flow was interrupted at 550 K, indicating the thermal decomposition of FeOCl (curve 1). In the case of curve 2 the $CO+Cl_2$ gases were changed to N_2 at 470 K. The reaction product was $FeCl_2(s)$, which was sublimed at about 950 K. The $FeCl_3$ formation and gasification can be observed during an isothermal chlorination at 470 K (Fig. 4B). After interrupting the flow of the active gas two mass loss steps can be seen during the anisothermal heating process, attributed to the decomposition of $FeOCl(s)$ to the sublimation of $FeCl_2(s)$.

In accordance with these results, the $FeO+Cl_2+CO$ system can be characterized by the following overall aquations:

$$4\ FeO(s) + Cl_2(g) = FeCl_2(s) + Fe_3O_4(s) \tag{5}$$

$$Fe_3O_4(s) + FeCl_2(s) + Cl_2(g) = FeCl_3(s) + FeOCl(s) + Fe_2O_3(s) \tag{6}$$

$$FeCl_2(s) + 1/2\ Cl_2(g) = 1/2\ Fe_2Cl_6(g) \tag{7}$$

$$FeCl_3(s) = 1/2\ Fe_2Cl_6(g) \tag{8}$$

$$FeOCl(s) = 1/3\ Fe_2O_3(s) + 1/6\ Fe_2Cl_6(g) \tag{9}$$

$$Fe_2O_3(s) + 3\ Cl_2(g) + 3\ CO(g) = Fe_2Cl_6(g) + 3\ CO_2(g) \tag{10}$$

When $COCl_2$ is the chlorinating agent, the reaction proceeds via intermediate $FeCl_2(s)$, similary to the $FeO+CCl_4$ system (7). In the case of Cl_2+CO the reaction starts at very low temperatures. As in the case of $FeO+Cl_2$ reaction (6), the intermedier products are $FeCl_2$, $FeCl_3$ and FeOCl. CO plays an important role in the chlorination process only above 850 K, when the formed Fe_2O_3 begins to react with chlorine by the assistance of CO.

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