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DTA Study of the Chlorination of Bauxite

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The chlorination processes of bauxite, which consists mainly of gibbsite (Al) and hematite (Fe), were studied in the presence of active carbon by means of a gas-flow type DTA apparatus. Of the two exothermic peaks appeared at about 270 and 490°C, the former was found to correspond to the chlorination of Fe and was influenced by the formation of water due to dehydration of gibbsite in bauxite, and the latter corresponded to the chlorination of Al. In order to examine the chlorination behaviors of bauxite in more detail, the chlorination of hydrated alumina, hematite and their mixtures were carried out too.

1. Introduction

In the previous work[1], a simple gas-flow DTA apparatus with a flow system by which Cl_2-gas can flow through the reference and the sample powder beds have been developed and applied to the study of chlorination of various Mg-containing ores. In this paper, the chlorination processes of bauxite and its constituents such as hydrated alumina and hematite were studied by means of this gas-flow type DTA apparatus.

2. Experimental

2.1 Materials

A chemical analysis of sample bauxite is shown in Table 1. The analysis was carried out according to the prescribed method[2]. Bauxite was ground to pass through a 200 mesh sieve. Bayerite, hematite (−150 mesh) and active carbon were all GR grade commercial reagents. Gibbsite was prepared from the aqueous solution of sodium aluminate.

Table 1 Chemical analysis of bauxite (wt%)

Al_2O_3*	Fe_2O_3**	SiO_2	TiO_2	Ig. loss
54.0	8.2	4.5	1.0	30.3

* gibbsite, ** hematite

2.2 DTA experiments

The gas-flow DTA apparatus[1] used consisted of two quartz tubes (i.d.=10mm) placed vertically in a furnace, the one used as a reference cell and the other as a sample cell. Cl_2-gas flowed through the reference and sample powders during the chlorination experiments. Active carbon was well mixed with bauxite in a V-type mixer for 1 h. In the standard DTA experiments, the mixing ratio of bauxite/carbon = 2 (wt. ratio), total sample weight of 500~700mg, heating rate of 5°C/min and Cl_2-gas flow rate of $30cm^3/min$ were employed.

In order to analyse the samples in the course of DTA runs, the samples heated up to various temperatures were rapidly quenched to room temperature after the cell was taken out of the furnace. The chlorides of constituents in bauxite were dissolved in water, and Al and Fe in the residue were analysed[2].

2.3 Model experiments

In order to examine the chlorination behavior of bauxite in more detail, the chlorination of mixtures of its components, i.e., hydrated alumina and hematite, were carried out. Mixing ratio was 1 : 1 : 1 for the alumina - hematite - carbon system, and 2 : 1 for the alumina - carbon or hematite - carbon system.

3. Results and discussion

Fig. 1 shows the chlorination processes of bauxite - carbon systems. Curve (a) shows the DTA curve of bauxite - active carbon system in the flowing Cl_2. Two exothermic peaks appear at about 270 and 490 °C. From the fractional conversion of Fe and Al of the chlorinated samples, it is thought that these peaks correspond to the chlorination of Fe and Al in the bauxite ore, respectively. However, the peak at 270 °C is abnormally large, compared with the peak at 490 °C corresponding to the

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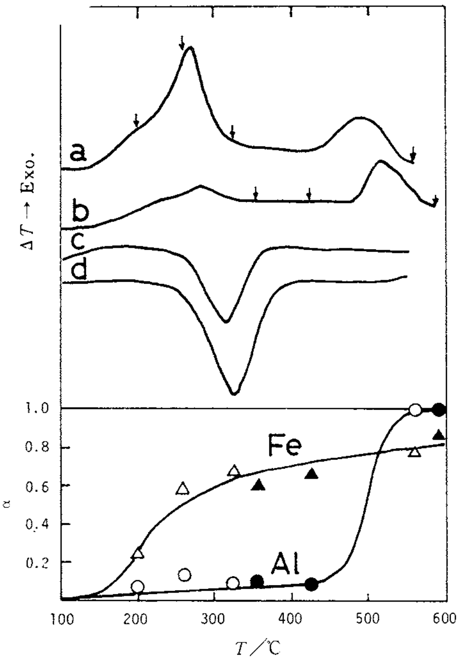

Fig. 1 DTA curves of bauxite (B) - active carbon (C) systems (2 : 1 in wt.) in chlorine (Cl_2) and nitrogen (N_2) and fractional conversions (α) of the chlorinated samples obtained at various temperatures shown in DTA curves. Flow-rate of Cl_2 and N_2: 30cm^3/min, heating rate: 5°C/min, total weight of sample: 500~700mg. B′: dehydrated bauxite.
a: B - C - (Cl_2), b: B′ - C - (Cl_2),
c: B - C - (N_2), d: B - (Cl_2)
○,△: α for curve (a) ●,▲: α for curve (b)

chlorination of Al. Curve (c) shows the DTA curve of the bauxite-carbon system in N_2. Only one endothermic peak corresponding to the dehydration of gibbsite appears at about 320°C. Curve (b) shows the DTA curve of the dehydrated bauxite (obtained from run c at 380°C) with carbon in the flowing Cl_2. The exothermic peak corresponding to the chlorination of Fe at about 290°C becomes small and peak corresponding to the chlorination of Al shifts to a little higher temperature. The behavior of the fractional conversion is same as the case of curve (a). On the basis of these data, it is thought that the large exothermic peak at about 270°C in the curve (a) was generated under the influence of the resulting water from the dehydration of gibbsite in bauxite. Curve (d) shows the DTA curve of bauxite alone in Cl_2. It is seen that no chlorination reaction occurs in the system without carbon in the temperature below 600°C.

