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THERMOANALYTICAL STUDY ON THE CHLORINATION OF MAGNESIUM-CONTAINING ORES

AN APPLICATION OF A SIMPLE GAS-FLOW DIFFERENTIAL THERMAL ANALYSIS TECHNIQUE

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ABSTRACT

A simple gas-flow DTA apparatus has been designed to investigate the chlorination reaction of Mg-containing complex ores (olivine, protoenstatite and talc) with Cl_2-gas in a temperature range of 25–1000°C. The apparatus consists of two quartz tubes of i.d. = 10 mm containing 1 g of reference material (α-Al_2O_3, −150 mesh) and 1 g of sample powders (−150 mesh) through which Cl_2-gas can flow to allow the reaction.

In the preliminary chlorination experiments with a constant Cl_2 flow-rate of 30–35 ml/min, the constituents of ores, MgO, FeO and Fe_2O_3, successfully showed the exothermic peak at 450, 150 and 450°C, respectively, and SiO_2 being inert against Cl_2 up to 950°C. Only MgO required carbon additive for the chlorination.

Mg in the ores is chlorinated only when they are mixed with carbon. Olivine (Mg_2SiO_4) shows two exothermic peaks at 880 and 950°C, which indicate that Mg in olivine has different reactivities. Protoenstatite ($MgSiO_3$) and talc ($Mg_3(Si_2O_5)_2(OH)_2$) give peaks at 950 and 750°C, respectively. The results of X-ray diffraction and chemical analysis revealed that the chlorination exothermic peaks of olivine and protoenstatite corresponded to the following reactions,

$$Mg_2SiO_4 + C + Cl_2 \rightleftharpoons MgSiO_3 + MgCl_2 + CO$$

$$MgSiO_3 + 0.25C + 0.25Cl_2 \rightleftharpoons 0.75MgSiO_3 + 0.25MgCl_2 + 0.25SiO_2 + 0.25CO$$

and that the chlorination of talc proceeded together with the decomposition reaction,

$$Mg_3(Si_2O_5)_2(OH)_2 \rightleftharpoons 3MgSiO_3 + SiO_2 + H_2O.$$

INTRODUCTION

Chloride metallurgy has been one of the most important techniques in process metallurgy. The advantages of the use of direct chlorination by Cl_2-gas as a method for extracting the metals from complex and/or low-grade ores have been demonstrated in recent investigations[1–3] for metals as Zr, Ti, W, Ta, Nd, and many others. Metals in the ores which consist of complex multiple oxide minerals are chlorinated, thereby showing the characteristic behavior at different temperatures. The DTA technique shall therefore be most successful to survey the thermal behavior of chlorination of the ores over the wide temperature range of 25–1000 °C and to find the starting temperature of chlorination, if the reaction of ore with Cl_2 shows any DTA peaks. Most DTA apparatus available at present, however, cannot be used for the study on chlorination because of strong corrosiveness of Cl_2 or chlorine compounds.

In this paper, a simple gas-flow DTA apparatus joined with the flowing-gas technique by which Cl_2-gas can flow through the reference and the sample powder beds has been developed, and applied to study the chlorination of various Mg-containing ores, viz. olivine, protoenstatite and talc, which have different structures and constituents.

EXPERIMENTAL

Materials

MgO, Fe_2O_3, SiO_2, talc, and graphite were all CR grade reagents supplied by Kanto Chem. Co. Ferric oxide was α-Fe_2O_3 containing a small amount of γ-Fe_2O_3. Talc showed 6.06% of weight losses when it was heated up to 1300 °C at 10 °C min^{-1}. Chemical analysis of talc gave the following composition (wt %): SiO_2, 58.96; MgO, 31.63; H_2O, 6.06.

FeO was prepared by thermal decomposition of $Fe(CO_2)_2$ (Kanto Chem. Co.) at 850 °C for 20 min in vacuum[4].

α-Cristobalite was obtained by calcining silicic acid anhydride in air at 1300 °C for 4 h.

Olivine was a natural ore from Tokachi, Hokkaido and the result of its chemical analysis was as follows (wt %): SiO_2, 43.63; MgO, 43.58; Fe_2O_3, 7.81; Al_2O_3, 1.69; CaO, 0.19; MnO, 0.24.

Three calcined olivine samples were prepared by heating in air at 1100 °C for 5 h, in air at 1350 °C for 5 h, and in nitrogen at 1100 °C for 6 h, respectively.

Protoenstatite was prepared from talc by calcining it in air at 1300 °C for 2 h. This sample contained a very small amount of α-cristobalite, and had the following composition (wt %): SiO_2, 62.68; MgO, 33.63; $Fe_2O_3+Al_2O_3$, 2.97; CaO, 0; MnO, 0.

All materials were sieved to obtain -150 mesh fractions except for talc and graphite which were available as -300 mesh powders.

Gas-flow DTA apparatus as a reactor of chlorination

Fig. 1 shows the schematic diagram of the gas-flow DTA apparatus used as a reactor for chlorination. Fig. 2 is a DTA cell tube. The apparatus consisted of two quartz tubes (i.d. = 10 mm) placed vertically in a furnace, one was used as reference cell and the other as sample cell, in which Cl_2-gas flowed through the reference and sample powders during the chlorination experiment. Pulverized sample and reference material were kept at a fixed position in the cell tube by underlying loosely packed quartz wool.

