

THERMAL ANALYSIS AND KINETICS OF OXIDATION OF “NbS₂”

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The thermal analysis and kinetics of oxidation of “NbS₂” to Nb₂O₅ were studied by thermogravimetry. The application of both isothermal and nonisothermal methods was necessary to establish the correct equation

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

This equation was valid for the reaction of sample reacted α in the interval 0.03 to 0.82–0.91. The apparent activation energy was determined to be 209.59 ± 2.36 kJ mol⁻¹ with the isothermal method and 209.28 ± 1.84 kJ mol⁻¹ with the nonisothermal method (5 deg min⁻¹) over the P_{O_2} range 8.9×10^{-2} to 2.0×10^{-1} atm and the temperature range 440 to 515°. The relationship between the rate constant k and P_{O_2} was also determined.

We earlier reported the kinetics of oxidation of vanadium and titanium sulfides [1, 2]. Factors which influence the kinetic parameters were discussed, and it was shown that experiments should be carried out in an appropriate range of oxygen partial pressure (P_{O_2}) to obtain realistic values of apparent activation energy E and preexponential factor A .

Tatsuki et al. [3] in our laboratory established the phase relations in the Nb–S system at high temperature. However no work has yet been done on the thermal analysis and kinetics of oxidation of niobium sulfide.

Until recently, mainly the isothermal method was used for kinetic studies. With the development of the methods and appropriate mathematical models [4], dynamic methods have become popular, since they are less tedious and also time-saving, and the results obtained with the two methods do not differ significantly [5–9]. Consequently, many investigators prefer to use the dynamic method alone. It will be shown in this paper, however, that there are cases such as the oxidation of niobium sulfide where it is essential to use both methods to demonstrate the correct mechanism clearly.

Experimental

Method

The TG-DTA measurements were performed with a Rapid Heating Rigaku Thermoflex TG-DTA unit. Twenty, 10, 5 and 2.5 mg quantities of the sample were weighed accurately in a platinum crucible of 2.5 × 5 mm diameter, distributed evenly with a pin when a small amount was used, and bedded down 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" α -alumina was used as the standard reference material. The controlling of P_{O_2} by mixing N₂-air and N₂-O₂, the characterization of the sample and the reaction products, and the other experimental work, were performed in the same way as described in a previous paper [10].

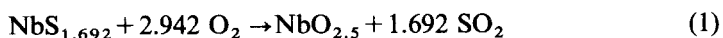
Sample preparation [3]

Reagent grade Nb₂O₅ (Wako Pure Chemical Industries Ltd., 99.9%) was taken in a mullite boat and was heated in a flow of H₂S at 700° for 24 h. The sample was then quenched to room temperature, ground, and again heated in H₂S at the same temperature for 24 h. The 3s-Nb_{1+x}S₂ phase was identified from the X-ray diffraction pattern of the finally quenched sample. The absence of the strongest peaks for Nb₂O₅ (Cu K α 2 θ = 28.5°) and NbO₂ (Cu K α 2 θ = 26.1°) was confirmed. The chemical composition of the prepared sample was determined to be NbS_{1.692} by oxidizing the disulfide completely to Nb₂O₅ in air at 700° for 48 h. The nonstoichiometric disulfide will be denoted as "NbS₂".

Results and discussion

Thermal analysis

The TG-DTA curves for the oxidation of "NbS₂" in air and in oxygen are shown in Fig. 1. The TG curve reveals a single step of weight loss and the DTA curve shows a very strong exothermic peak. The reaction started at 440°, and the sample temperature rose sharply to over 530° and 810° in air (for more than a 5 mg quantity of the sample) and in oxygen flows, respectively. The X-ray diffraction pattern of the sample at the end of heating showed only Nb₂O₅ peaks. The good agreement between the calculated weight loss (9.68%) and the observed weight loss (9.6%) after correcting the TG pen drift suggests that the oxidation reaction takes place as



