

BRIEF COMMUNICATION

Synthesis of Titanium Sulfides under High Pressure

KATSUYUKI OSHIMA, MASAO YOKOYAMA, HIROFUMI HINODE,
MASATAKA WAKIHARA, AND MASAO TANIGUCHI

*Department of Chemical Engineering, Tokyo Institute of Technology,
Ookayama, Meguro-ku, Tokyo 152 Japan*

Received November 22, 1985; in revised form March 24, 1986

Titanium sulfides were synthesized in the temperature range 600–750°C and in the pressure range 10–200 MPa with an apparatus used for hydrothermal synthesis. Stoichiometric TiS_2 cannot be prepared under atmospheric pressure, but was synthesized under high pressure. Also the phase relationship between TiS_2 and TiS_3 has been established under high pressure up to 200 MPa, and the pressure–temperature phase diagram for Ti–S system is presented. © 1986 Academic Press, Inc.

Introduction

In the Ti–S system, there was a continuous transition from the CdI_2 -type structure of TiS_2 to NiAs-type structure of TiS giving the several intermediate phases when titanium was added (1). The phase equilibria (2, 3) and the electrochemical studies (4) of this system have been recently reported. Besides, stoichiometric TiS_2 are of technical interest recently because of its layered structure with the van der Waals layer. A special case is titanium disulfide, a promising cathode material for secondary lithium batteries (4). However, TiS_2 shows nonstoichiometric compositional ranges TiS_x ($x < 2$) or $\text{Ti}_{1+y}\text{S}_2$ ($y > 0$) (2, 3). The excess titanium is occupied in the van der Waals layer and it impedes the intercalation of cation, e.g., lithium ion. Whittingham *et al.* prepared nonstoichiometric TiS_2 by contaminating TiS_3 from titanium sponge between 450 and 600°C in a temperature gradi-

ent which fixes the sulfur pressure (4). Yamamoto *et al.* prepared an almost stoichiometric TiS_2 by the reaction between Ti and TiS_2 at 1000°C under high pressures (5).

We report the phase equilibria of $\text{TiS}_{1.4}$ – TiS_2 under controlled sulfur partial pressure in the range from 10^{-8} to 1 atm (3). According to our investigation, stoichiometric TiS_2 could not be prepared, even at 1 atm sulfur partial pressure. Hence we have attempted the synthesis of stoichiometric TiS_2 by using an apparatus usually used for hydrothermal synthesis and also studied the relationship between TiS_2 and TiS_3 under high pressure.

Experimental

(1) *Apparatus.* In the present work, we used an apparatus (6) generally employed for high pressure hydrothermal synthesis. Figure 1 shows a test tube-type vessel

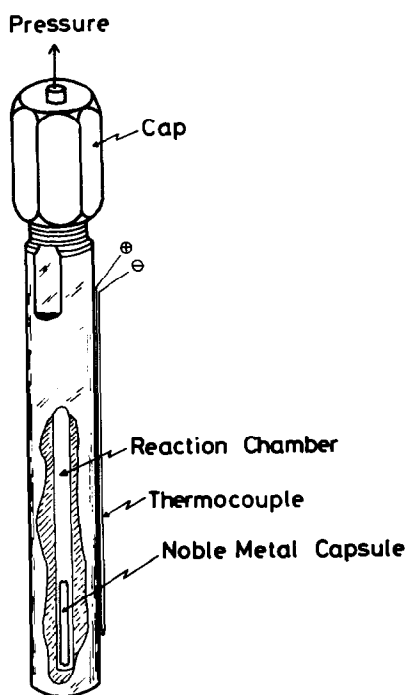
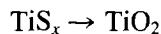


FIG. 1. Schematic figure of the stellite test tube-type vessel.

which is made of stellite (a Co-Cr-W alloy). A gold capsule which contains the sample is inserted into the vessel which is heated and then subjected to a given pressure. The maximum temperature and pressure of the apparatus were set to 800°C and 250 MPa, respectively, for safety considerations. Since the thermocouple is usually set on the outside of the vessel and given that the internal temperature of vessel corresponds to the actual reaction temperature, the difference between the inside and outside temperatures was checked using a Pt-Pt13%Rh thermocouple before starting the experiment. It was found that the inner temperature was lower than the outside one by 26–37°C in the temperature range of 600 to 750°C.