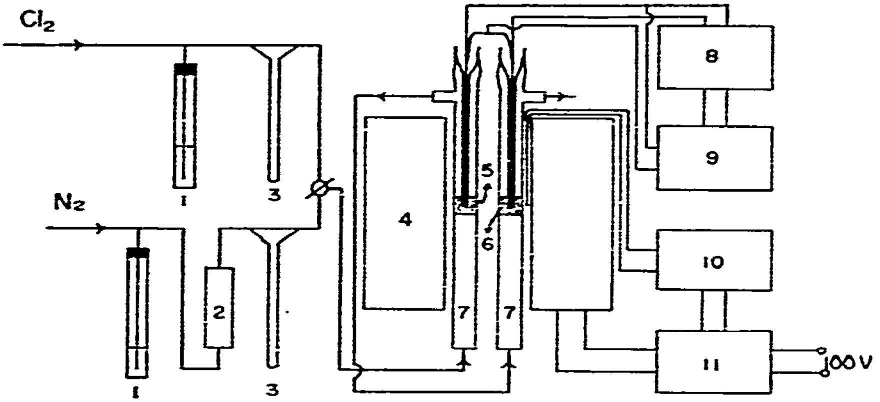


Fig. 1. Schematic diagram of gas-flow DTA apparatus. 1, Flow-rate controller; 2, silica gel; 3, flow meter; 4, furnace; 5, reference material; 6, sample; 7, DTA cell; 8, recorder; 9, amplifier; 10, program-controller; 11, volt-slider.

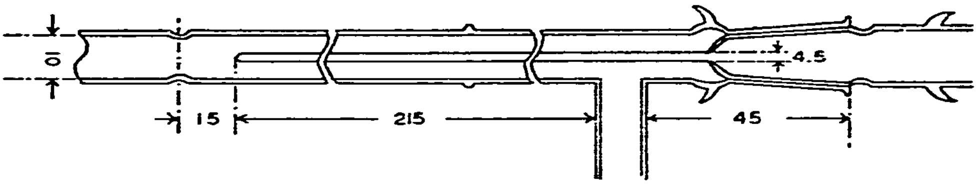


Fig. 2. Quartz DTA cell; unit of dimension: mm.

Chromel–alumel thermocouples (d = 0.3 mm) were protected by a fine quartz tube (o.d. = 4.5 mm) from corrosive atmospheric gas such as Cl_2 and they were placed at the center of the sample and reference materials in the cells. The heating rate of the furnace was controlled by the ECP-51B Type program controller (Ohokura Electric Ins.) and the differential temperature was recorded by the 25SB4-IR-6 Type millivolt recorder (Ohokura) through the AM1001B Type micro-voltmeter (Ohokura). 1 g of α-Al_2O_3 (−150 mesh, Merck) calcined at 1290°C for 3 h was used as reference material. X-ray diffraction and chemical analysis showed that α-Al_2O_3 did not react with Cl_2-gas in the temperature range up to 1000°C. The temperature range applicable to this apparatus was up to 1000°C, and the strong corrosive gases such as Cl_2 and HCl could flow at a range of gas flow-rate from 0 ml min^{-1} (standard static technique) to 300 ml min^{-1} (fluidized bed technique).

In the standard DTA experiments, 1 g of sample, at a heating rate of 5°C min^{-1} and a Cl_2-gas flow-rate of 30–50 ml min^{-1} were employed. Carbon was well mixed with the sample in an agate mortar.

In order to analyse the changes of sample in the course of DTA runs, the samples heated up to various temperatures were rapidly quenched to room temperature by throwing water on the sample cell immediately after the cell was taken out of the furnace. N_2-gas stream was passed through the apparatus to stop the reaction and to displace Cl_2 prior to quenching the samples.

It must be kept in mind, that for a successful operation of this simple apparatus, the heating rate and the gas flow-rate should be kept constant during the experiment.

Chemical analysis and estimation of conversion

The analysis of constituents of sample ores was carried out according to the prescribed method[5].

The fractional conversion, α, for the chlorination of Mg to $MgCl_2$ was defined by the following relation,

$$\alpha(\%) = \frac{\text{Mg in MgCl}_2\text{ formed by the reaction, Mg(R)}}{\text{Total Mg in the starting sample, Mg(T)}} \times 100 \qquad (1)$$

In the case of MgO sample, Mg(T) was estimated by EDTA-chelatometric titration of Mg^{2+} in 0.1 N HNO_3 solution containing dissolved sample, and Mg(R) was determined by $AgNO_3$-titration of Cl^- in aqueous solution of the reacted sample.

In the case of complex ores, the gravimetric analysis was used for determining the Mg^{2+} content, because chelatometry is not possible due to unfavorable effects of other metallic ions which coexist with Mg^{2+} in the solution. First, the reacted sample was dissolved in water and filtered. The ions such as Fe^{3+}, Fe^{2+} and Al^{3+} in the filtrate were removed as precipitates of the hydroxides by adding NaOH. Then, Mg^{2+} remaining in the filtrate was precipitated as $MgNH_4 \cdot PO_4 \cdot 6H_2O$ by adding a saturated solution of $(NH_4)_2 \cdot HPO_4$. The precipitate was converted to $Mg_2P_2O_7$ by ignition and its weight was corrected for MgO.

X-ray diffraction

The diffractometer used was Geigerflex 2141 Type (Rigaku Denki Co.) and was operated at the following conditions: Cu-target, Ni-filter, 25 kV, 10 mA, and 1 sec-time constant; Co-target for sample of iron compounds, Fe-filter, 35 kV, 10 mA, and 2 sec-time constant.

Thermogravimetry

The apparatus consisted of a quartz spring (sensitivity: 3.25×10^{-3} g/mm) with a small quartz basket and a quartz reaction tube (o.d. = 40 mm) connected to the vacuum system. The weight change was measured by a cathetometer as a function of temperature.

