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# THERMAL ANALYSIS AND KINETICS OF OXIDATION OF "$TiS_2$" AND "$Ti_2S_3$" *

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## ABSTRACT

The thermal analysis and kinetics of oxidation of "$TiS_2$" and "$Ti_2S_3$" to $TiO_2$ (anatase) were studied by using both isothermal and non-isothermal thermogravimetry in the oxygen partial pressure, $P_{O_2}$, range from 1 to $10^{-3}$ atm. The initial stage of the oxidation process ($\alpha = 0.03$ to 0.65) was controlled by

$$[-\ln(1-\alpha)]^{1/1\ 5} = kt$$

The apparent activation energies for this stage were determined to be $142.93 \pm 2.17$ and $160.13 \pm 7.17$ kJ $mol^{-1}$ for "$TiS_2$" and "$Ti_2S_3$", respectively over the temperature range 375–450°C and $P_{O_2}$ range $4.50 \times 10^{-2}$ to $1.29 \times 10^{-1}$ atm. Insufficient $P_{O_2}$ ($< 4.50 \times 10^{-2}$ atm) was shown to be a major contributing factor to the decrease of $E$ with increasing amount of sample. The latter stage of oxidation ($\alpha = 0.65$ to $> 0.90$) was controlled by

$$\left[\left(1/(1-\alpha)^{1/3}\right)-1\right]^2 = kt$$

and the activation energies were found to be $126.30 \pm 5.96$ and $156.97 \pm 13.4$ kJ $mol^{-1}$ for "$TiS_2$" and "$Ti_2S_3$", respectively, over the same temperature and pressure ranges as mentioned above.

## INTRODUCTION

The technical importance of transition metal sulfides is due to their physicochemical properties and industrial applications; of equal importance, for similar reasons, is a knowledge of the mechanisms and kinetics of thermal oxidation of these sulfides. A great majority of the reported kinetic studies [1–3] were performed to determine optimum conditions for process metallurgy. Consequently, the reported values of the kinetic parameters, apparent activation energy $E$ and pre-exponential factor $A$, are not free from the influences of certain factors, such as amount of sample, particle

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* Dedicated to Professor Seki in honour of his contribution to Calorimetry and Thermal Analysis.

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size, atmosphere, heating rate, etc. These factors should be controlled to obtain values which are only relevant to the oxidation process. Simon [4] suggested that for gas–solid reactions a very small amount of sample ($< 1$ mg) of very small particle size at a low heating rate in a self-generated atmosphere should be studied. He has shown that the values of $E$ decreased regularly with increased amounts of sample. We observed a similar trend when oxidizing "$V_5S_8$" and $V_3S_4$ [5]. In addition to this, we found that $E$ increases with increasing $P_{O_2}$. The reason for this could not be found for vanadium sulfides, since at higher $P_{O_2}$ two or more reactions may take place simultaneously to make the kinetic study meaningless. Recently, we reported a very brief account of the oxidation and kinetics of the initial stage of oxidation of titanium sulfides [6], of which no report was available in the literature. Considering the simplicity of the oxidation process, a vivid study on the influence of $P_{O_2}$ on $E$ has been made, and a full account of the kinetics of oxidation of "$TiS_2$" and "$Ti_2S_3$" are reported in this paper.

## EXPERIMENTAL

### *Measurement method*

The TG–DTA measurements were done with a Rapid Heating Rigaku Thermoflex TG–DTA unit. Samples of 20, 10, 5 and 2.5 mg were weighed in a platinum crucible of 2.5 × 5 mm diameter, distributed evenly with a pin when a small amount was used, and bedded by tapping 2 or 3 times on a metal surface from a height of about 5 mm. An equal amount of high-purity "dead-burnt" $\alpha$-alumina was used as the standard reference material. The control of $P_{O_2}$ by mixing $N_2$–air and $N_2$–$O_2$, and monitoring it by the EMF method [7], the characterization of the samples and the reaction products, and other experimental procedures were performed in the same way as reported before [5,8].

