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Synthesis of Vanadium Sulfides under High Pressure

MASAO YOKOYAMA, MASAHIRO YOSHIMURA,* MASATAKA WAKIHARA, SHIGEYUKI SOMIYA,* AND MASAO TANIGUCHI†

*Department of Chemical Engineering, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152 and *Department of Material Science and Engineering, Tokyo Institute of Technology, 4259, Nagatsuta-cho, Midori-ku, Yokohama 227, Japan*

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Vanadium sulfides were synthesized in a temperature range of 350–750°C and in a pressure range of 10–250 MPa (1 MPa = 9.87 atm), with an apparatus used for hydrothermal synthesis. The nonstoichiometric compositional range of the $V_{1+x}S_2$ phase, which cannot be prepared under atmospheric pressure, is $VS_{1.661}$–$VS_{1.732}$ ($0.155 < x < 0.204$). It was impossible to synthesize vanadium disulfide VS_2 under the present experimental conditions. Equilibrium phase diagrams for the V_5S_8–S system under 100 and 200 MPa have been proposed on the basis of the present results. Also, the phase relationship between V_5S_8 and $V_{1+x}S_2$ has been established and a pressure–temperature phase diagram for the V–S system has been drawn.

Introduction

In the vanadium–sulfur system, various nonstoichiometric compounds are present and have recently been investigated with respect to composition and physical properties. For example, monosulfide VS and disulfide VS_2 have NiAs- and CdI_2-type structures, respectively, and V_5S_8 (monoclinic structure) becomes an antiferromagnet below (approximately 30 K (*1*, *2*). These interesting properties are due to the behavior of the *d* electrons of vanadium atoms in every second metal layer of vanadium sulfide.

Vanadium disulfide is considered as one of the important compounds used as cathode materials in high energy secondary batteries in which other transition metal disulfides have been used (*3*, *4*). A comprehensive report, however, has not yet been published concerning the synthesis of the VS_2 using the dry process.

A few years ago some of the present authors (*5–7*) reported the phase equilibria of the V–S system as having a compositional range of VS–V_5S_8 under controlled sulfur partial pressure in the range from 10^{-14} to 1 atm. According to their investigations, the vanadium sulfide in equilibrium with sulfur vapor pressure of 1 atm is the V_5S_8 ($VS_{1.6}$); also, considerably higher pressure is indispensable in order to obtain VS_2 at high temperatures. Onoda *et al.* (*8*) attempted to synthesize VS_2 by thermal decomposition of VS_4 at 700–800°C under 20 kbar using a piston–cylinder apparatus. However, they were not able to synthesize VS_2 but ob-

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† To whom all correspondence should be addressed.

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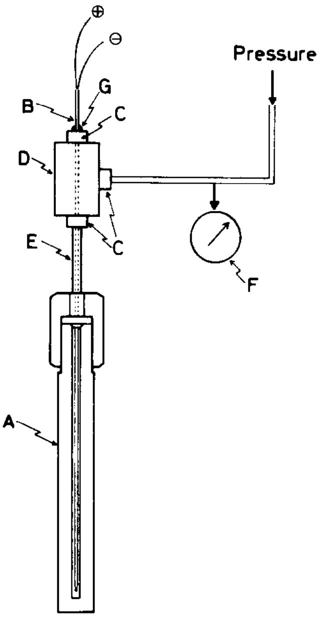

FIG. 1. Schematic diagram of the apparatus for temperature measurement under high pressure: (A) test-tube type vessel (stellite); (B) seath thermocouple; (C) ground; (D) tee; (E) nipple; (F) pressure gauge; (G) welding.

tained $VS_{1.8\pm0.1}$ instead (trigonal $V_{1+x}S_2$: $x = 0.11$). The trigonal $V_{1+x}S_2$ phase ($x = 0.2$) was also obtained by thermal decomposition of higher sulfides under reduced pressure by Jellinek (9), but the details of the composition range about the $V_{1+x}S_2$ phase have not been reported thus far. For this reason, we have studied the phase equilibria of V–S system under high pressure using an apparatus usually employed for hydrothermal synthesis.