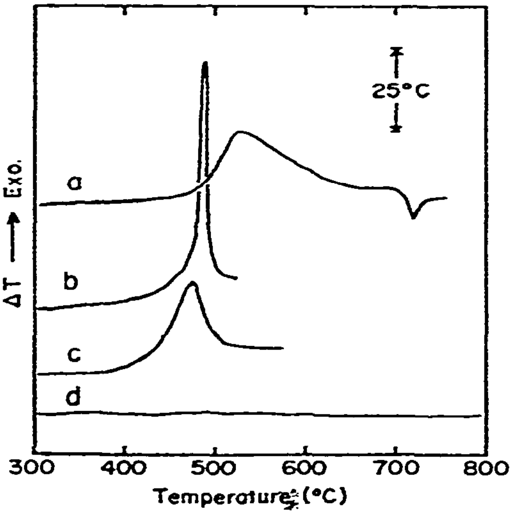
RESULTS AND DISCUSSION

In order to obtain the fundamental data needed for discussion of the chlorination behavior of magnesium-containing ores, the chlorination of MgO, FeO, Fe_2O_3 and SiO_2, which are the principal constituents of the ores, was examined as a preliminary investigation and as a test for availability of the apparatus.

Chlorination of the constituents

MgO. Fig. 3 shows DTA curves of Cl_2–MgO–C systems; the mixing molar ratio of C/MgO was changed from 0 to 3. At C/MgO = 0, there is no thermal deflection on curve (d) and even when MgO was isothermally treated in Cl_2-gas at 640°C for 4 h, no formation of $MgCl_2$ was observed. In the case of C/MgO > 0, however, the sharp exothermic peak which corresponds to formation of $MgCl_2$, appears at around 500°C. This peak shifts to lower temperatures with increasing amount of carbon. From these results, it is found that chlorination of MgO is promoted by adding carbon and this promoting effect is associated with the amount of carbon. Chemical analysis of the sample obtained just after the exothermic peak showed that α was about 50%. For the case of C/MgO = 2, the reacting amounts of carbon and MgO at $\alpha = 51.1\%$ were found to be consistent with the stoichiometry, $MgO + C + Cl_2 \rightleftharpoons MgCl_2 + CO$. The endothermic peak at about 720°C on curve (a) corresponds to the melting point of $MgCl_2$ formed.

Furthermore, the isothermal chlorination experiments at 500°C were carried out in order to compare them with the results of the DTA experiments described above. The results are shown in Fig. 4. At C/MgO = 0, α is negligibly small at 7 h.



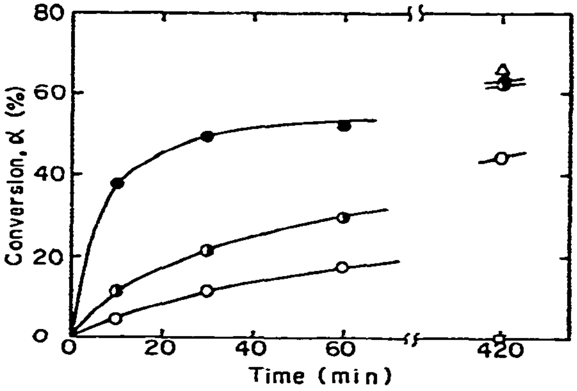


Fig. 3. DTA curves for the chlorination of MgO–C systems. C/MgO (molar ratio): curve (a) = 1; (b) = 2; (c) = 3; (d) = 0. Flow-rate of Cl_2, 35 ml min^{-1}; heating rate, 5°C min^{-1}.

Fig. 4. Isothermal chlorination of MgO at 500°C. C/MgO (molar ratio): ○ = 0.5; ◑ = 1; ● = 2; △ = 3; □ = 0.

At C/MgO = 1 and 2, the initial stage indicating the rapid chlorination corresponds to the exothermic DTA peak in Fig. 3. All curves tend to converge to about $\alpha = 60\%$ as the reaction proceeds. From this fact, it is considered that $MgCl_2$ formed on the surface of the MgO particle acts as a barrier against further progress of the reaction.

The reducing action of carbon on MgO was examined by means of TG to find its role in the chlorination reaction. When the disc with the mixture of MgO with carbon was heated up to 1000 °C at a heating rate of 5 °C min^{-1} in N_2 (30 mm Hg), no weight change was observed. This leads to the conclusion that carbon does not reduce MgO to Mg metal in the MgO–C–N_2 system, but acts as a reducing reagent in the MgO–C–Cl_2 system.

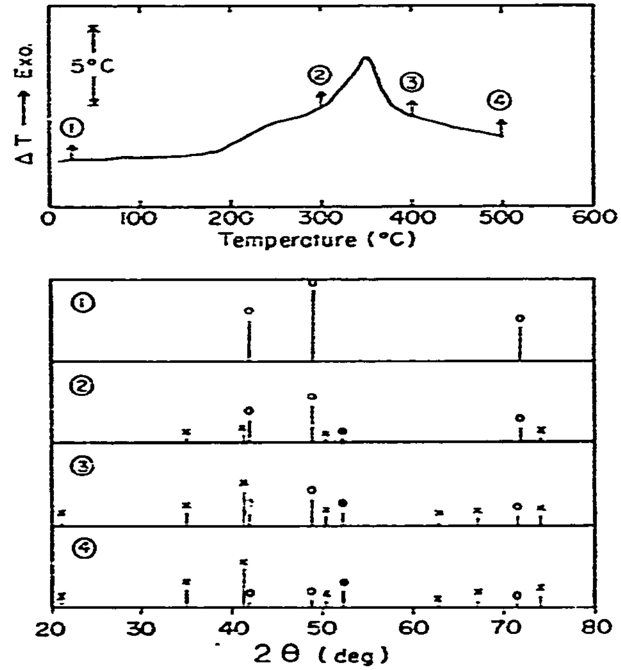


Fig. 5. DTA curve of FeO in N_2 and X-ray diffraction patterns of samples obtained at various temperatures shown on DTA curve. Flow-rate of N_2, 50 ml min^{-1}; heating rate, 5 °C min^{-1}. ○ = FeO; ● = α-Fe; × = Fe_3O_4.