### *Sample preparation [9]*

High-purity sulfur powder (Yoneyama Chem. Ind. Ltd., 99.5%) and titanium powder (Soekawa Chemicals, 99.9%) were used for the preparation of titanium sulfides:

*$TiS_2$*. Titanium and sulfur powders were mixed in the ratio of 1 : 2.1, ground in acetone, dried overnight under vacuum, sealed in an evacuated quartz tube and heated at 400°C for 24 h. The tube was then placed in another furnace having two constant temperature zones (800 and 400°C) and heated for 6 days. The temperatures of the furnace were then set to 530 and 360°C, respectively, and heating was continued for 4 days before quenching. The sample side of the tube was always kept at the higher temperature. The $TiS_2$

phase was identified from its X-ray powder diffraction pattern (Cu $K\alpha$), and the composition was determined to be $TiS_{1.972}$ by oxidizing the sample in air to $TiO_2$.

*$Ti_2S_3$.* The mixing ratio of titanium and sulfur for $Ti_2S_3$ was 1 : 1.75. At first the mixture, sealed in an evacuated quartz tube following the same procedures as described for $TiS_2$, was heated at 400°C for 24 h and then at 950°C for 24 h and quenched. The phase and composition were identified as $Ti_2S_3$ and $TiS_{1.740}$, respectively.

## RESULTS AND DISCUSSION

### *Thermal analysis*

The TG–DTA curves for the oxidation of nonstoichiometric "$TiS_2$" and "$Ti_2S_3$" in air and in oxygen at 10°C $m^{-1}$ are shown in Figs. 1 and 2, respectively. The TG curves show only a single weight loss step with a corresponding sharp exothermic DTA peak. The oxidation reaction for "$TiS_2$" and "$Ti_2S_3$" started around 365 and 369°C, respectively. The reactions became very violent from 382°C for "$TiS_2$" and from 387°C for "$Ti_2S_3$", and the sample temperatures rose abruptly from the programmed temperature, like the oxidation of vanadium sulfides to $V_2O_3$ [8]. The rise in sample temperatures is shown by the sharp peaks in curve T in Figs. 1 and 2. The X-ray diffraction patterns of the oxidized samples showed only $TiO_2$ (anatase) peaks. However, there was a slight disagreement between the calculated (28.1% for "$TiS_2$" and 22.9% for "$Ti_2S_3$") and observed (27.5%

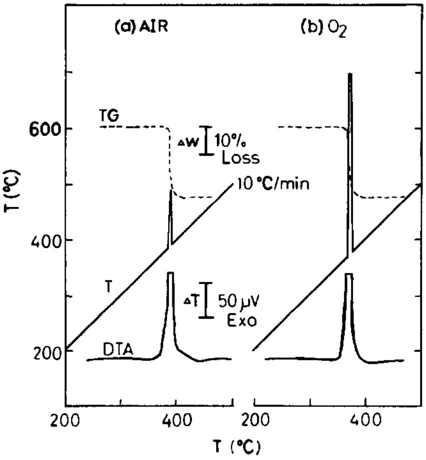

Fig. 1. TG–DTA curves for "$TiS_2$" when heated in (a) air and in (b) oxygen (sample size: 10 mg, 250–270 mesh; gas flow: 2 ml $s^{-1}$).

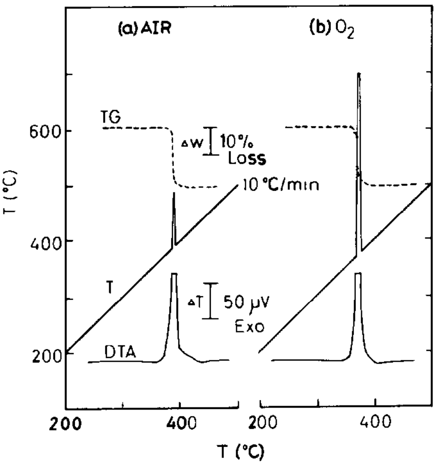

Fig. 2. TG–DTA curves for "$Ti_2S_3$" when heated in (a) air and in (b) oxygen (sample size: 10 mg, 250–270 mesh; gas flow: 2 ml $s^{-1}$).

for "$TiS_2$" and 22.5% for "$Ti_2S_3$") weight losses at the end of heating. Electron probe micro analysis of the oxidized samples revealed the presence of ca. 1.5% unreacted sulfide. On the basis of the above analysis, the oxidation reaction can be written as

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

where $x = 1.972$ for "$TiS_2$" and 1.740 for "$Ti_2S_3$".