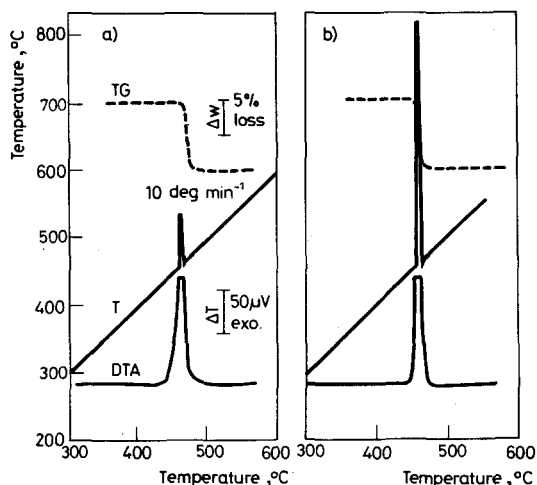


Fig. 1 TG-DTA curves when heating "NbS₂" in a) air and in b) oxygen (sample amount: 10 mg, 250-270 mesh; gas flow: 2 ml s⁻¹)

The TG-DTA curves obtained by heating 2.5 mg sample at different P_{O_2} are depicted in Fig. 2. The Figure shows that when a small amount of sample was used, the sample temperature did not rise for moderate heating rates (≤ 5 deg min⁻¹), even when heating was performed in an air flow. In all cases, only Nb₂O₅ was formed as the reaction product.

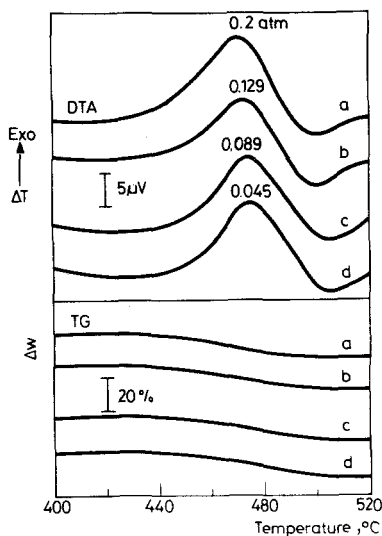


Fig. 2 The TG-DTA curves when heating "NbS₂" at 5 deg min⁻¹ in different P_{O_2} , (sample amount: 2.5 mg, 250-270 mesh; gas flow: 2 ml s⁻¹)

Kinetics of oxidation

It is clear from Fig. 2 that kinetic study of the oxidation of "NbS₂" according to Eq. (1) is possible at any suitable P_{O_2} below 2.0×10^{-1} atm if a small amount of sample is used.

On the basis of the above results and previous experience, 2.5 mg of the sample was taken to determine the kinetic parameters. The sample was oxidized at temperatures between 440° and 515°, selected from the dynamic TG experiments. Blank experiments, with an equal amount of α -alumina taken instead of the sample, were always performed for each isothermal run and to deduce the correct α vs. t data. A typical α vs. t plot is depicted in Fig. 3.

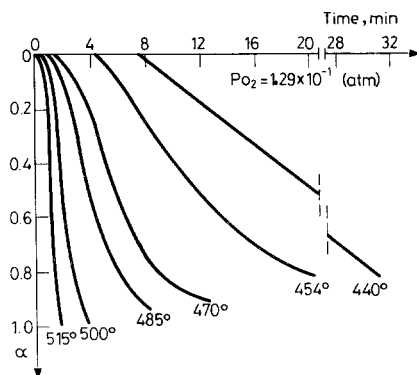


Fig. 3 Typical α vs. t plots for the oxidation of "NbS₂" at a definite P_{O_2} over the whole range of temperature examined (sample amount: 2.5 mg, 250–270 mesh; gas flow: 2 ml s⁻¹)