FeO. Fig. 5 shows the DTA curve of FeO alone in the flowing N_2 atmosphere (50 ml min^{-1}) and X-ray diffraction patterns of four samples which were taken at the temperatures (points ①–④) shown by the arrows. From these results, it is found that the exothermic peak at around 350 °C corresponds to the disproportionation of FeO to α-Fe and Fe_3O_4. In the case of FeO with carbon (C/FeO = 2), the similar X-ray result was also obtained from samples heated up to 200 and 400 °C. Moreover, no effect of α-Al_2O_3 on both DTA curve and X-ray diffraction pattern was recognized, when α-Al_2O_3 was added to the FeO–C system (FeO, 148 mg; C, 52 mg; α-Al_2O_3, 800 mg) as a diluent.

Fig. 6 shows DTA curves in the flowing Cl_2 atmosphere (30 ml min^{-1}). Curve (a) shows the result of FeO without carbon (FeO, 200 mg; α-Al_2O_3, 800 mg), in which a sharp exothermic peak appears at about 150°C. The X-ray diffraction pattern of the sample, which was taken at 250°C (point ①) and then washed with water, shows that a small amount of Fe_3O_4 is formed, but FeO and $FeCl_2$ are not present as seen in the figure. This shows that almost all FeO was chlorinated at around 150°C and $FeCl_2$ formed was washed out with water. Curve (b) shows the DTA result of FeO mixed with carbon (FeO, 144 mg; C, 56 mg; α-Al_2O_3, 800 mg). The DTA curve and X-ray diffraction pattern of sample obtained at 400°C were similar to those shown by the sample for curve (a). This similarity means that carbon has no promoting effect in such a low temperature chlorination.

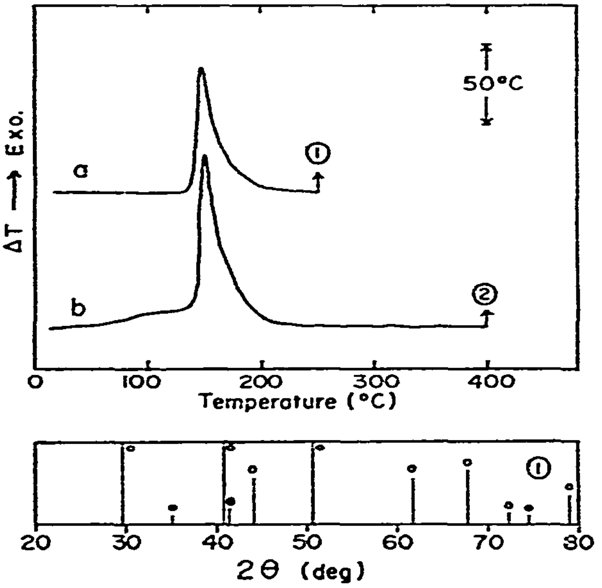


Fig. 6. DTA curves of FeO and FeO–C system in Cl_2, and X-ray diffraction pattern of FeO-sample heated up to 250°C in Cl_2 (curve (a)). Flow-rate of Cl_2, 30 ml min^{-1}; heating rate, 5°C min^{-1}. Curve (a): FeO = 200 mg, α-Al_2O_3 = 800 mg; curve (b): FeO = 144 mg, C = 56 mg, α-Al_2O_3 = 800 mg. ○ = α-Al_2O_3, ● = Fe_3O_4.

Fe_2O_3. Fig. 7 shows the DTA curve of Fe_2O_3 with carbon (Fe_2O_3, 870 mg; C, 130 mg) in the flowing Cl_2 atmosphere (30–35 ml min^{-1}) and the X-ray diffraction patterns of the same Fe_2O_3–C mixtures which were treated in the flowing N_2 atmosphere. The exothermic peak at about 450°C corresponds to chlorination of Fe_2O_3. This peak temperature is much higher than that of FeO (Fig. 6). In the flowing N_2, the Fe_2O_3–C mixture does not show any thermal deflections on the DTA curve in the range from 25 to 1000°C, and the X-ray diffraction pattern of sample heated up to 450°C shows no essential change as seen in the figure. Therefore, it is thought that Fe_2O_3 is not reduced with carbon at temperatures before the chlorination reaction proceeds.

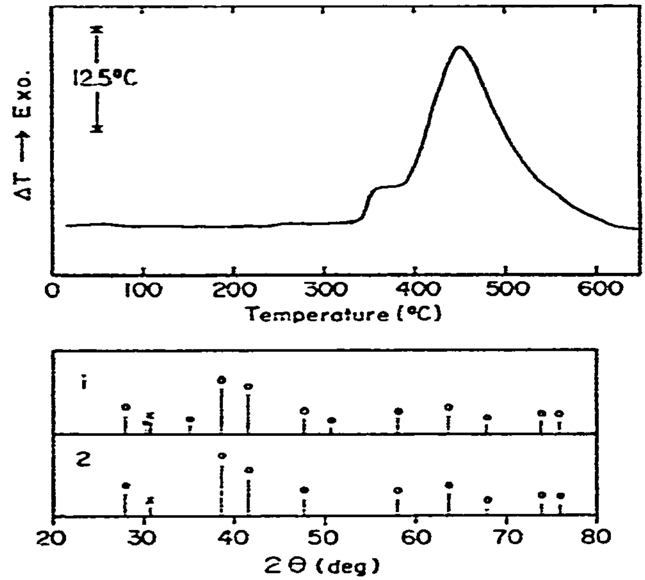


Fig. 7. DTA curve of Fe_2O_3–C system in Cl_2 and X-ray diffraction patterns of samples heated in N_2. Flow-rate of Cl_2 and N_2: 30–35 ml min^{-1}; heating rate: 5°C min^{-1}. X-ray chart: 1 = sample at 25°C; 2 = sample at 450°C. ○ = α-Fe_2O_3; ● = γ-Fe_2O_3; × = graphite.

Our experimental results differ from those shown by Ivashentsev[6]. The reason seems to be due to the difference in reactivity of Fe_2O_3 and FeO samples which were prepared by the different ways.

