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THERMAL ANALYSIS AND KINETICS OF THE OXIDATION OF VANADIUM AND TITANIUM SULFIDES

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ABSTRACT

The kinetics of the oxidation of "V_5S_8" and V_3S_4 to V_2O_3, and "TiS_2" and "Ti_2S_3" to TiO_2 was studied by using both isothermal and nonisothermal thermogravimetry. The kinetic equations are

$1-(1-\alpha)^{1/1.5}$ = kt for the vanadium sulfides and

$[-\ln(1-\alpha)]^{1/1.5}$ = kt for the titanium sulfides

INTRODUCTION

Oxidation processes of some metal-sulfide systems (Fe-S, Cu-S, Zn-S, Ni-S, etc.) have been studied vigorously, but others, such as V-S and Ti-S systems, yet warrant special attention. Although several authors [1,2,3] have studied the oxidation of VS, V_4S_5 and V_2S_3, there are no reports on the oxidation of V_5S_8 and V_3S_4, the two other most important phases of the V-S system. In the present report, we have made an effort to study the thermal oxidation process and the kinetics of oxidation of the V_5S_8, V_3S_4, TiS_2 and Ti_2S_3 phases.

EXPERIMENTAL

Measurement method: TG-DTA measurements were done with a rapid heating Rigaku-Thermoflex TG-DTA unit. Five, ten or twenty mg of the sample was weighed accurately in a platinum crucible of 2.5 x 5 mm diameter, distributed evenly without pressing and was tapped 2 or 3 times on a metal surface. High purity "dead burnt" α-alumina was used as the standard reference material. The oxygen partial pressure (Po_2) in the reaction chamber was controlled by mixing air and N_2 [4].

Sample preparation: Nonstoichiometric "V_5S_8" ($VS_{1.567}$) was obtained by heating [400°C(6h)→ 950°C(20h)→ 400°C(24h)] reagent grade NH_4VO_3 powder (99% pure) in a mullite boat in a flow of H_2S gas (1 atm). Stoichiometric V_3S_4 ($VS_{1.342}$) was prepared by heating the "V_5S_8" sample in a flow of H_2S/H_2 ($Ps_2=10^{-4}$atm) at 900°C for 3h.

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Nonstoichiometric "TiS_2" ($TiS_{1.972}$) was prepared by heating [400°C (1 day)→ 800°C(6 days)] a stoichiometric weighed mixture (for TiS_2) of Ti (99.9% pure) and S (guaranted reagent) in an evacuated quartz tube. The mass was then heated again for 4 days in a furnace which has a temperature gradient (360°-550°C). In order to obtain non-stoichiometric "Ti_2S_3" ($TiS_{1.740}$) weighed mixture of Ti and S was heated [400°C(1 day)→ 950°C(1 day)] in an evacuated quartz tube.

The phases were identified by X-ray powder diffractometry, and the compositions were determined by oxidizing the V-sulfides to V_2O_5 and Ti-sulfides to TiO_2 in flowing air.

RESULTS AND DISCUSSION

Thermal analysis: Fig.1a shows the TG-DTA curves of "V_5S_8" (250-325 mesh) in air flow at 0.5° and 10°C/min. At lower heating rate, the TG curve (A) shows 5 steps of weight change. V_3S_4 also shows the same oxidation steps. The X-ray analysis of the products at the end of each step, except step 1, together with the weight change calculated for these steps suggests that the oxidation steps are

$$VS_x \xrightarrow{I} O_{2(absorption)} \xrightarrow{II} VO_2+VS_{x(unreacted)} \xrightarrow{III} V_2O_3 \xrightarrow{IV} VO_2 \xrightarrow{V} V_2O_5$$

Weight chemical analysis revealed that traces of $VOSO_4$ form at step II. At higher heating rate (B), step III is absent; however, the rise of sample temperature at step III (starting temperature is around 355°C), is much higher than that at lower heating rates.

Fig.2b shows the TG-DTA curves of "TiS_2" (250-275 mesh) in air flow at 10°C/min. Both TG and DTA curves show a single step. X-ray analysis of the end product showed the presence of only TiO_2 (Anatase) phase. The weight change calculated for this step shows that the sample (also "Ti_2S_3") oxidizes stoichiometrically to TiO_2.

