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THERMAL ANALYSIS AND KINETICS OF OXIDATION OF "Cr_3S_4" AND "Cr_2S_3"

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ABSTRACT

The thermal analysis and kinetics of oxidation of monoclinic "Cr_3S_4", trigonal "Cr_2S_3" and rhombohedral "Cr_2S_3" phases were studied by using both thermogravimetry and high temperature X-ray diffraction technique. The oxidation reactions of Cr_xS ($x=0.677\sim 0.751$) were as follows:

low temperature range (450°~ 500°C);

$$Cr_xS + \frac{3y}{4}O_2 = Cr_{x-y}S + \frac{y}{2}Cr_2S_3 \qquad (1)$$

high temperature range (500°~ 645°C);

$$Cr_xS + \frac{3x+4}{4}O_2 = \frac{x}{2}Cr_2O_3 + SO_2 \qquad (2)$$

Both the reactions were dependent on temperature, partial pressure of oxygen and phases of chromium sulfides. Reaction (1) was the preferred oxidation of chromium metal in the sulfides and the oxidation reaction obeyed the parabolic law. Reaction (2) ($0.01 \leq \alpha \leq 0.65$) was controlled by $1-(1-\alpha)^{1/3} = kt$. The phase transition of $Cr_{x-y}S$ during low temperature oxidation was also discussed.

INTRODUCTION

Chromium sulfides (Cr_3S_4, Cr_2S_3, etc.) are formed as a result of corrosion of Cr-base commercial alloys. There are reports on the sulfidation and oxidation of metallic chromium, but very little has been done on the thermal oxidation of chromium sulfides. When heating Cr_7S_8 coated Cr and bulk Cr_7S_8 in O_2 (100 torr) at 1050°C, Tedmon et al.[1] observed the formation of Cr_2O_3 and higher sulfides (undefined) without the evolution of SO_2. The kinetics in the initial stage of oxidation were parabolic, but in the later stage the rate decreased sharply. Tudo [2] reported that chromium sulfides started to gain weight from around 100°C when heated in O_2. Formation of $Cr_2(SO_4)_3$ and Cr_2O_3 was observed around 600°C but no SO_2 was detected below 580°C. Tudo also observed phase transition during this oxidation process. However, the phases of higher sulfides formed in

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the course of oxidation were not identified. There is also discrepancy regarding the formation of $Cr_2(SO_4)_3$.

In these circumstances, the purpose of this paper was to investigate the kinetics and oxidation processes of three principal phases, e.g. monoclinic Cr_3S_4 (m-"Cr_3S_4"), trigonal Cr_2S_3 (t-"Cr_2S_3") and rhombohedral Cr_2S_3 (r-"Cr_2S_3") in the Cr-S system under different experimental conditions.

EXPERIMENTAL

Measurement method

The TG-DTA measurements were performed with a Rapid-Heating Rigaku Thermoflex TG-DTA unit. Experimental procedures including the control of PO_2, the characterization of samples and oxidation products, the determination of rate equations, etc. have been reported elsewhere [3,4].

Sample preparation

Reagent grade Cr_2O_3 powder (Yoneyama Chem. Ind. Ltd., over 99% pure) was placed in a mullit boat and heated in a flow of H_2S gas (1 atm) at 950°C for 48h. Complete sulfidation of the sample was ascertained, and the composition of the heated sample was determined to be $CrS_{1.480}$. This sample was heated [5,6] at different Ps_2 (10^{-8} $\sim$1 atm) at 800°C for 5$\sim$16h to prepare m-"Cr_3S_4" ($Cr_{0.751}S$), t-"Cr_2S_3" ($Cr_{0.702}S$) and r-"Cr_2S_3" ($Cr_{0.677}S$). The phases were identified from the X-ray powder diffraction pattern, (CuK_α), and the compositions were determined by oxidizing the samples in air at 900°C for 24h to Cr_2O_3.