The same oxidation process was observed irrespective of $P_{O_2}$ ($1.02 \times 10^{-1}$ to $1.00 \times 10^{-3}$ atm) and heating rates (1 to 20°C $min^{-1}$). The TG–DTA

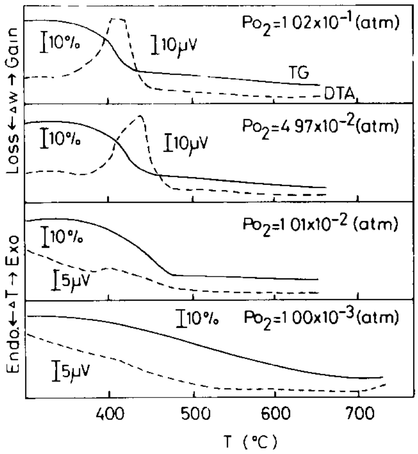

Fig. 3. TG–DTA curves for "$TiS_2$" when heated at 5°C $min^{-1}$ in different $P_{O_2}$ (sample size: 5 mg, 250–270 mesh; gas flow: 2 ml $s^{-1}$).

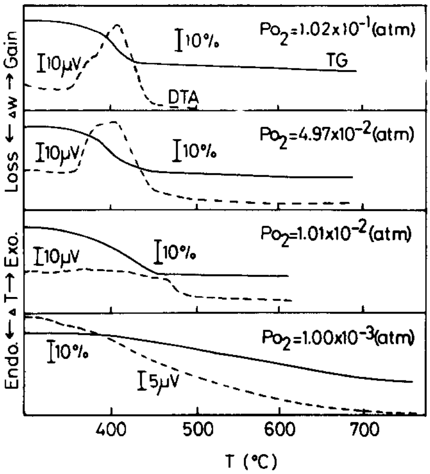

Fig. 4. TG–DTA curves for "$Ti_2S_3$" when heated at 5 °C $min^{-1}$ in different $P_{O_2}$ (sample size: 5 mg, 250–270 mesh; gas flow: 2 ml $s^{-1}$).

curves for "$TiS_2$" and "$Ti_2S_3$" obtained at different $P_{O_2}$ and at a heating rate of 5 °C $min^{-1}$ are shown in Figs. 3 and 4, respectively. It is clear from these figures that at lower $P_{O_2}$ a kinetic study of the oxidation of these sulfides is possible according to eqn. (1) if a small amount of sample is taken. Under these conditions there is no rise in sample temperature due to the heat of reaction, and there is no side reaction either.

## *Kinetics from isothermal TG*

### *$\alpha$ vs.* t *plot*

The samples were oxidized isothermally between 365 and 475 °C, selected from the non-isothermal analysis. A blank experiment, with an equal amount of $\alpha$-alumina instead of the sample, was performed at each temperature to correct the drift of the TG pen during the instantaneous rise in furnace temperature [5]. The corrected TG traces were then used to calculate the fraction reacted at a definite time $t$. Typical plots of $\alpha$ vs. $t$ for "$TiS_2$" and "$Ti_2S_3$" are shown in Fig. 5.

### *Rate equation and Arrhenius plot*

The most appropriate rate equation is considered to be the one which gives the best straight line fit when a number of possible rate equations [5] are plotted against time. However, very often two or more equations might look fit for a particular set of data obtained for a definite $P_{O_2}$ or for a particular sample size. Therefore, all the plots obtained for the whole range of temperature for different $P_{O_2}$ and sample sizes must be examined care-

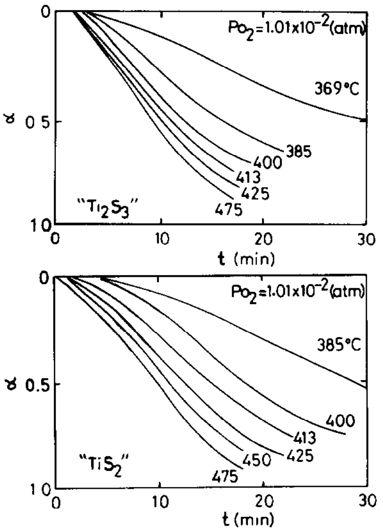

Fig. 5. Typical $\alpha$ vs. $t$ plots for "$TiS_2$" and "$Ti_2S_3$" (sample size: 5 mg, 250–270 mesh; gas flow: 2 ml $s^{-1}$).

fully before zeroing in on any rate equation. Such examination showed that the reaction represented by eqn. (1) conforms to the rate equation

$$[-\ln(1-\alpha)]^{1/1.5} = kt \qquad (2)$$

as shown in Fig. 6, and is valid for $\alpha = 0.03$ to 0.65. The latter stage will be discussed below. The above equation indicates that the "random nucleation and growth accompanied by ingestion of nuclei" mechanism controls the oxidation reaction. Figure 7 shows that a knee appears in the Arrhenius plot. This may be due either to an alteration of reaction site energy distribution going from one Arrhenius region to another, according to Dollimore et al. [10], or to a decrease in $P_{O_2}$ during the progress of the reaction, especially at higher temperatures (Fig. 9).