Experimental

1. Apparatus

In the present work, we used an apparatus (Fig. 1) generally employed for high-pressure hydrothermal synthesis. A test-tube type vessel is made of stellite (an alloy of Co, Cr, W, etc.). A noble metal (Au, Pt, etc.) capsule which contains the sample was inserted into the vessel (o.d. 25.4 mm. i.d. 6.0 mm). It was heated and then subjected to a given pressure. The maximum temperature and pressure of this apparatus were set at 800°C (±5°C) and 400 MPa (±5 MPa), respectively, for safety reasons. A thermocouple was usually attached to the outside of the vessel and at the same position as that of the capsule during the reactions. As the inside temperature of the vessel actually corresponds to the reaction temperature, we checked the difference between the inside and the outside temperatures using a seath thermocouple (Fig. 1) before starting the experiment. The inner temperature was lower than the outside one by 20–35°C.

2. Experimental Procedure

Vanadium sulfides as starting materials were prepared by the following methods: (a) reaction of NH_4VO_3 (Wako pure chemical 99.9%) with H_2S gas at 400°C for 6 hr, and then at 1000°C for 20 hr to obtain a composition corresponding roughly to $VS_{1.5}$; and (b) synthesis of the VS_4 phase, in which both the sample prepared by (a) and pure sulfur powder (99.9%) were mixed in the S/V ratio of 4:5 and then sealed in a Pyrex tube followed by heating at 450°C for 3 days. The unreacted sulfur was transported to the cold zone of the tube by heating the sample zone at about 400°C. VS_4 phases with compositions in the range $VS_{3.2}$–$VS_{3.5}$ were always prepared by this method.

Next, we mixed the above starting material with sulfur powder in appropriate ratios. About 100 mg of the mixed sample was put into a gold capsule (o.d. 3.0 mm. i.d. 2.6 mm, and L 35 mm) and was sealed by arc-melting (a.c. 25–30 V). (The ratio "S/V" of the sealed material will be labeled as "sealed composition" VS_y in this paper.) Then the capsule was heated high pressure for 1–10 days (sulfur-rich samples were left for longer times). The temperature range

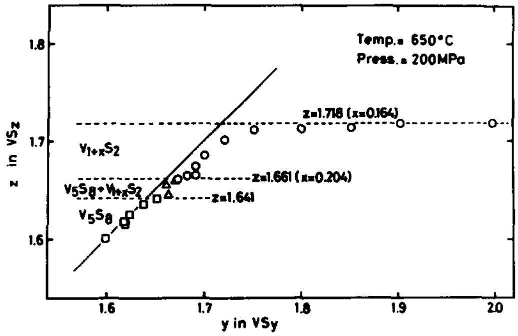

FIG. 2. Relation between the sulfur composition of the sealed materials (y) and that of the products (z) for the V–S system at 650°C under 200 MPa.

was 350–750°C and the pressure range was 10–25 MPa for the reactions. Finally, the capsule was quenched to room temperature before the pressure was released. The product contained unreacted sulfur which was removed by heating the products at 200°C in vacuum.

Phase identification of vanadium sulfide samples was made by X-ray powder diffractometry with CuK_α radiation (Rigaku Denki Co. Ltd.), and the compositions were determined by oxidation of the sulfide to V_2O_5 air at 600°C for 24 hr:

$$\underset{a(g)}{VS_z} \longrightarrow \underset{b(g)}{VO_{5/2}}$$

where $z = 2.837a/b - 1/0.589$.

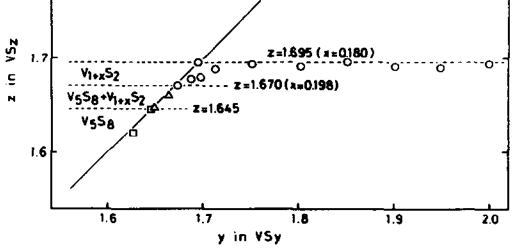

FIG. 3. Relation between the sulfur composition of the sealed materials (y) and that of the products (z) for V–S system at 750°C under 100 MPa.