SiO_2. DTA experiments on silicic acid anhydride and α-cristobalite containing carbon ($C/SiO_2 = 2$) in the flowing Cl_2 (30–35 ml/min) showed no temperature deflection over the range between 25 and 950°C. The X-ray diffraction pattern of SiO_2 obtained at 950°C showed no structural change owing to the chemical reaction of SiO_2 with Cl_2. SiO_2 can thus be regarded as inert towards Cl_2 up to 950°C.

Chlorination of the ores

Olivine. Fig. 8 shows DTA curves of four mixtures of olivine–C of different ratios and of carbon alone in the flowing Cl_2 (30–35 ml min^{-1}); curves (a), (b), (c), and (d) correspond to the results from ores (1000 mg) containing carbon of 111, 250, 500, and 0 mg, respectively. Curves (a)–(c) have a large exothermic peak at around 950°C and a small one at about 870°C, and curve (c) shows another broad exothermic peak at about 700°C. In curve (d), there is no thermal deflection. The DTA result from the sample of the same mixing ratio as for curve (b) showed no peak in the flowing N_2 atmosphere. Curve (e) is the DTA result of carbon alone (600 mg) in the flowing Cl_2 atmosphere. In this case, two exothermic peaks at 870 and 950°C which appeared in curves (a)–(c) are not seen, but a broad exothermic peak appeared at about 700°C, which seems to correspond to the peak at the same temperature on curve (c). This peaks is probably due to some interactions of Cl_2 with carbon, such as heat of adsorption. However, the exact identification of the peak cannot be made at present.

The results of X-ray analysis[7] of the residues, which were obtained by washing the samples heated up to temperatures indicated by points ⑦, ⑧ and ⑨ on curve (b),

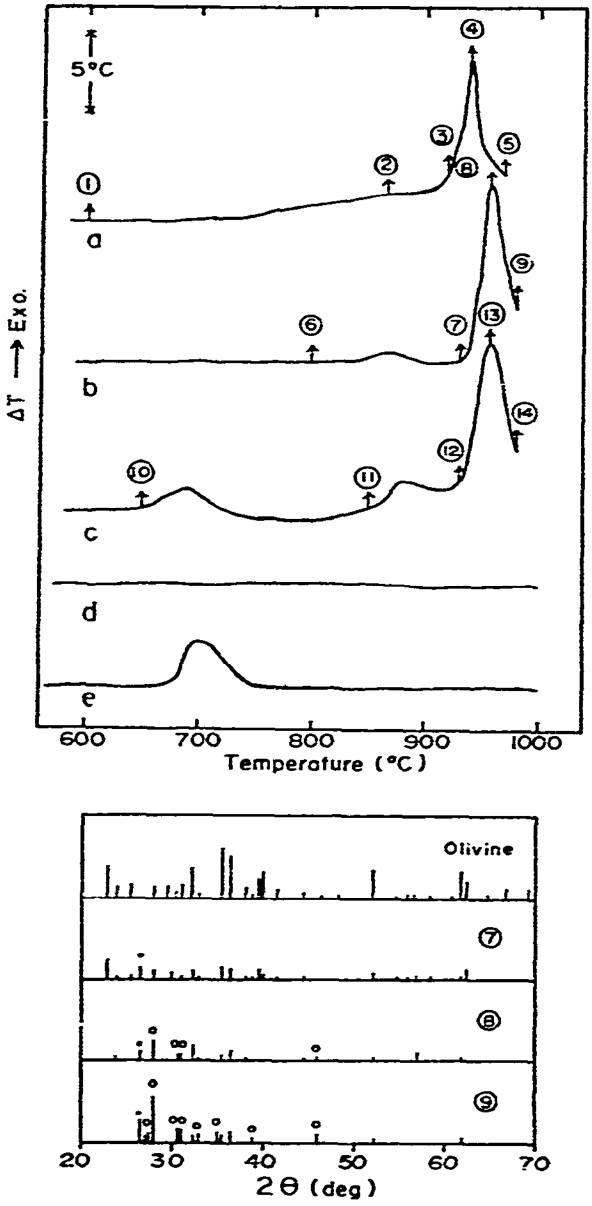


Fig. 8. DTA curves of olivine–C systems and C in Cl_2, and X-ray diffraction patterns of olivine and the samples heated up to various temperatures; ⑦, ⑧, and ⑨ for curve (b). Curve (a): olivine = 1000 mg, C = 111 mg; curve (b): olivine = 1000 mg, C = 250 mg; curve (c): olivine = 1000 mg, C = 500 mg; curve (d): olivine = 1000 mg, C = 0 mg; curve (e): olivine = 0 mg, C = 600 mg. Flow-rate of Cl_2, 30–35 ml/min; heating rate, 5°C min^{-1}. ● = Graphite; ○ = protoenstatite; no mark = olivine.

are given in Fig. 8 which shows the increase in the intensity of protoenstatite (○ mark) with increasing temperature. The X-ray diffraction pattern of the sample obtained at 980°C (point ⑨) shows that almost all olivine has changed to protoenstatite and the chemical analysis gives an α value of 50%. The reason why the α value of the sample heated up to 980°C shows such a low value seems to be due to a lower reactivity of Mg in protoenstatite.

Fig. 9 shows α values of samples obtained at various temperatures (points ①–⑭) on the DTA curves (a), (b) and (c) in Fig. 8. From these α values, it is concluded that the two exothermic peaks at about 870 and 950°C were the result of the chlorination of Mg in olivine to $MgCl_2$, and these two peaks may result from two kinds of Mg having different reactivities for the chlorination. The small α value (about 5%) shown over the range of 600–800°C was probably due to the uncertainties of chemical analysis, because there are no thermal deflections in this temperature range and α is independent of the amount of carbon additive and of temperature.