### *Influence of sample amount and insufficient* $P_{O_2}$ *on* E

Different amounts of samples, e.g. 20, 10, 5 and 2.5 mg, were oxidized at a fixed $P_{O_2}$ ($1.01 \times 10^{-2}$ atm) to check the effect of sample size on the apparent activation energy $E$. The variation of $E$ with sample size is shown in Fig. 8. This figure shows that the value of $E$ decreases greatly with increasing sample size. Several reasons for this were described in a previous paper [5]. Figure 9 can be shown as evidence for the insufficiency of oxygen for larger amounts of samples. The peaks in Fig. 9 show the increase in EMF (i.e. decrease in $P_{O_2}$), monitored by the CSZ electrolytic method,

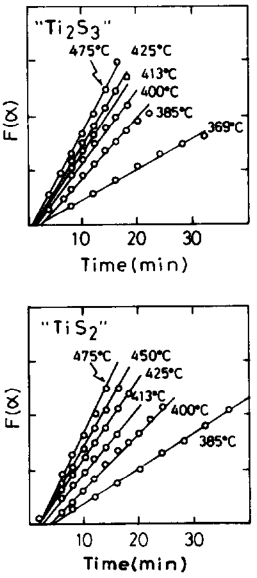

Fig. 6. Plots of rate equation ($F(\alpha) = [-\ln(1-\alpha)]^{1/1.5}$) vs. time at a $P_{O_2}$ of $1.01 \times 10^{-2}$ atm (sample size: 5 mg, 250–270 mesh; gas flow: 2 ml $s^{-1}$).

during heating different amounts of "$TiS_2$" sample at various temperatures. Three things are clear from this measurement:

(a) $P_{O_2}$ ($1.01 \times 10^{-2}$ atm), set for the isothermal study is more or less insufficient for all the sample sizes studied,

(b) for such insufficient $P_{O_2}$, once the oxidation reaction starts, the availability of oxygen in the reaction chamber gradually decreases and varies with sample size and temperature,

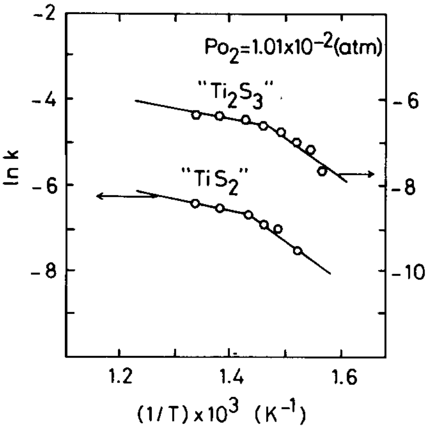

Fig. 7. Arrhenius plots for the initial stage of oxidation of "$TiS_2$" and "$Ti_2S_3$" (sample size: 5 mg, 250–270 mesh; gas flow: 2 ml $s^{-1}$).

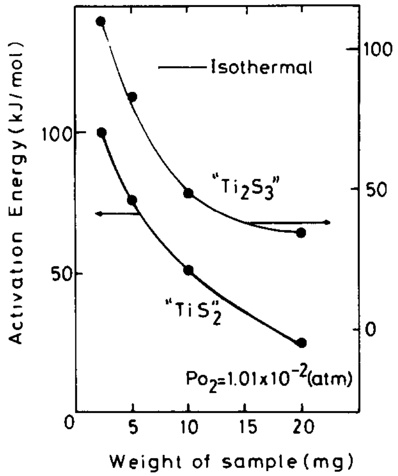

Fig. 8. Variation of $E$ with sample size at a definite $P_{O_2}$ for "$TiS_2$" and "$Ti_2S_3$".

(c) the oxygen intake becomes almost constant after a certain temperature, especially for larger sample sizes. This may be one of the major reasons why the rate of change of $k$ with respect to temperature does not improve noticeably and gives a lower value of $E$ for larger sample sizes in comparison with that for smaller sample sizes.