(2) *Experimental procedure.* Titanium sulfides starting materials were prepared by the following method. Titanium metal and

sulfur were mixed in the molar ratio of $Ti/S = 1/1.9$. The mixture was sealed in a evacuated quartz tube and heated at 400°C for 1 day and then at 900°C for 4 days. The sulfide obtained was not contaminated with metal oxides. This material was then mixed with sulfur powder in the appropriate ratios ($Ti/S = 1/3$). About 100 mg of the mixed sample was put into a gold capsule which was sealed by arc-melt (A.C 25–30 V) and then heated under high pressure for 1–3 days. The solid-liquid reaction between titanium sulfide and sulfur was carried out at different temperatures and pressures between 600–750°C and 10–200 MPa, respectively. Finally the capsule was quickly cooled to room temperature before releasing the pressure. The product contained unreacted sulfur (so-called excess sulfur), which was removed by heating the products at 200°C under vacuum. Phase identification of the titanium sulfides was made by X-ray powder diffractometry using $CuK\alpha$ radiation. The compositions were determined by the oxidation of the sulfide to TiO_2 in air at 900°C for 6 hr according to



The composition x in TiS_x can be calculated with the equation

$$x = 2.492 \times (a/b) - 1.494 \quad (1)$$

where $a(g)$ and $b(g)$ are the weight of TiS_x and TiO_2 samples. Equation (1) was derived from the relation: $a/(\text{formula weight of } TiS_2) = b/(\text{formula weight of } TiO_2)$.

Results and Discussion

(1) *Pressure dependence of the maximum sulfur content of the products.* According to Rau (7), the saturated vapor pressure of sulfur at 650°C is 9.030 atm, and at 750°C it is 22.63 atm. Therefore sulfur is present in the liquid state at all times within our present experimental conditions. The pressure dependence of the maximum sulfur

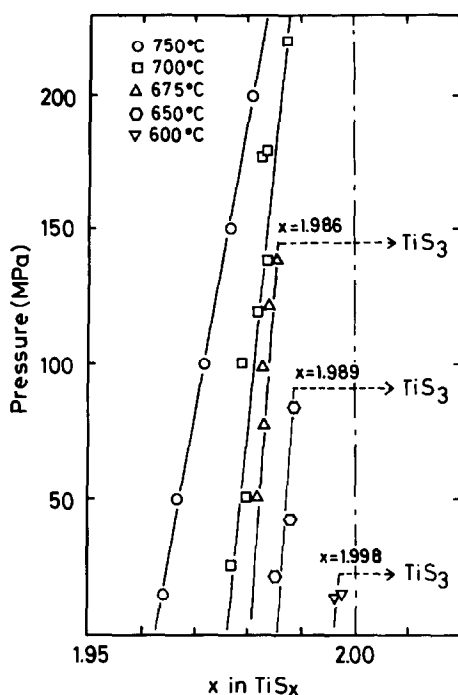


FIG. 2. Pressure dependence of sulfur composition of the products.

content of the products TiS_x in equilibrium with liquid sulfur at constant temperatures shown in Fig. 2. Reference to this figure shows that the sulfur content (x) increases with increasing pressure at each temperature, and also found that the phase transformation of TiS_2 to TiS_3 may occur at 600, 650, and 675°C under 23, 97, and 150 MPa, respectively. The maximum sulfur content (x) in TiS_x of the single TiS_2 phase decreases with increasing temperature of reaction being nearly stoichiometric at 600°C under 15 MPa pressure.

(2) *Pressure-temperature phase diagram for the Ti-S system.* Figure 3 shows the relationship between pressure and temperature for the transformation of TiS_2 to TiS_3 . It is seen that the transformation temperature increases with increasing pressure. By applying the root mean square method, we obtained the following relationship between pressure (P) and temperature (T):

$$P = 1044 - 2.42 \times T - 3.54 \times 10^{-4} \times T^2 - 1.09 \times 10^{-7} \times T^3 + 4.50 \times 10^{-9} \times T^4. \quad (2)$$

(3) *Compositional dependence of the lattice parameters in the phase TiS_2 .* The lattice parameters of samples quenched from the reaction temperatures to room temperature were calculated as a hexagonal unit cell from indexed data (8), and the results are shown in Fig. 4. Whittingham (4) reported the lattice parameters $a = 3.408 \text{ \AA}$, $c = 5.6953 \text{ \AA}$ for stoichiometric TiS_2 (closed circle in Fig. 4). The parameter a decreased slightly with increasing sulfur content, and the change in the parameter c was very small (3) between $\text{TiS}_{1.975}$ and TiS_2 . This tendency agrees well with that reported by Jeannin and Benard (9) and Jeannin (10).