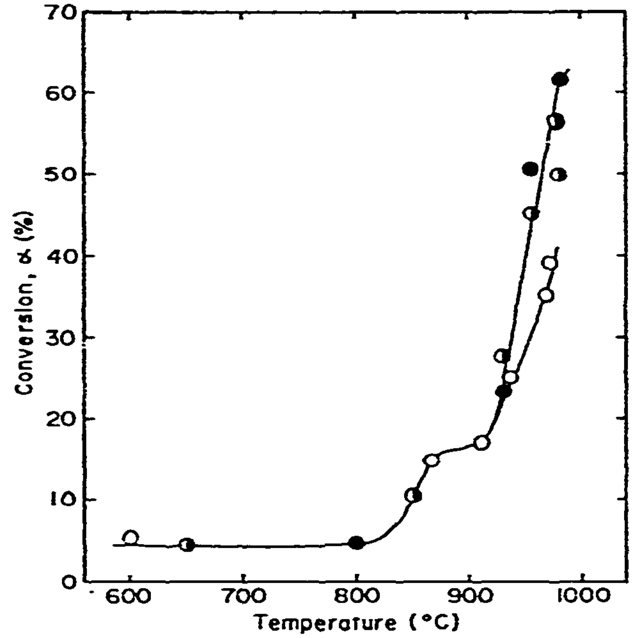


Fig. 9. Fractional conversions, α, of the chlorinated olivine samples obtained at various temperatures shown on DTA curves (a), (b) and (c) in Fig. 8. ○ = curve (a); ● = curve (b); ◑ = curve (c) in Fig. 8.

Calcined olivine. Fig. 10 shows DTA curves of calcined olivine (1000 mg) with carbon (250 mg) in the flowing Cl_2 atmosphere (30–35 ml min^{-1}). Curves (a) and (c) correspond to the results of the olivine samples calcined in air at 1100 and 1350°C, and curve (b) to the sample calcined in N_2 at 1100°C.

In curves (a) and (b), three exothermic peaks (peaks 1, 2 and 3) appear at about 850, 880 and 930–950°C. It is assumed that a broad exothermic peak observed for the uncalcined olivine at about 870°C (Fig. 8) splits into two peaks; a small peak 1 and a large peak 2. This indicates that olivine ore originally contains three kinds of Mg having different reactivities for the chlorination, and the difference of reactivity becomes appreciable when it was calcined in air or N_2 prior to the chlorination.

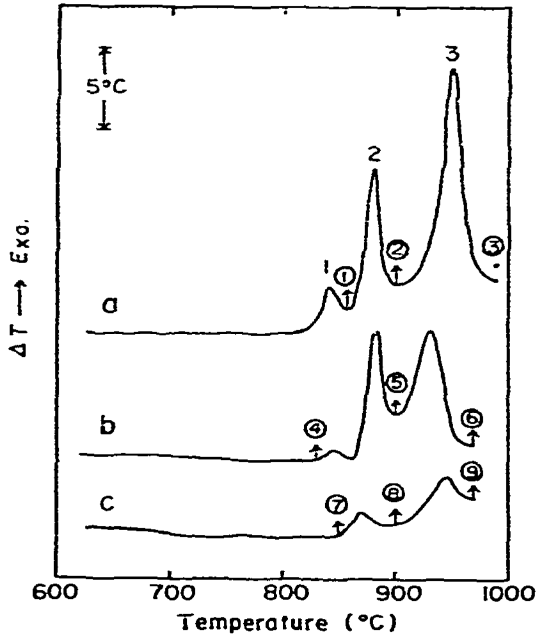


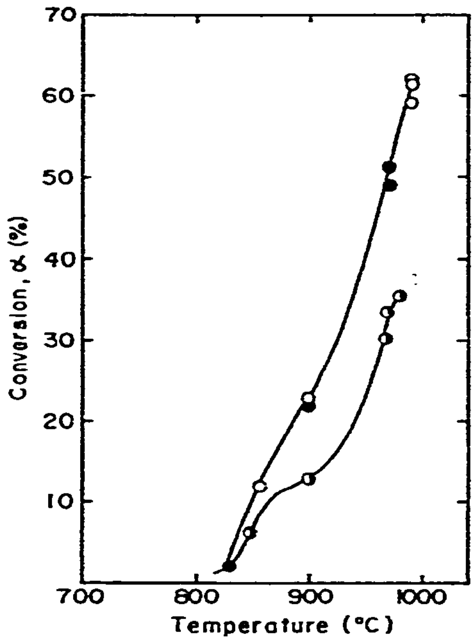
Fig. 10. DTA curves of calcined olivine–C systems in Cl_2. Flow-rate of Cl_2, 30–35 ml min^{-1}; heating rate, 5°C min^{-1}. Calcined olivine, 1000 mg and carbon, 250 mg. Curve (a): calcined olivine in air at 1100°C; curve (b): calcined olivine in N_2 at 1100°C; curve (c): calcined olivine in air at 1350°C.

Curve (c) shows two broad DTA peaks. On the basis of the observation that the sample treated in air at 1350°C partly melted and solidified during the treatment, it is considered that these broad peaks are due to the low reactivity of this sample caused by the high temperature treatment.

In the case of no carbon, the sample calcined at 1100°C for 5 h showed no DTA peak in the flowing Cl_2, no conversion, and no changes of the X-ray diffraction pattern. Further, the DTA experiment on the same sample containing carbon carried out in N_2 also showed the same results. These results may indicate that Mg in the calcined olivine does not react individually with Cl_2 or carbon in the range of 25–1000°C. When both Cl_2 and carbon coexist with olivine in the reaction system, the chlorination reaction of Mg may proceed.

Fig. 11 shows α values of the samples obtained at various temperatures (points①–⑨) on the DTA curves in Fig. 10. It is observed that the sample heated at 1350°C (◑ mark) shows lower α values than samples heated at 1100°C.

Protoenstatite. The sample was prepared by calcinating talc in air at 1300°C for 2 h. Fig. 12 shows the DTA curve of protoenstatite (1000 mg) containing carbon additive (100 mg) measured in the flowing Cl_2 (30–35 ml min^{-1}), and X-ray diffraction patterns of the starting sample and the chlorinated sample at 980 °C.