Three rate equations, from among all the possible rate equations listed in an earlier paper [1], gave almost perfect straight lines when plotted against time (Figs 4a, b, c). Variation of P_{O_2} slightly favors the rate equation plotted in Fig. 4b. The values of k , calculated from the slopes of the lines in Figs 4a, b, c, are plotted against the inverse of temperature (K) in Fig. 5. Again they gave good straight lines, and the values of E calculated from these lines were very close to one another (Table 1). As a result, selection of the appropriate rate equation through use of the isothermal method alone was very difficult. All three equations were then used to calculate the values of E nonisothermally by the Coats and Redfern method (Figs 4a, b, c), and they are listed in Table 1. The best agreement between the values of E obtained with both methods was found for the equation plotted in Fig. 4b. It is clear now from this results that a three-dimensional phase boundary reaction or a contracting volume model is the right mechanism for the oxidation reaction represented by Eq. (1). This

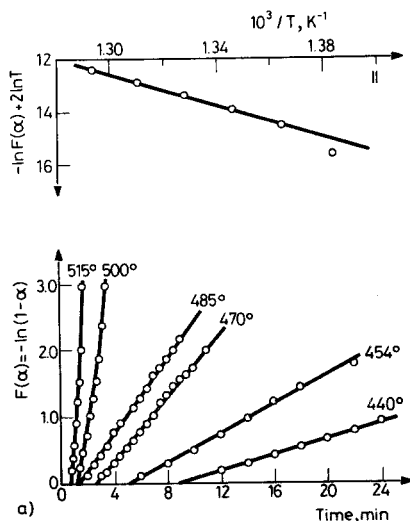


Fig. 4a $F(\alpha)$ vs. t plots, where $F(\alpha)$ corresponds to unimolecular decay controlling rate equation, I isothermal method, and II Coats and Redfern's linearization plot for nonisothermal method (5 deg min⁻¹), (P_{O_2} : 1.29×10^{-1} atm, sample amount: 2.5 mg, 250–270 mesh; gas flow: 2 ml s⁻¹)

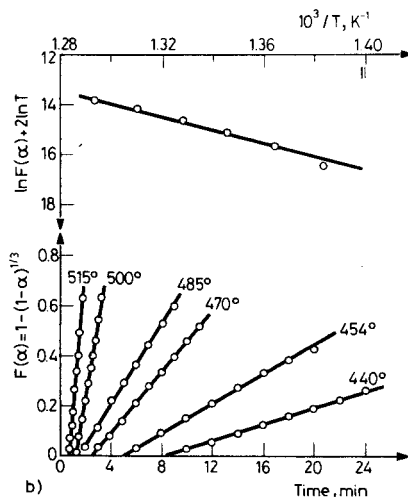


Fig. 4b $F(\alpha)$ vs. t plots, where $F(\alpha)$ corresponds to three dimensional phase boundary controlling rate equation, I isothermal method, and II Coats and Redfern's linearization plot for nonisothermal method (5 deg min⁻¹) (P_{O_2} : 1.29×10^{-1} atm; sample amount: 2.5 mg, 250–270 mesh; gas flow: 2 ml s⁻¹)

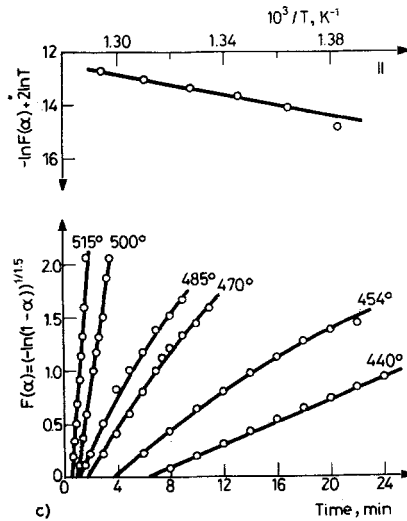


Fig. 4c $F(\alpha)$ vs. t plots, where $F(\alpha)$ corresponds to random nucleation and growth accompanied by ingestion of nuclei controlling rate equation, I isothermal method, and II Coats and Redfern's linearization plot for nonisothermal method (5 deg min⁻¹), (P_{O_2} : 1.29×10^{-1} atm; sample amount: 2.5 mg, 250–270 mesh; gas flow: 2 ml s⁻¹)