After the reactions, it was observed that a slight amount of vanadium sulfide reacted with the gold capsule, and a very fine layer of a new Au–V–S compound was present only on the inner surface of the capsule. The compositional analysis showed the compound to be AuV_3S_5. Details concerning the properties of AuV_3S_5 will be published elsewhere.

Results and Discussion

1. Dependence of Sulfur Content (z) *of the Products* VS_z *Composition* (y) *in* VS_y

The relation between sulfur content (z) of synthesized samples and sealed composition (y), at 650°C under 200 MPa and at 750°C under 100 MPa, are shown in Figs. 2 and 3, respectively. According to Rau (10), the saturated vapor pressure of sulfur at 650 and 750°C are 9.030 and 22.63 atm, respectively. Therefore sulfur exists always in the liquid state under the present experimental conditions. When y is less than 1.7, z is nearly equal to y at 650°C under 200 MPa. The z value is, however, constant (1.718) when y is larger than approximately 1.72. Therefore, the maximum sulfur content in VS_z in equilibrium with liquid sulfur under high pressure in this condition is $VS_{1.718}$. The V_5S_8 phase is stable below z = 1.641, and the $V_{1+x}S_2$ phase is present in the compositional range of $1.661 < z < 1.178$ ($0.164 < x < 0.204$) at 650°C under 200 MPa, as shown in Fig. 2. The upper limit of the compositional range of the V_5S_8 phase ($z = 1.641$) agrees well with the results obtained by Saeki *et al.* (*11*). The nonstoichiometric compositional range of the $V_{1+x}S_2$ phase is found to be $VS_{1.670}$–$VS_{1.695}$ at 750°C under 100 MPa, as shown in Fig. 3.

2. Equilibrium Phase Diagram for V_5S_8*–S System under High Pressure*

Figure 4 shows the temperature dependence of the maximum sulfur content of the

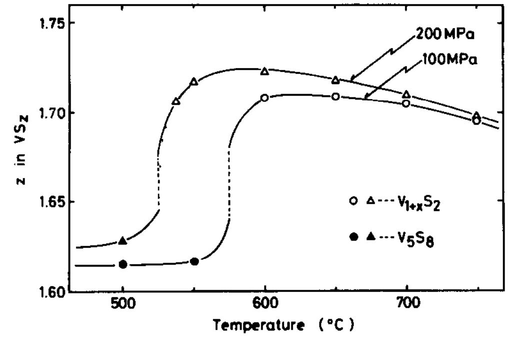

FIG. 4. Temperature dependence of maximum sulfur content in VS_z for products under pressure of 100 and 200 MPa.

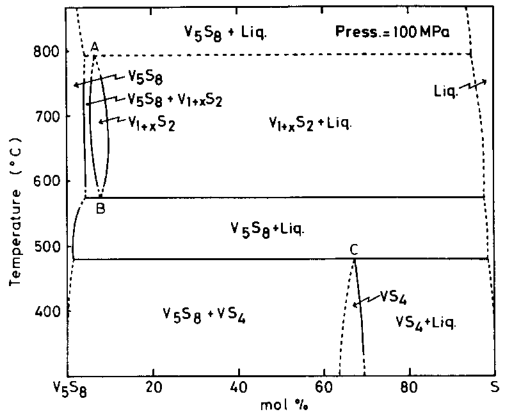

FIG. 6. Equilibrium phase diagram for V_5S_8–S system under a pressure of 100 MPa.

products VS_z in equilibrium with the liquid sulfur under high pressure as mentioned in the previous section. The temperature dependence (350–750°C) of the maximum sulfur content in VS_z under 100 MPa is shown in Fig. 5. The $V_{1+x}S_2$ phase is stable at temperatures above 575°C, and the V_5S_8 phase is stable below this temperature. Under 200 MPa the $V_{1+x}S_2$ phase exists at temperatures above 525°C, and the V_5S_8 phase exists below this temperature (Fig. 4). It is seen from Fig. 5 that the VS_4 phase is stable at a temperature lower than 450°C under 100 MPa. Based on the present results, the equilibrium phase diagrams for the V_5S_8–S systems under 100 and 200 MPa are presented in Figs. 6 and 7, respectively. The stable single-phase region of $V_{1+x}S_2$ was not present when synthesized under atmospheric pressure. However, it was encountered under 100 and 200 MPa, as shown in these figures. The stable region under 200 MPa is slightly wider than that under 100 MPa. The following metatectic reaction may take place at points A and B (Fig. 6):

$$V_5S_8 + \text{Liq.} = V_{1+x}S_2$$

Also, the same reaction may take place at points A′ and B′ (Fig. 7) and a different