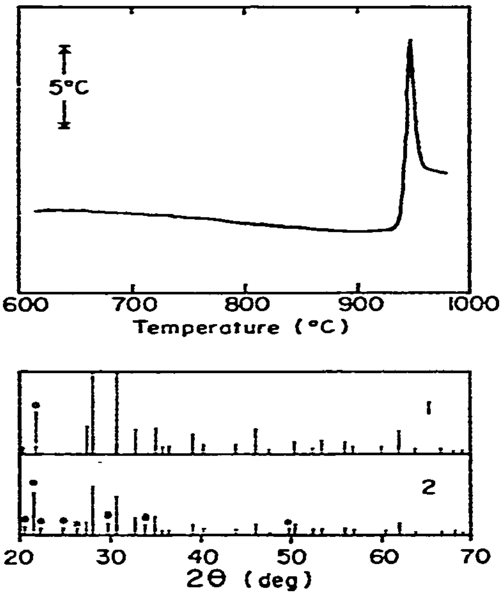


Fig. 11. Fractional conversion, α, of the calcined olivine samples obtained at various temperatures shown on DTA curves in Fig. 10. ○ = curve (a); ● = curve (b); ◑ = curve (c) in Fig. 10.

Fig. 12. DTA curve of protoenstatite–C system in Cl_2, and X-ray diffraction patterns of protoenstatite and sample obtained at 980 °C. Flow-rate of Cl_2, 30–35 ml min^{-1}; heating rate, 5 °C min^{-1}. Protoenstatite, 1000 mg and carbon, 100 mg. X-ray chart: 1 = sample at 25 °C; 2 = chlorinated sample at 980 °C. ○ = α-Cristobalite; × = graphite; ● = $MgCl_2$ and its hydrates; no mark = protoenstatite.

An exothermic peak appears at about 950 °C, and the X-ray diffraction pattern of the chlorinated sample shows the presence of $MgCl_2$ formed. On the other hand, in the case of no carbon additive, not any DTA peak could be observed. From these results, it is found that the exothermic peak at about 950 °C was caused by chlorination of protoenstatite mixed with carbon to $MgCl_2$. At 980 °C α was measured to be 20.5–30.6% (mean value for five samples was 25.1%). The exothermic peak is located at almost the same temperature as that of olivine (Fig. 8), but the α value is very small.

When comparing α values of olivine (α = about 60% at 980 °C) and of protoenstatite (α = about 25% at 980 °C), it is found that the chlorination of olivine proceeds at around 980 °C according to the following processes:

$$Mg_2SiO_4+C+Cl_2 \rightarrow MgSiO_3+MgCl_2+CO \qquad \text{(Fig. 8)} \qquad (2)$$

$$MgSiO_3+0.25C+0.25Cl_2 \rightarrow 0.75MgSiO_3+0.25MgCl_2+0.25SiO_2+0.25CO \qquad \text{(Fig. 12)} \qquad (3)$$

or eqn (2)+(3)

$$Mg_2SiO_4+1.25C+1.25Cl_2 \rightarrow 0.75MgSiO_3+1.25MgCl_2+0.25SiO_2+1.25CO \quad (4)$$

where Mg_2SiO_4 and $MgSiO_3$ correspond to olivine and protoenstatite, respectively.

Talc. Curve (a) in Fig. 13 shows the DTA curve of talc (300 mg) in static air measured by Rigaku DTA apparatus (Rigaku 8001 Type). Three peaks appear at about 625, 860 and 1000°C. Curv (b) is the result of TG experiment at the same conditions as of curve (a). A steep weight decrease observed at 900–1050°C corresponds to the endothermic peak at 1000°C of curve (a).

X-Ray diffraction patterns of the samples obtained at various temperatures of DTA curve (a) show that at point ④ (995°C) a small amount of protoenstatite (○ mark) is formed. At point ⑤ (1062°C) the diffraction lines corresponding to talc

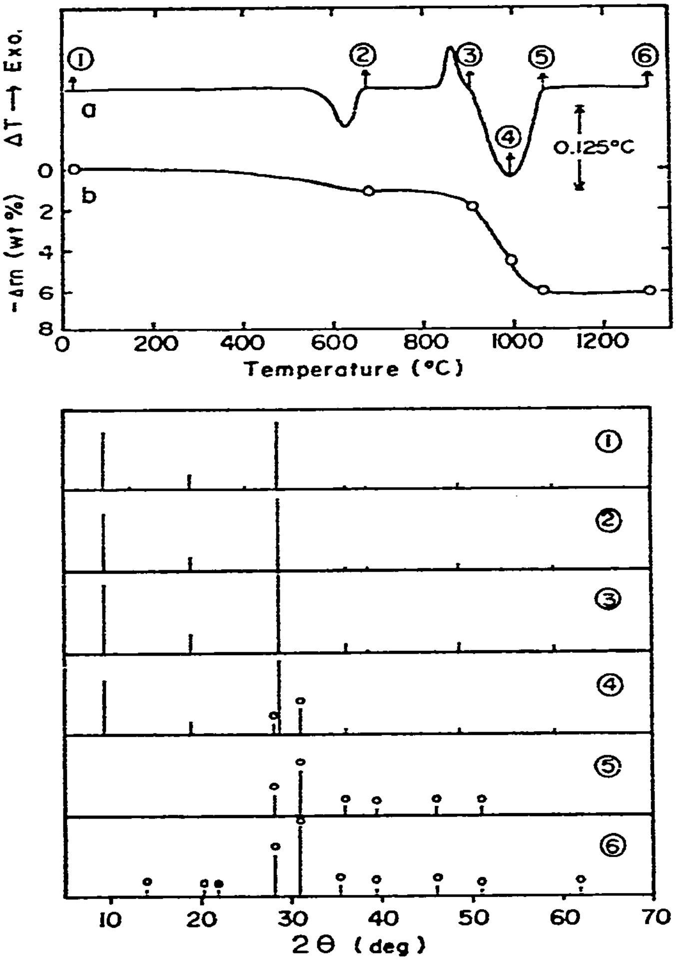


Fig. 13. DTA and TG curves of talc measured in static air, and X-ray diffraction patterns of samples obtained at various temperatures shown on DTA curve (a). Heating rate: 10°C min^{-1}; talc: 300 mg; ○ = Protoenstatite; ● = α-cristobalite; no mark = talc.

disappear and all the lines correspond to protoenstatite. At point ⑥ (1300°C) the strongest diffraction (101) line of α-cristobalite appears at $2\theta = 21.9°$. Furthermore, when the sample was heated in air at 1300°C for 2 h, an increase in the intensity of the diffraction line of α-cristobalite was found.