RESULTS AND DISCUSSION

Oxidation process

The TG-DTA curves for the oxidation of nonstoichiometric m-"Cr_3S_4", t-"Cr_2S_3" and r-"Cr_2S_3" at a Po_2 of 0.110 atm, at 10°C/m are shown in Fig. 1. All the TG traces recorded a slight gain in weight from around 100°C (not indicated in the figure) and a sharp loss from 630°, 635° and 725°C for the rhombohedral, trigonal and monoclinic phases, respectively. A sharp exothermic peak corresponding to the weight loss appeared in the DTA curves. An example of the effect of Po_2 on the TG-DTA profile is shown in Fig.2. The final

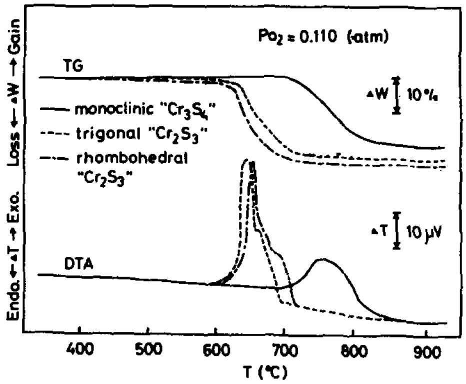

Fig.1 TG-DTA curves at 10°C/m (Sample: 10mg, 250~270mesh).

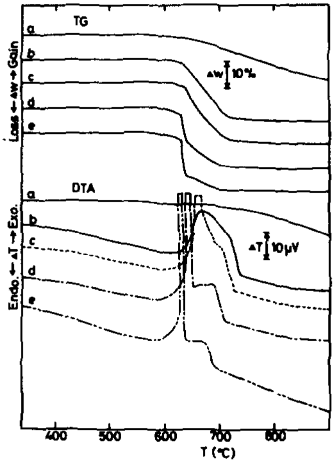

Fig.2 TG-DTA curves of t-"Cr_2S_3" at 10°C/m (Sample: 10mg, 250~270mesh; Po_2: a) 0.006, b) 0.044, c) 0.110 d) 0.209 and e) 0.412 atm)

oxidation product for all the samples was Cr_2O_3. The presence of SO_2 could not be detected in the outlet gas during the weight gain, and in all cases only Cr_2O_3 was found to be formed from 400°C.

The low temperature weight gain (ca. 4% without SO_2) and high temperature weight loss (ca. 20% with SO_2) became clear when the samples were heated isothermally. A typical example is shown in Fig.3 which indicates that the limiting temperature for these two reactions is 500°C when heating t-"Cr_2O_3" in air. This temperature increased with the decrease of Po_2, and it is almost the same for the rhombohedral phase. However, for m-"Cr_3S_4", this temperature could not be distinguished since the sample continued to gain weight even at higher temperature. The samples were examined after heating isothermally at different temperatures, but unlike Tudo [2], the formation of $Cr_2(SO_4)_3$ could not be detected. From this results, it is concluded that the oxidation reactions of chromium sulfides (Cr_xS) are

low temperature range: $Cr_xS + \frac{3y}{4}O_2 \xrightarrow{<500°C} Cr_{x-y}S + \frac{y}{2}Cr_2O_3$ (1)

high temperature range: $Cr_xS + \frac{3x+4}{4}O_2 \xrightarrow{>500°C} \frac{x}{2}Cr_2O_3 + SO_2$ (2)

Phase transition during low temperature oxidation

The transition of the monoclinic "Cr_3S_4" to trigonal Cr_2S_3 phase, and of the trigonal "Cr_2S_3" to rhombohedral Cr_2S_3 phase as generalize in Eq. (1) were observed from the high temperature X-ray

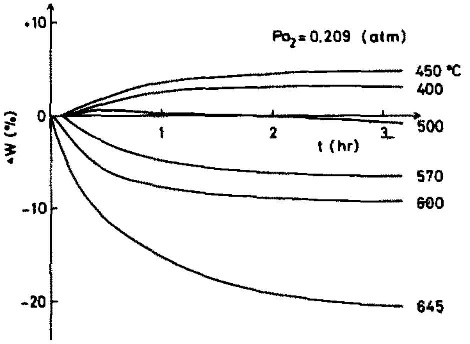

Fig.3 Isothermal TG curves for t-"Cr_2S_3" (Sample: 2.5mg, 250~270mesh).