*Dependence of* E *and* A *on* $P_{O_2}$

Values of $E$ and $A$ for 5 and 2.5 mg quantities of samples for different $P_{O_2}$ are listed in Table 1. A close examination of this table shows that if

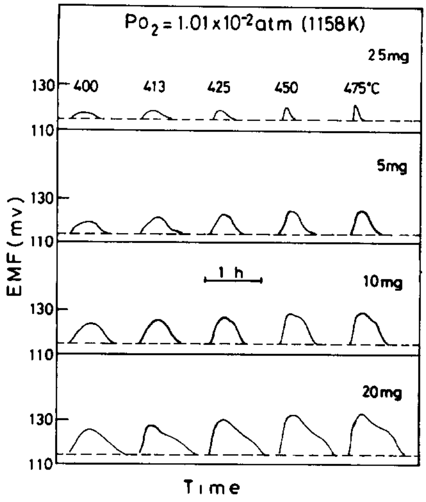

Fig. 9. Variation of EMF, i.e. $P_{O_2}$ with sample size and isothermal heating temperatures (sample: "$TiS_2$", 250–270 mesh; gas flow: 2 ml $s^{-1}$).

TABLE 1

Activation energy and pre-exponential factor for the initial stage of isothermal oxidation of $TiS_x$ at different $P_{O_2}$

| $P_{O_2}$ (atm) | $E_1$ [a] (kJ $mol^{-1}$) | $A_1$ (1/s) | $E_2$ [a] (kJ $mol^{-1}$) | $A_2$ (1/s) | RT [b] (°C) |
|---|---|---|---|---|---|
| "$TiS_2$" (5 mg, 250–270 mesh) | | | | | |
| 0.102 | 152.5 | $9.30 \times 10^8$ | 56.4 | $4.08 \times 10^1$ | 441.3 |
| 0.050 | 127.1 | $8.67 \times 10^6$ | 36.1 | 1.92 | 435.2 |
| 0.010 | 75.7 | $5.75 \times 10^2$ | 21.5 | $5.53 \times 10^{-2}$ | 417.6 |
| 0.001 | 53.9 | 4.83 | 13.7 | $3.82 \times 10^{-3}$ | 397.2 |
| "$Ti_2S_3$" (5 mg, 250–270 mesh) | | | | | |
| 0.102 | 156.6 | $2.65 \times 10^9$ | 40.9 | 9.24 | 436.2 |
| 0.050 | 106.1 | $3.08 \times 10^5$ | 22.0 | $1.90 \times 10^{-1}$ | 425.3 |
| 0.010 | 83.0 | $3.26 \times 10^3$ | 14.8 | $9.35 \times 10^{-2}$ | 408.6 |
| 0.001 | 25.5 | $3.72 \times 10^{-2}$ | 3.7 | $7.47 \times 10^{-4}$ | 395.5 |

| "$TiS_2$" (2.5 mg, 250–270 mesh) | | | "$Ti_2S_3$" (2.5 mg, 250–270 mesh) | | |
|---|---|---|---|---|---|
| $P_{O_2}$ (atm) | E (kJ $mol^{-1}$) | A (1/s) | E (kJ $mol^{-1}$) | A (1/s) | Temp. range (°C) |
| 0.129 | 146.0 | $3.74 \times 10^8$ | 167.9 | $2.67 \times 10^{10}$ | 375–455 |
| 0.089 | 141.6 | $1.54 \times 10^8$ | 150.6 | $1.02 \times 10^9$ | 375–480 |
| 0.045 | 141.2 | $1.19 \times 10^8$ | 161.9 | $6.75 \times 10^9$ | 375–450 |
| 0.010 | 100.3 | $2.28 \times 10^5$ | 108.7 | $6.07 \times 10^5$ | 375–450 |

Fraction reacted $\alpha = 0.03$ to 0.60–0.65. $kt = [-\ln(1-\alpha)]^{1/1\ 5}$.

[a] $E_1$ and $E_2$ are for high and low temperature regions in the Arrhenius plot. [b] RT is the reflection temperature.

sufficient $P_{O_2}$ is available in the reaction chamber for oxidation, the value of $E$ becomes constant within the range of experimental error. It can be concluded from the above findings that for determining the values of $E$ and $A$ of the oxidation of sulfides, the appropriate $P_{O_2}$ range, sample size, etc., must be determined first.