From these results, the decomposition of talc to protoenstatite is found to begin rapidly at about 900°C in air according to the following equation,

$$Mg_3(Si_2O_5)_2(OH)_2 \rightarrow 3MgSiO_3 + SiO_2 + H_2O. \qquad (5)$$

Next, the chlorination experiments in the temperature range of 25–950°C were carried out in the flowing Cl_2 (30–35 ml min^{-1}) by means of gas-flow DTA apparatus. The results of DTA and X-ray analysis are shown in Fig. 14. The DTA curve (a) of talc (1000 mg) containing carbon (94 mg) shows a sharp exothermic peak at about

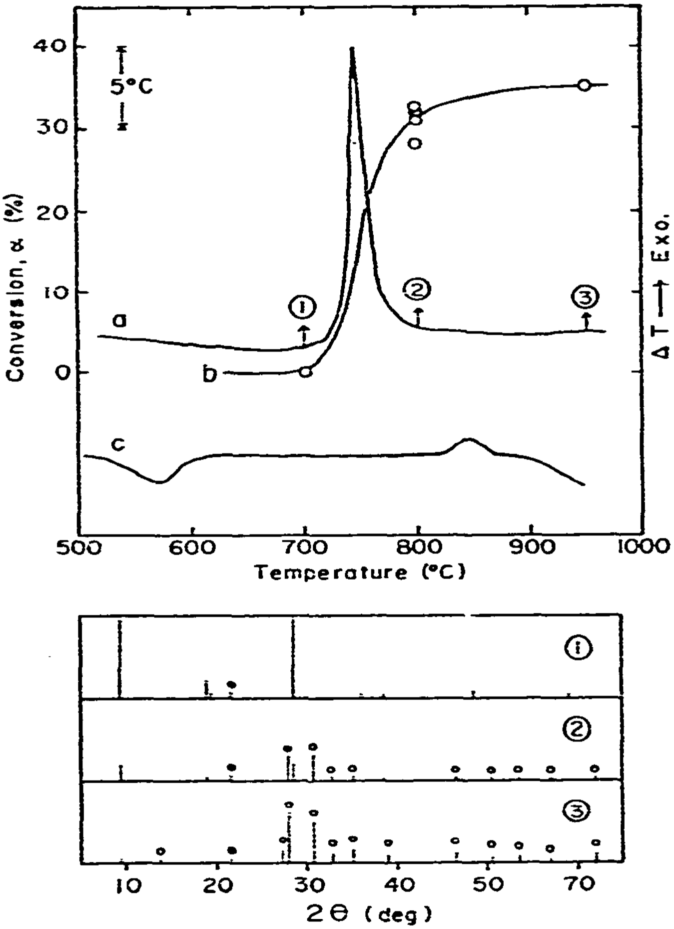


Fig. 14. DTA curves of talc–C system in Cl_2 (curve (a)) and in N_2 (curve (c)); fractional conversions (curve (b)), and X-ray diffraction patterns of samples obtained at various temperatures shown on DTA curve (a). Flow-rate of Cl_2: 30–35, N_2: 40 ml min^{-1}; heating rate: 5°C min^{-1}. Talc, 1000 mg and C, 94 mg. ○ = Protoenstatite; ● = graphite; no mark = talc.

750 °C. X-ray analysis of residues prepared by washing the samples which were heated up to three temperatures indicated on DTA curve (a), shows that the formation of protoenstatite occurred at 800 °C (point ②). The sample obtained at 950 °C (point ③) has no X-ray lines of talc.

Curve (b) shows the relationship between α and temperature, which indicates that the exothermic peak is a result of the chlorination. This α–T curve and X-ray results may show that, in Cl_2 atmosphere, the decomposition and the chlorination of talc occur simultaneously at lower temperatures compared with the decomposition temperature found in air (Fig. 13). In the case of talc alone, however, in Cl_2 atmosphere there was not any DTA peak, and the α value at 950 °C was zero.

Curve (c) shows the DTA result in the flowing N_2 atmosphere for the same sample used for curve (a). The result is similar to that obtained for talc alone in air (Fig. 13).

From these results, it is concluded that the decomposition of talc is not promoted by carbon alone and for the chlorination of talc the coexistence of Cl_2 and carbon is needed.

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REFERENCES

1 A. W. Henderson, *J. Metals*, (1964) 155.
2 K. Funaki, *Chem. and Chem. Ind. (Chem. Soc. Japan)*, 24 (1971) 120.
3 *Chem. Eng. News*, 29 (1971) 31.
4 P. L. Gunther and H. Z. Rehaag, *Z. Anorg. Allgem. Chem.*, 243 (1939) 60.
5 The Mineral. Soc. Japan, *Experimental Mineralogy*, Kyoritsu, Tokyo, 1966, p. 58.
6 Y. I. Ivashentsev, *J. Tomskogo Gas. Univ., Ser. Khim.*, 170 (1964) 146; *C. A.*, 63 (1965) 4306*e*.
7 H. S. Yoder, Jr. and T. G. Sahama, *Amer. Mineral.*, 42 (1957) 475.