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The Phase Relation of the Titanium-Sulfur System

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The phase relation of the titanium–sulfur system was studied in the range from $TiS_{1.38}$ through $TiS_{1.96}$ at 900 °C by the use of the thermobalance method under controlled sulfur pressure. It was found that four phases, (a) Ti_2S_3 (4H) with a short-range ordering of titanium vacancies, (b) the superstructure of Ti_2S_3 (4H) due to the ordering of titanium vacancies, (c) Ti_2S_3 (4H), and (d) TiS_2 (2H), exist in this composition range. The Ti_5S_8 phase of the 12R type reported previously was not detected for any composition.

Several phases have been reported in the TiS–TiS_2 range, namely, TiS (2H), Ti_8S_9 (9R), Ti_4S_5 (10H), Ti_3S_4 (21R), Ti_2S_3 (4H), Ti_5S_8 (12R), and TiS_2 (2H).[1] (The structure designations in the Ramsdell notation are given in the parentheses). The structures are based on close-packed sulfur layers; hexagonal close packing for TiS or TiS_2, and more complex stacking sequences for the intermediate phases. Titanium atoms occupy octahedral holes in the sulfur framework. Polytypism was observed by Tronc and Huber[2] in the composition around $TiS_{1.70}$.

In the composition range near $TiS_{1.5}$, the existence of the 4H-type has been reported by Jeannin[3] from his study of the phase relation in the Ti–S system. The structure of this 4H-type was also studied by Wadsley[4] and by Norrby and Franzen;[5] it was described as follows: the stacking sequences of sulfur layers are represented by chchch.., that is, there is alternating cubic and hexagonal close packing. Titanium atoms occupy the octahedral holes fully and partially in the alternating titanium layers. Recently, the existence of two superstructures related to the 4H-type was found, and the atomic arrangements were determined by means of X-ray diffractometry and high-resolution electron microscopy.[6–8] These superstructure arise from the ordered arrangement of titanium vacancies in partially occupied titanium layers and have been designated as the $(4H)_2$ type and the $(4H)_3$ type respectively.

The phase diagram of the Ti–S system has not been established because of the discrepancies between the experimental data reported by different investigators, as has been pointed out by Kjekshus and Pearson,[9] and Jeannin.[10] The reasons for these discrepancies may be as follows: (1) an equilibrium state is difficult to be attained because of the sluggishness of the transformation rate or the existence of an energy subminimum state, or (2) in the previous investigations, studies were performed for quenched specimens. The high-temperature states might not be held through the quenching processes.

In the present work the phase relation was examined by means of a thermobalance method, that is, an *in situ* observation, under a sulfur partial pressure controlled by H_2S–H_2 mixture gas. The aim is to give the phase relation including the superstructure, which has not yet been reported in any phase diagrams in the Ti–S system. Although the P_{S_2}-composition relation was reported by Abendroth and Schleton,[11] their data were not sufficiently accurate for determining the phase relation.

Experimental

The starting materials, Ti_2S_3 and TiS_2, were prepared by the following procedure. A mixture of titanium metal powder (purity 99.0%) and sulfur (purity 99.9999%) was sealed in an evacuated silica tube and heated in an electric furnace. Reaction was allowed to take place for a few days at 350 °C and subsequently at 900 °C. Quenching was made to water.

The chemical compositions of the starting materials were determined by oxidizing them to TiO_2 at 800 °C in air for several hours. The titanium content was calculated from the weight of TiO_2, while the sulfur content was determined by the weight change in converting sulfide to oxide within a reproducibility of $x=\pm0.004$ in TiS_x.

About 2 g of the starting materials, Ti_2S_3 or TiS_2, were placed in a silica crucible and suspended by means of a silica spring balance in an electric furnace, into the bottom of which H_2S–H_2 mixture gas was introduced at the rate of 5.0 $cm^3\ s^{-1}$. To attain an equilibrium at 900 °C, the sample weight was allowed to change as a result of the absoption or libration of sulfur gas. The equilibrium composition was determined by an *in situ* observation, that is, a measurement of the increase or decrease in the length of the silica spring using a cathetometer. The attainment of an equilibrium state was judged by the following conditions: (1) the sample weight does not change with time, and (2) the compositions determined through a sulfurization process of a sulfur-poor material and through a desulfurization of a sulfur-rich material agree with one another in the same atmosphere.

The oxygen and H_2O in the H_2 and H_2S had to be removed, as titanium sulfide is easily oxidized. The oxygen in the H_2 was allowed to react with hydrogen, while the H_2O was eliminated by passing the mixture gas over P_2O_5. If these procedures had not been performed, the TiO_2 would have occured as an impurity. Once produced, TiO_2 could not be sulfurized easily in the H_2S–H_2 atmosphere at 900 °C. In the present work, the production of titanium oxide could be ignored during the experiment, because an identical P_{S_2}-compoistion relation was obtained in repeated equilibrating experiments.