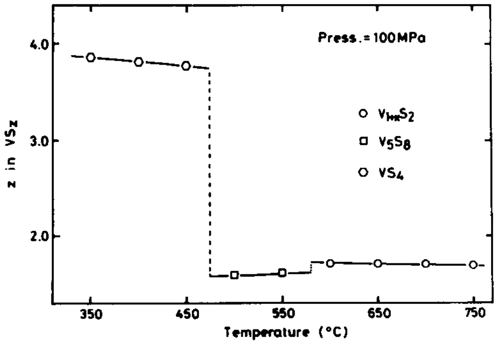

FIG. 5. Maximum sulfur content in VS_z of the product over the temperature range from 350 to 750°C under a pressure of 100 MPa.

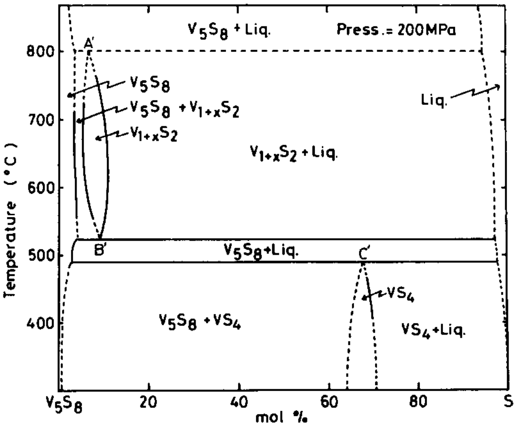

FIG. 7. Equilibrium phase diagram for V–S system under a pressure of 200 MPa.

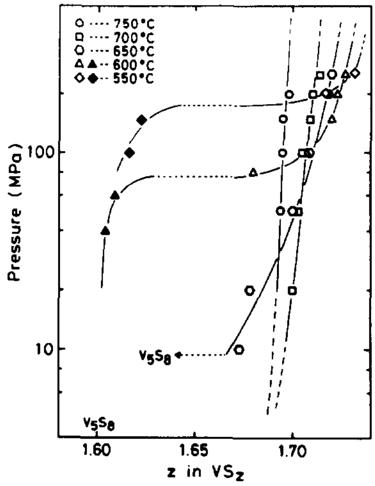

FIG. 8. Pressure dependence of the sulfur content of the products at constant temperature. Solid symbols represent the V_5S_8 phase; open circles represent $V_{1+x}S_2$.

metatectic reaction may take place at points C (Fig. 6) and C′ (Fig. 7):

$$VS_4 = V_5S_8 + \text{Liq.}$$

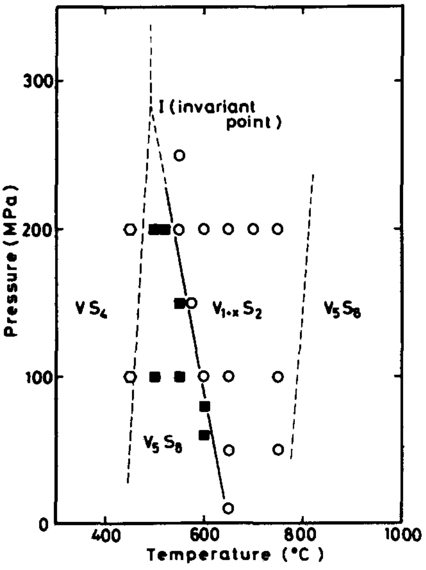

FIG. 9. Pressure–temperature phase diagram for the V–S system.