### *Latter stage of oxidation ($\alpha = 0.65$ to $< 0.90$)*

The rate-controlling process of the oxidation of titanium sulfides changes from the initial "random nucleation and growth accompanied by ingestion of nuclei" process to the final diffusion-controlled process, developed by Zhuravlev et al. [11] as

$$\left[\left(1/(1-\alpha)^{1/3}\right) - 1\right]^2 = kt \qquad (3)$$

Plots of this rate equation against time are shown in Fig. 10. From the slopes of the lines in this figure, values of $k$ were estimated and plotted against the inverse temperature (K) in Fig. 11 to obtain the values of $E$ and $A$. These values are given in Table 2. This change of rate-controlling process is thought to be due to the higher density of the $TiO_2$ layer formed in the initial stage.

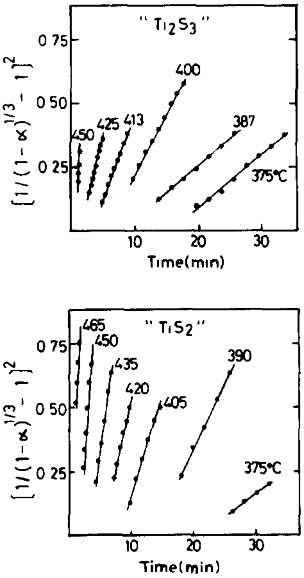

Fig. 10. Plots of Zhuravlev equation vs. time for the latter stage of oxidation of "$TiS_2$" and "$Ti_2S_3$" (sample size: 2.5 mg, 250–270 mesh; gas flow: 2 ml $s^{-1}$; $P_{O_2}$: $8.90 \times 10^{-2}$ atm).

*Other factors*

(1) Particle size (e.g. −250, 250–270, 325–400 mesh) did not have any marked influence on the observed activation energy values.

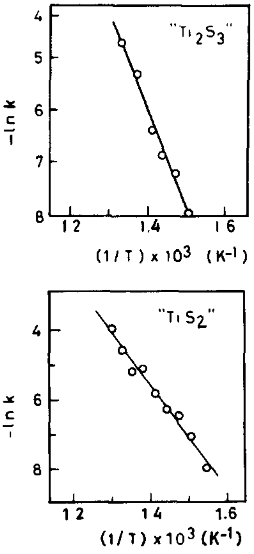

Fig. 11. Arrhenius plots for the latter stage of oxidation of "$TiS_2$" and "$Ti_2S_3$" (sample size: 2.5 mg, 250–270 mesh; gas flow 2 ml $s^{-1}$; $P_{O_2}$: $8.90 \times 10^{-2}$ atm).

TABLE 2

Activation energy and pre-exponential factor for the latter stage of isothermal oxidation of $TiS_x$ at different $P_{O_2}$

| "$TiS_2$" (2.5 mg, 250–270 mesh) | | | "$Ti_2S_3$" (2.5 mg, 250–270 mesh) | | |
|---|---|---|---|---|---|
| $P_{O_2}$ (atm) | $E$ (kJ $mol^{-1}$) | $A$ (1/s) | $E$ (kJ $mol^{-1}$) | $A$ (1/s) | Temp. range (°C) |
| 0.129 | 119.2 | $1.55\times10^{6}$ | 141.1 | $6.69\times10^{7}$ | 375–455 |
| 0.089 | 125.9 | $5.93\times10^{6}$ | 165.5 | $7.46\times10^{8}$ | 375–475 |
| 0.045 | 133.8 | $7.33\times10^{7}$ | 173.3 | $3.07\times10^{9}$ | 375–450 |

Fraction reacted $\alpha = 0.60$–$0.65$ to $> 0.90$. $kt = [1/(1-\alpha)^{1/3}-1]^2$.

(2) Changing the sample holder from platinum to silica had no noticeable influence on the values of $E$.

(3) Dependence of rate constant $k$ on $P_{O_2}$ could not be determined since the slope of the plots of $-\log k$ vs. $-\log P_{O_2}$ varies greatly with temperature.