It can be concluded from the above results that the kinetic study of the oxidation of V-sulfides to V_2O_3 and Ti-sulfides to TiO_2 according to eqns (1) and (2) is possible if the rise of sample temperature during oxidation can be prevented, and it can actually be done by reducing the Po_2.

$$VS_x + (x + 0.75)O_2 = VO_{1.5} + xSO_2 \qquad (1)$$

where, x=1.567 for "V_5S_8" and 1.342 for V_3S_4

$$TiS_x + (x + 1)O_2 = TiO_2 + xSO_2 \qquad (2)$$

where, x=1.972 for "TiS_2" and 1.740 for "Ti_2S_3"

Kinetic study: Fig.2a shows the fraction reacted (α) vs time (t) curves for "V_5S_8" at a Po_2 of 0.01 atm when heated isothermally. It has been found that equation (3), which corresponds to "index of reaction" [5] (superficially analogous to rate of reaction) of m=1/3 (z and $\beta=1$) indicating the unidirectional kinetic of a sphere,

$$1-(1-\alpha)^{1/1.5} = kt \qquad (3)$$

gives the best straight line fit for both "V_5S_8" and V_3S_4 (α = 0 to 70-90%) and hence controls the oxidation reaction. Fig.3 shows the Arrhenius plots for "V_5S_8" and V_3S_4. Fig.2b shows the α vs. t curves for "TiS_2". It has been found that equation (4), which corresponds

$$[-\ln(1-\alpha)]^{1/1.5} = kt \qquad (4)$$

to random nucleation and subsequent growth mechanism, gives the best straight line fit for the oxidation. A knee appears in the Arrhenius plot (fig.4) for the Ti-sulfides. There are two well accepted reasons for this; the introduction of a new phase during the progress of the reaction [3], and the alteration of reaction-site energy distribution going from one Arrhenius region to another [6]. The latter one seems to be applicable here, since repeated X-ray analysis of the oxidation product failed to detect the presence of any other phase but TiO_2 (Anatase).

Apparent activation energy E and preexponential factor A were also determined nonisothermally for eqns (1) and (2) in the same Po_2 by employing the graphical method of Coats and Redfern [7] (fig.5). Values of E and A from both the isothermal and nonisothermal methods are given in table 1. The use of equations (3) and (4) in fig.5a and 5b respectively, and comparable values of E and A left no doubt regarding the authenticity of the observed mechanisms.

The present study reveals that, unlike the decomposition of carbonates which proceeds by a similar mechanism [8], the mechanism of the oxidation of sulfides differs for different sulfides.

TABLE 1

The values of E (kJ mol^{-1}) and A (sec^{-1}) for V-sulfides and Ti-sulfides

Sample	Isothermal		Nonisothermal		
	E	A	E	A	Heating Rate
"V_5S_8"	30.9	0.146	32.3	0.095	20°C/m
V_3S_4	33.2	0.212	42.2	0.437	20°C/m
"TiS_2"	75.7 (21.5)	575	87.0	3298	2°C/m
"Ti_2S_3"	83.0 (14.8)	3263	86.7	4206	2°C/m

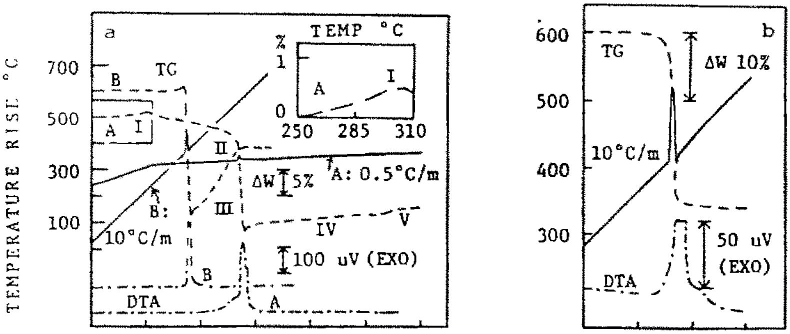

FIG.1 TG-DTA curves in air (2cc/sec); a: "V_5S_8" (insert; step I of curve A), b: "TiS_2"

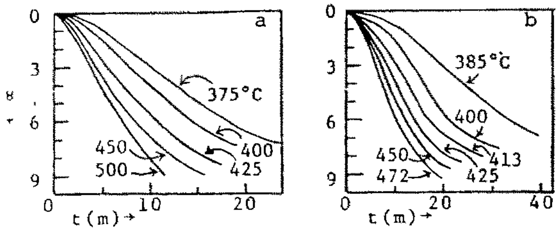

FIG.2 α vs. t curves; a: "V_5S_8", b: "TiS_2"

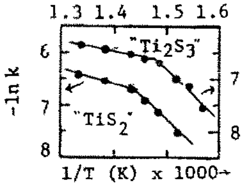

FIG.4 Arrhenius plot for TiS_x

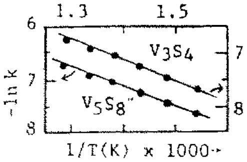

FIG.3 Arrhenius plot for VS_x

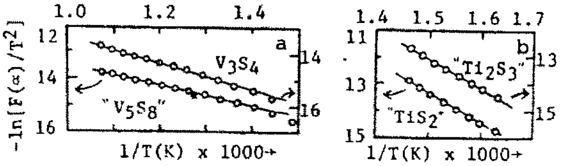

FIG.5 Coats and Redfern's linearization plots; a: VS_x [$F(\alpha)=1-(1-\alpha)^{1/1.5}$], b: TiS_x [$F(\alpha)=(-\ln(1-\alpha))^{1/1.5}$]

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