3. Pressure Dependence of the Maximum Sulfur Content of the Products

The pressure dependence of the maximum sulfur content of the products VS_z in equilibrium with the liquid sulfur at constant temperature is shown in Fig. 8. It is seen from the figure that the sulfur content (z) increases with increasing pressure at each temperature. Under the present experimental conditions (at 550°C under 250 MPa), the maximum sulfur-rich compound was found to be $VS_{1.732}$ ($V_{1+x}S_2$ phase). Accordingly, it is assumed that VS_2 may only be prepared under ultra-high pressures. As shown in Fig. 8, the phase transformation at V_5S_8 to $V_{1+x}S_2$ may occur at 550° and 600°C under 70 and 180 MPa, respectively, but the vanadium sulfides which belong to $V_{1+x}S_2$ could only be obtained above 650°C.

4. Pressure–Temperature Phase Diagram for the V–S System

The phase diagram of Fig. 9 shows the relationship between pressure and temperature for the transformation of the V_5S_8 phase to $V_{1+x}S_2$. It is found that the dP/dT line of the phase boundary has a negative slope (the solid line in Fig. 9). The VS_4 phase is stable below 450°C, and the extrapolated boundary line between the VS_4 and the V_5S_8 phases joins with the boundary line between the V_5S_8 phase and the $V_{1+x}S_2$ phase at point I in Fig. 9. At this point, four phases, i.e., VS_4, V_5S_8, $V_{1+x}S_2$, and liquid sulfur, coexist. Therefore, it represents an invariant point in the binary (V–S) system according to the phase rule ($f = c - p + 2$). The phase boundary between the V_5S_8 phase at high temperature and the $V_{1+x}S_2$ phase has not yet been determined due to our experimental limitations.

5. Compositional Dependence of Lattice Parameters of Vanadium Sulfides

The measured lattice parameters of the NiAs–CdI_2-type subcell (pseudo-orthohex-

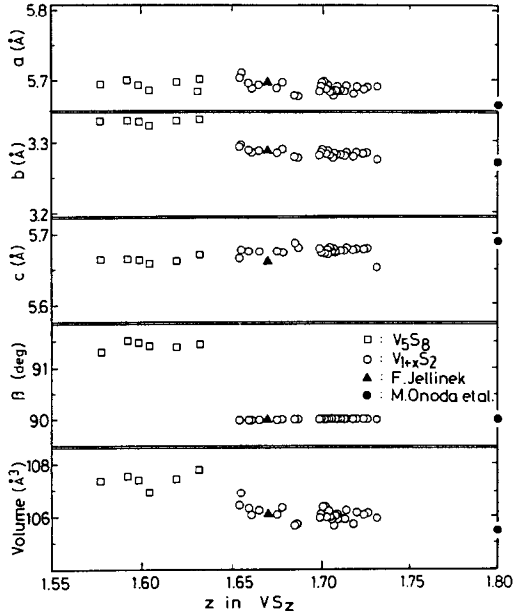

FIG. 10. Compositional dependence of lattice parameters in the range from $VS_{1.55}$ to $VS_{1.8}$.

agonal) of the $V_{1+x}S_2$ with the composition $VS_{1.58}$–$VS_{1.63}$ are shown in Fig. 10, along with those of $VS_{1.67}$ reported by Jellinek (*9*), and of $VS_{1.8}$, reported by Onoda *et al.* (*8*). It is seen from the Fig. 10 that the parameters suddenly change close to the sulfur composition (z in VS_z) of approximately 1.65, particularly for cases b with respect to volume. This significant change indicates the phase transformation of V_5S_8 to $V_{1+x}S_2$. The lattice parameters of the $V_{1+x}S_2$ phase obtained by us are in good agreement with those of Jellinek (*9*) and of Onoda *et al.* (*8*).

Conclusion

In the present work, vanadium sulfides with higher sulfur compositions were synthesized and their phase relationships under high pressure were determined. The nonstoichiometric range of the $V_{1+x}S_2$ phase under the present experimental conditions was found to be $VS_{1.661}$–$VS_{1.732}$ ($0.155 < x < 0.204$). The equilibrium phase diagrams for the V_5S_8–S system under 100 and 200 MPa and the pressure–temperature phase diagram for the V–S system under pressures up to 300 MPa were also drawn. However, it was not possible to synthesize stoichiometric VS_2 under the present set of conditions.

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