For identification, the powder samples were prepared by heating weighed quantities of titanium and sulfur at 900 °C in evacuated silica tubes, after which they were quenched. The powder X-ray diffraction patterns were taken by the counter-diffractometer method using Ni-filtered Cu *Ka* ration. Electron-diffraction patterns were taken from the crushed particles by means of the 100 kV electron microscope.

Results

Phase Relation in the Composition Range of $TiS_{1.38}$—

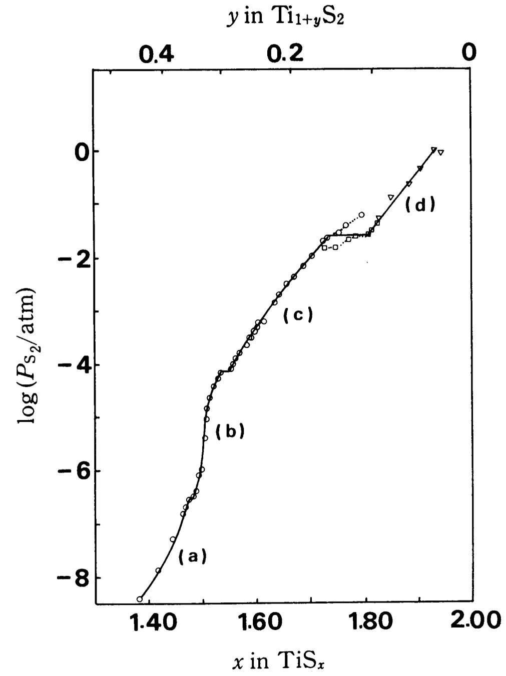
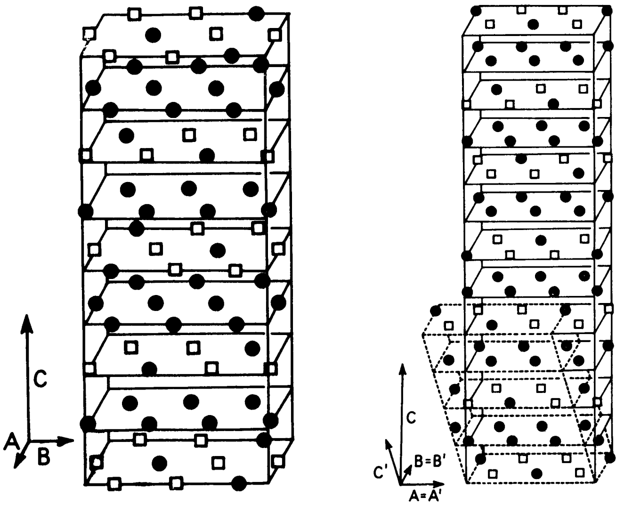


Fig. 1. P_{S_2}-composition relation of Ti–S system.
(a) is the range of Ti_2S_3 (4H) with short-range ordering of titanium vacancies, (b) the range of Ti_2S_3 $(4H)_{super}$, (c) the range of Ti_2S_3 (4H), and (d) the range of TiS_2 (2H).
○: Starting material; Ti_2S_3 (4H), method; H_2S–H_2 mixture gas, □: starting material; TiS_2 (2H), method; H_2S–H_2 mixture gas, ▽: starting material: TiS_2 (2H), method: quartz Bourdon gauge.



Ti_2S_3 $(4H)_2$ Ti_2S_3 $(4H)_3$

Fig. 2. Crystal structure of Ti_2S_3 $(4H)_2$ and Ti_2S_3 $(4H)_3$. For Ti_2S_3 $(4H)_2$ three axes of the monoclinic unit cell are represented by A, B, and C. For Ti_2S_3 $(4H)_3$, A, B, and C represent three axes of the rectangular unit cell, and A′, B′, and C′ represent them of the reduced monoclinic unit cell which is indecated by the dotted lines (see Ref. 5). Sulfur layers are eliminated.
●: Ti atoms, □: Ti vacancies.

$TiS_{1.96}$. The P_{S_2}-composition relation determined as described above is shown in Fig. 1. The P_{S_2} value was calculated from the gas-mixing ratio and the reaction temperature by the use of the thermodynamical data listed in the JANAF thermochemical tables.[12] Figure 1 shows that four ranges exist: (a)—$TiS_{1.475}$, (b) $TiS_{1.483}$—$TiS_{1.535}$, (c) $TiS_{1.550}$—$TiS_{1.730}$, and (d) $TiS_{1.810}$—. The details will be presented below.