### *Kinetics from non-isothermal* TG

The Coats and Redfern method [5,12] was used for the non-isothermal study. Typical plots for "$TiS_2$" and "$Ti_2S_3$" are shown in Fig. 12. The apparent activation energy $E$ (Table 3) was then determined for 5 and 2.5 mg quantities of samples over the same $P_{O_2}$ range applied for the isothermal study. The good agreement between the values determined by this and

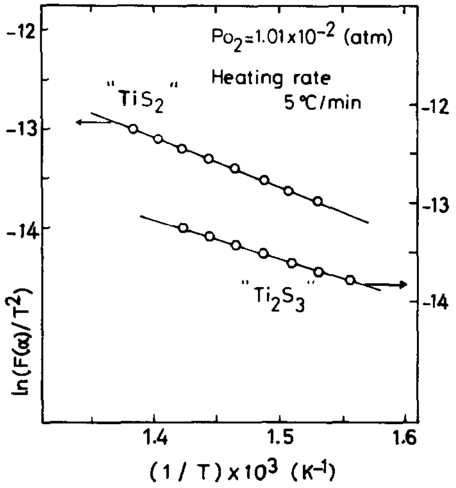

Fig. 12. Coats and Redfern linearization plots for "$TiS_2$" and "$Ti_2S_3$" (sample size: 2.5 mg, 250–270 mesh; gas flow: 2 ml $s^{-1}$).

TABLE 3

Activation energy for the non-isothermal (5°C $\mathrm{min}^{-1}$) oxidation of $TiS_x$ at different $P_{O_2}$

| $P_{O_2}$ (atm) | $E$ (kJ $\mathrm{mol}^{-1}$) for "$TiS_2$" | $E$ (kJ $\mathrm{mol}^{-1}$) for "$Ti_2S_3$" |
|---|---|---|
| Sample amount: 5 mg, 250–270 mesh | | |
| 0.102 | 141.7 | 147.3 |
| 0.050 | 134.6 | 111.4 |
| 0.010 | 82.0 | 67.2 |
| 0.001 | 34.2 | 24.5 |
| Sample amount: 2.5 mg, 250–270 mesh | | |
| 0.129 | 148.31 | 162.2 |
| 0.089 | 146.7 | 155.9 |
| 0.045 | 138.1 | 158.4 |
| 0.010 | 98.5 | 104.3 |

isothermal methods proves the accuracy of the rate equation determined by the isothermal method for the initial part of the reaction represented by eqn. (1).

## CONCLUSIONS

Both "$TiS_2$" and "$Ti_2S_3$" oxidize directly to $TiO_2$ as

$$TiS_x + (1+x)O_2 \underset{(b)\,369°C}{\overset{(a)\,365°C}{\rightarrow}} TiO_2 + xSO_2$$

where $x =$ (a) 1.972 for "$TiS_2$" and (b) 1.740 for "$Ti_2S_3$".

Two different mechanisms control the above oxidation process. The initial stage of the reaction is controlled by the "random nucleation and growth accompanied by ingestion of nuclei" mechanism and is expressed as

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

where $\alpha = 0.03$ to 0.65. The latter stage is a diffusion-controlled process developed by Zhuravlev et al. [11]:

$$\left[\left(1/(1-\alpha)^{1/3}\right) - 1\right]^2 = kt$$

where $\alpha = 0.65$ to $> 0.90$.

For a larger sample size and an inadequate supply of oxygen, i.e. for insufficient $P_{O_2}$, progress of the reaction is hampered, and the rate constant $k$ becomes less dependent on the isothermal heating temperature. But for a small amount of sample and an adequate supply of oxygen, i.e. for sufficient $P_{O_2}$, the rate constant increases smoothly with temperature. However, care must be taken to select the upper $P_{O_2}$ limit so that the sample temperature does not rise due to the exothermic heat of reaction.

For the initial stage of oxidation, the values of $E$ obtained from both the isothermal and non-isothermal methods ($142.93 \pm 2.17$ and $144.36 \pm 4.48$ kJ mol$^{-1}$, respectively, for "$TiS_2$", and $160.13 \pm 7.17$ and $158.83 \pm 2.59$ kJ mol$^{-1}$, respectively, for "$Ti_2S_3$" over the temperature range 375 to 450°C and $P_{O_2}$ range $4.50 \times 10^{-2}$ to $1.29 \times 10^{-1}$ atm) agree very well with each other. The values of $E$ for the latter stage were found to be $126.30 \pm 5.96$ and $156.97 \pm 13.14$ kJ mol$^{-1}$ for "$TiS_2$" and "$Ti_2S_3$", respectively. These values are considered accurate since the influences of $P_{O_2}$, sample amount, heat of reaction, particle size, etc., on $E$ were kept to the minimum possible level.

The insufficiency of $P_{O_2}$ during oxidation is thought to be one of the major contributing factors to the decrease of $E$ with increasing sample size.

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