Fig. 2 shows the model experiments. Curves (e) and (f) show the DTA curves of the hematite-bayerite-carbon systems in Cl_2 and N_2, respectively. The curves similar to the bauxite-carbon systems (a and c in Fig. 1) were obtained. Curve (g) without carbon is similar to bauxite without carbon (d in Fig. 1). The small endothermic peaks at 220~230°C in the curve (f) and (g) correspond to the decomposition of a part of bayerite to boehmite. Curve (h)~(k) show that the reaction behaviors of gibbsite and bayerite are analogous. The exothermic peak at 200~300°C seems to be due to the reaction among water resulting from the dehydration of gibbsite or bayerite, Cl_2 and active carbon. Curve (l) shows the DTA curve of dehydrated alumina (obtained

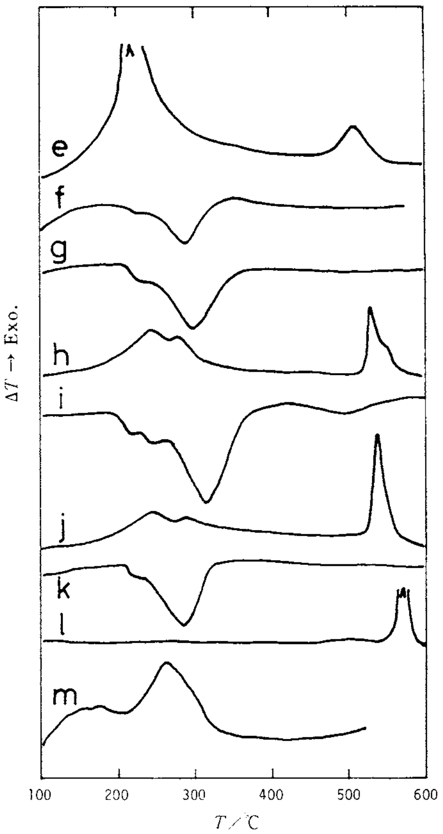

Fig. 2 DTA curves of gibbsite (Al_G), bayerite (Al_B), dehydrated bayerite ($Al_{B'}$), hematite (Fe) and mixtures between them in chlorine (Cl_2) and nitrogen (N_2). Flow-rate of Cl_2 and N_2: 30cm^3/min, heating rate: 5°C/min, total weight of sample: 500~700mg. C: active carbon
e : Fe - Al_B - C - (Cl_2) f: Fe - Al_B - C - (N_2),
g : Fe - Al_B - (Cl_2) or (N_2), h: Al_G - C - (Cl_2),
i : Al_G - (Cl_2), j : Al_B - C - (Cl_2),
k : Al_B - C - (N_2), l : $Al_{B'}$ - C - (Cl_2),
m: Fe - C - (Cl_2)

from run k at 370°C) with carbon in Cl_2, and no exothermic peak at 200~300°C is observed. Curve (m) is the result for the hematite - carbon system in Cl_2.

Acknowledgements

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References

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Thermochemical Studies of Au + Te

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Enthalpies of mixing of gold + tellurium have been measured at 769 K by a high temperature calorimeter. The results are in agreement with the values by Castanet *et al.*, but differ from those by Predel and Piehl. The enthalpy of fusion of $AuTe_2$ was also determined. These allow to evaluate the enthalpy of formation of $AuTe_2$(s).

Introduction

In the previous papers we have reported a series of enthalpies of liquid solution of B-metal + chalcogen systems.[1-4] The results indicated that these systems show large negative enthalpies of mixing in the liquid state, and the minima in the enthalpy – composition diagram appear at the compositions of the solid compounds at lower temperature. Both Castanet *et al.*[5] and Predel and Piehl[6] have measured the enthalpies of mixing in gold + tellurium system. Their values disagree each other, partly because of quite different experimental temperatures. In this paper the results obtained in our laboratory and the enthalpy of fusion of $AuTe_2$ are reported and are discussed in terms of bond formation in the liquid state.

Experimental

The calorimeter and the experimental procedure are the same as described in the previous paper.[1] For the determination of the enthalpy of fusion of the compound, the solution calorimetry method with the same experimental procedure as in the above mixing was applied. The $AuTe_2$ was dissolved in liquid tin both below and above the melting point. The concentrations of $AuTe_2$ in tin solvent after the dissolution were 1.2 and 1.5 mol per cent. In order to prepare the compound, the mixture of the nominal composition was sealed in an evacuated quartz tube and heated up to 775 K for 24 h. The purities of gold and tellurium were better than 99.99 mass per cent and that of tin was 99.96 mass per cent.

Results and Discussion

The observed enthalpies of mixing are shown in Table 1 and are plotted in Fig. 1 with the data of the previous authors. The present results are in good agreement with the values at 737 K by Castanet *et al.* and are much more endothermic than those of Predel and Piehl at 1281 K. In the second column of the Table 1, $H^E(s)$ is the raw value with solid gold. Subtracting the enthalpy of fusion times mole fraction of gold from $H^E(s)$, $H^E(l)$ is evaluated. The difference of heat capacities of liquid and solid was neglected. In Fig. 2 are plotted $H^E(l)$ referred to the pure liquid metals and the partial molar enthalpy of tellurium evaluated by derivative of $H^E(l)$ equation of fourth order of composition:

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