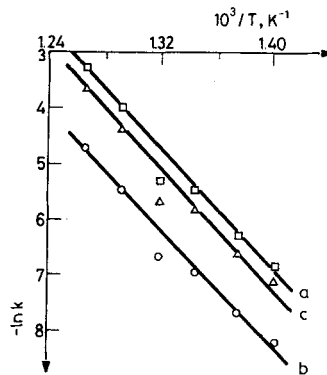


Fig. 5 Arrhenius plots for all possible rate equations depicted in Figs 4a, b, c $\square -\ln(1-\alpha)$, $\triangle [-\ln(1-\alpha)]^{1/1.5}$, $\circ 1-(1-\alpha)^{1/3}$

rate equation, $1-(1-\alpha)^{1/3} = kt$, is valid for values of α in the interval 0.03 to 0.82–0.91. It is noticeable here however, that both methods yield almost perfect straight lines for all three rate equations, and a decision as to the correct rate equation is difficult from either of them alone. Tanaka et al. [11] encountered similar difficulties when studying the kinetics of dehydration of magnesium oxalate dihydrate and ultimately selected the rate equation by comparing the results

Table 1 Activation energy, for the isothermal and nonisothermal methods, obtained for "NbS₂" when using different possible kinetic equations at a P_{O_2} of 1.29×10^{-1} atm

kt	Isothermal E , kJ/mol	Nonisothermal (5 deg/min) E , kJ/mol
a) $-\ln(1-\alpha)$	215.84	285.39
b) $1-(1-\alpha)^{1/3}$	212.62	210.00
c) $[-\ln(1-\alpha)]^{1/1.5}$	210.46	186.10

Sample amount: 2.5 mg, 250–270 mesh

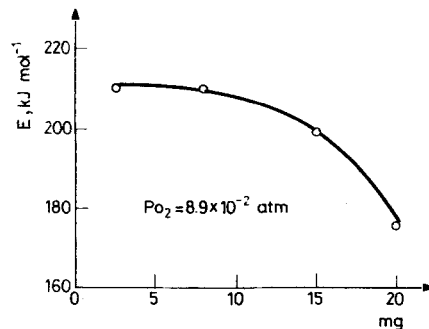
obtained with both methods. It is therefore concluded that both isothermal and dynamic methods should be applied to be sure about the correctness of the selected rate equation, and hence about the accuracies of the observed kinetic parameters.

The values of E and A determined for different P_{O_2} are given in Table 2. These results conform to the previous findings [2] that the values of E become stable when an adequate supply of oxygen is available. The influence of the sample amount on E was also tested at a fixed P_{O_2} (8.9×10^{-2} atm). The observed values of E for different sample amounts are plotted in Fig. 6. It is seen from this Figure that, for a

Table 2 Activation energy preexponential factor for the oxidation of "NbS₂" at different P_{O_2}

P_{O_2} (atm)	Isothermal E , kJ/mol	A , 1/s	Nonisothermal (5 deg/min) E , kJ/mol
0.200	206.86	4.94×10^{11}	211.10
0.129	212.62	8.95×10^{11}	210.00
0.089	209.29	5.42×10^{11}	206.75
0.045	198.73	7.22×10^{10}	202.00

Sample amount: 2.5 mg, 250–270 mesh

**Fig. 6** Variation of apparent activation energy E with sample amount at a definite P_{O_2} (sample: "NbS₂", 250–270 mesh; gas flow: 2 ml s^{-1})

sufficient P_{O_2} , the sample amount (up to a certain extent) does not have a very drastic effect on the observed values of E .

Figure 7 shows the plot of $-\log k$ vs. $-\log P_{O_2}$. It is seen that k varies considerably and linearly with temperature. From the slopes of these plots, the dependence of the rate constant k on P_{O_2} (8.9×10^{-2} to 2.0×10^{-1} atm) was calculated as $k = c' (p_{O_2})^{0.342 \pm 0.034}$ over the temperature range 440 to 495°.

The particle size (e.g. -250, 250-270, 325-400 mesh) had very little effect on the observed kinetic parameters in the P_{O_2} range studied.