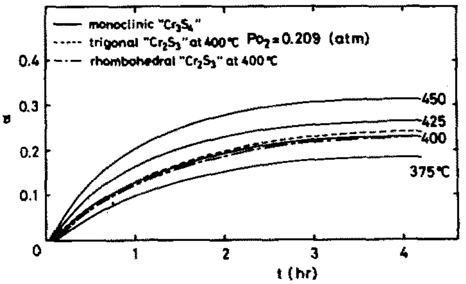

Fig.4 α vs. t plots for low temperature oxidation (Sample: 2.5mg, 250~270mesh).

diffraction pattern. The phase transition occurred by the relative increase in sulfur content due to the preferred oxidation of Cr in the sulfides.

Kinetics of low temperature oxidation (Eq. 1)

Typical α vs. t plots for the oxidation of Cr_xS according to Eq. (1) are shown in Fig.4. For r-"Cr_2S_3", the maximum weight gain was observed at 400°C. This can be explained by the fact that r-Cr_2S_3 has the smallest nonstoichiometry of the three phases [5] and less amount of Cr is available for oxidation, i.e. with the dissolution of a small amount of sulfur in the matrix, the highest limit of the rhombohedral phase is attained. It is clear from the α^2 vs. t plot shown in Fig.5 that the reaction initially obeys parabolic law, and after about 3h, the rate becomes slower than parabolic. The apparent activation energies were 140~145 kJ/mol and were independent of the sulfide phases. These values coincide with that of the oxidation of metallic chromium (150 ± 13 kJ/mol) at temperatures between 300 600°C reported by Young et al. [7]. This finding suggests that the rate determining step of Eq. (1) is the diffusion of Cr through the Cr_2O_3 layer since the diffusion of Cr through the sulfide is quite high [5].

Kinetics of high temperature oxidation (Eq. 2)

Kinetics of oxidation of m-"Cr_3S_4" could not be studied since both reactions (1) and (2) occur simultaneously at high temperature. It is seen from the F(α) vs. t plots in Fig.6 that reaction (2) was controlled ($0.01 \le \alpha \le 0.65$) by three-dimensional phase boundary

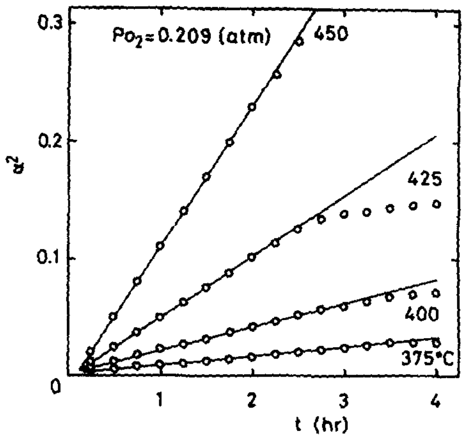

Fig.5 α^2 vs. t plots for m-"Cr_3S_4" (Sample: 2.5mg, 250~270mesh).

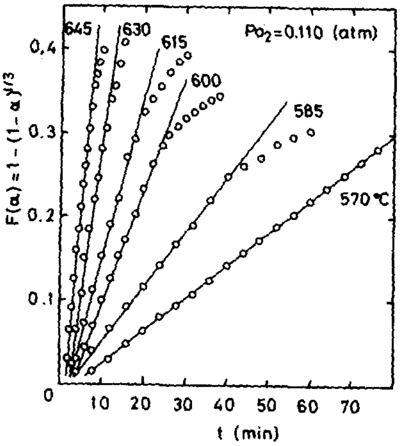

Fig.6 $F(\alpha)$ vs. t plots for r-"Cr_2S_3" (Sample: 2.5mg, 250~270mesh).

reaction. The activation energies were found to be 188~194 kJ/mol and 224~227 kJ/mol for t-"Cr_2S_3 and r-"Cr_2S_3", respectively over the Po_2 range of 0.006~0.209 atm.

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