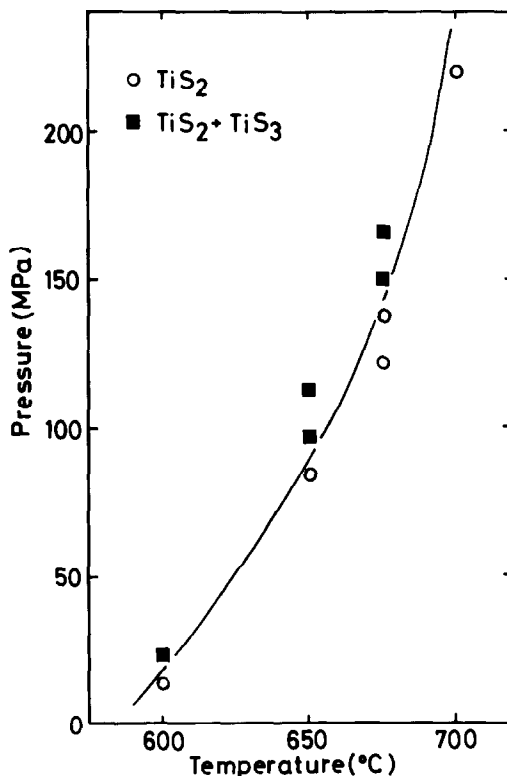


FIG. 3. Relation between pressure and temperature for the phase transition from TiS_2 to TiS_3 .

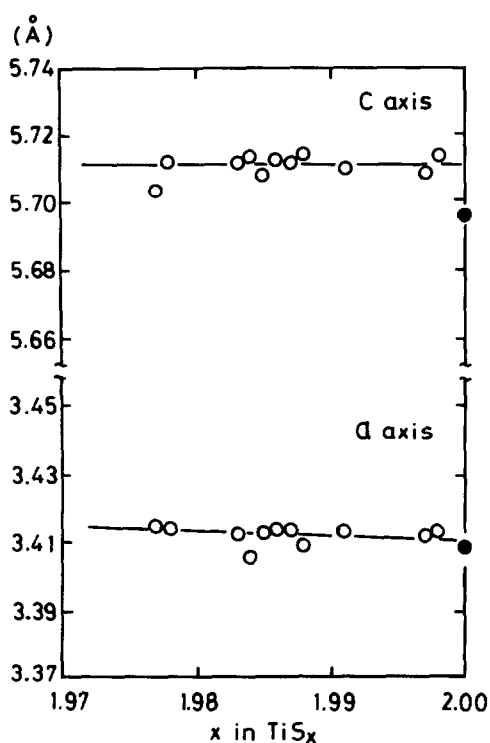


FIG. 4. Compositional dependence of lattice parameters of TiS_x . Closed symbol refer to the data by Whittingham.

Also this behavior coincides with our previous results on TiS_x ($x < 1.95$) (3). Our parameter a is almost the same as that of Whittingham (4), but the parameter c in the present study is slightly larger than that of Whittingham.

Conclusion

In the present work, titanium sulfides with various sulfur compositions were synthesized under high pressure and their phase relationships were determined. The pressure-temperature phase diagram for the Ti-S system under pressures up to 200 MPa was established, and the phase transformation of TiS_2 to TiS_3 shown. Stoichiometric TiS_2 was prepared at 600°C under 15 MPa pressure.

References

1. G. A. WIEGER AND F. JELLINIK, *J. Solid State Chem.* **1**, 62 (1979).
2. M. SAEKI AND M. ONODA, *Bull. Chem. Soc. Jpn.* **55**, 3144 (1982).
3. M. WAKIHARA, Y. MIZUGUCHI, H. HINODE, AND M. TANIGUCHI, *J. Less-Common Met.* **105**, 311 (1985).
4. M. S. WHITTINGHAM AND J. A. PANELLA, *Mater. Res. Bull.* **16**, 37 (1981).
5. T. YAMAMOTO, S. KIKKAWA, AND M. KOIZUMI, *Mater. Res. Bull.* **18**, 1451 (1983).
6. M. YOKOYAMA, M. YOSHIMURA, M. WAKIHARA, S. SOMIYA, AND M. TANIGUCHI, *J. Solid State Chem.* **60**, 182 (1985).
7. H. RAU, T. R. N. KUTY, AND J. R. F. GUEDES DE CARVALHO, *J. Chem. Thermodyn.* **5**, 833 (1973).
8. Powder Diffraction File, Joint Committee on Powder Diffraction Standards, International Center for Diffraction Data, Swarthmore, PA, 1980, Cards 27-908, 15-853.
9. Y. JEANNIN AND B. BENARD, *C. R. Acad. Sci.* **248**, 2875 (1959).
10. Y. JEANNIN, *C. R. Acad. Sci.* **251**, 246 (1960).