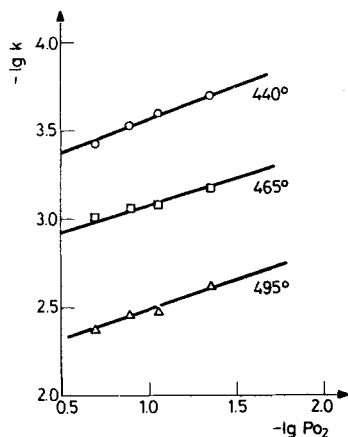


Fig. 7 Plots of $-\log k$ vs. $-\log P_{O_2}$ at different temperatures (sample: "NbS₂", 250-270 mesh; gas flow: 2 ml s⁻¹)

Conclusions

"NbS₂" is oxidized directly to Nb₂O₅ in accordance with $NbS_{1.692} + 2.942 O_2 \xrightarrow{440^\circ} Nb_{2.5} + 1.692 SO_2$.

Both the isothermal and nonisothermal methods of analyzing TG data over wide ranges of temperature and oxygen pressure must be used to single out the correct rate equation. For "NbS₂" the oxidation is controlled by a three-dimensional phase boundary reaction, or in general by the shrinking core kinetic model of spherical particles, as $1 - (1 - \alpha)^{1/3} = kt$ where $\alpha = 0.03$ to $0.82-0.91$.

The value of E determined with the isothermal method is 209.59 ± 2.36 kJ mol⁻¹ and that with the nonisothermal method is 209.28 ± 1.84 kJ mol⁻¹ over the P_{O_2} range 8.9×10^{-2} to 2.0×10^{-1} atm and the temperature range 440 to 515°. However, care must be taken to select the upper P_{O_2} limit so that the sample

temperature does not rise due to any unwanted exothermic heat of reaction. The rate constant k increases smoothly with temperature, and the observed relationship between k and P_{O_2} is

$$k = c' (P_{O_2})^{0.342 \pm 0.031}.$$

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Zusammenfassung — Die thermische Analyse und die Kinetik der Oxydation von „NbS₂“ zu Nb₂O₅ wurden thermogravimetrisch untersucht. Die Anwendung sowohl der isothermen als auch der nicht-isothermen Methode war notwendig, um die richtige Gleichung $1 - (1 - \alpha)^{1/3} = kt$ aufzustellen. Diese Gleichung ist gültig für Werte von α (Anteil der umgesetzten Probenmenge) im Intervall von 0,03 bis 0,82–0,91. Für die scheinbare Aktivierungsenergie wurde mit der isothermen Methode ein Wert von $209,59 \pm 2,36 \text{ kJ} \cdot \text{mol}^{-1}$ und mit der nicht-isothermen ($5 \text{ Grad} \cdot \text{min}^{-1}$) ein Wert von $209,28 \pm 1,84 \text{ kJ} \cdot \text{mol}^{-1}$ über den P_{O_2} -Bereich von $8,9 \cdot 10^{-2}$ bis $2,0 \cdot 10^{-1} \text{ atm}$ und den Temperaturbereich von $440\text{--}515^\circ$ erhalten. Auch die Abhängigkeit der Geschwindigkeitskonstante k von P_{O_2} wurde ermittelt.

Резюме — С помощью термогравиметрии изучен термический анализ и кинетика окисления «NbS₂» до Nb₂O₅. Применение изотермического и неизотермического методов было вызвано необходимостью подтвердить правильность уравнения $1 - (1 - \alpha)^{1/3} = kt$. Данное уравнение было справедливым для реагирующего образца с α в интервале от 0,03 до 0,82–0,91. Кажущаяся энергия активации, определенная изотермическим методом, была равной $209,59 \pm 2,36 \text{ кдж/моль}$, а неизотермическим — $209,28 \pm 1,84 \text{ кдж/моль}$ (при температурном интервале $440\text{--}515^\circ$, нагреве $5^\circ/\text{мин}$ и $P_{O_2} 8,9 \cdot 10^{-2}\text{--}2,0 \cdot 10^{-1}$). Установлена взаимосвязь между константой скорости k и P_{O_2} .