(a) Phase up to the $TiS_{1.475}$ Composition: The powder X-ray diffraction pattern of the specimen quenched in the $TiS_{1.38}$—$TiS_{1.475}$ range was that of the Ti_2S_3 (4H) type. However, in the electron-diffraction pattern with an incident beam parallel to the c axis, super spots are observed. In order to assign the integral indices, the hexagonal cell constant, a, of the supercell was taken to be $\sqrt{3}$ times that of the 4H type. The diffuse-scattering distribution was observed along the super-spot rows in the pattern with an incident beam perpendicular to the c axis. These results suggest that titanium vacancies are in a long-range order state along the a and b axes and in a short-range order state along the c axis. A detailed analysis of the structure is now in progress.

(b) Phase in the $TiS_{1.483}$—$TiS_{1.535}$ Composition Range: The powder X-ray pattern of the quenched specimen at the composition of $TiS_{1.48}$—$TiS_{1.49}$ or $TiS_{1.51}$—$TiS_{1.53}$ was identical with that of the $(4H)_2$-type superstructure reported previously.[6] The quenched specimen at the composition close to $TiS_{1.50}$ exhibit a powder pattern of the $(4H)_3$ type superstructure whose data were also reported.[6] The superstructures, $(4H)_2$ and $(4H)_3$, arise from ordering of titanium atoms and vacancies in the partially occupied titanium layer and the piling up of the ordered-arrangement layers along the c axis. The titanium arrangements in $(4H)_2$ and $(4H)_3$ are shown in Fig. 2.

The P_{S_2}-composition curve in the (b) range in Fig. 1 does not indicate the boundary of the existence range of the two super-structures, $(4H)_2$ and $(4H)_3$. Either of the following two possibilities can be true; (1) Both the $(4H)_2$ and $(4H)_3$ types may appear at 900 °C within the (b) range; The phase boundary between $(4H)_2$ and $(4H)_3$ is not detected because the experimental procedure is insufficiently precise; or (2) only one of the two structures occurs at 900 °C, and the other appears through the quenching process. As it is difficult to decide which case occurs, the tentative designation "$(4H)_{super}$" is used for the phase in the $TiS_{1.483}$—$TiS_{1.535}$ range.

(c) Phase in $TiS_{1.550}$—$TiS_{1.730}$ Composition Range: Judging the result of X-ray and electron diffractometry, the structure of the quenched sample in this range is the same as that of Ti_2S_3 (4H).

(d) Phase in Compositions Richer in Sulfur than $TiS_{1.810}$: The sample richer in sulfur than $TiS_{1.810}$ gave powder patterns of the TiS_2 (2H) type. Because of the limitations in the sulfur partial pressure controlled by an H_2S–H_2 gas method, most of the P_{S_2} values of the TiS_2 phase shown in Fig. 1 were estimated from the total pressure measurement by means of a quartz Bourdon gauge. The details of the method and results were reported in a previous paper.[13]

Determination of the Phase Boundaries of Ti_2S_3 (4H) and TiS_2. The P_{S_2}-composition curve obtained by the sulfurization of Ti_2S_3 (4H) does not agree with that obtained by the desulfurization of TiS_2 (2H) in the $TiS_{1.730}$—$TiS_{1.810}$ range, as is shown by the dotted lines in Fig. 1. The horizontal part, representing a two-phase region, does not emerge in this range, because the transformation process was so slow that the equilibrium state was not established. The quenched specimens gave the diffraction patterns of the mixture of TiS_2 (2H) and Ti_2S_3 (4H).

In order to estimate the length of time required to attain equilibrium in this range, powder specimens of Ti_2S_3 (4H) and TiS_2 (2H), put on different sides of an inverted U-type evacuated silica tube, were kept at 900 °C for a week. The quenched specimens on both sides differ from each other in composition and structure. Equilibrium was not established even after a week.

As has been described above, the phase boundary of Ti_2S_3 (4H) and TiS_2 (2H) could not be determined through the equilibration process. After the X-ray diffraction patterns were examined in detail, it was found that TiS_2 (2H) began to be formed at $P_{S_2}=0.023$ atm in the sulfurization process, while in the desulfurization process Ti_2S_3 (4H) began to be formed at the identical P_{S_2} value. This P_{S_2} value corresponds to that of the two-phase region, as is shown by the solid line in Fig. 1.

Discussion

The composition range corresponding to (a), (b), and (c) in Fig. 1 was regarded as a homogeneity range of the Ti_2S_3 (4H) phase by the previous researchers. In the present work, four phases, that is, (a) Ti_2S_3 (4H) with a short range order of titanium vacancies, (b) the superstructure of Ti_2S_3 (4H) due to the ordering of titanium vacancies, (c) Ti_2S_3 (4H), and TiS_2 (2H), were found by an *in situ* observation.

From the P_{S_2}-composition curve shown in Fig. 1, Gibbs free energies for the reactions at 900 °C were calculated:

$$\mathrm{TiS}_{1.475}(4\mathrm{H}) + ((1.483-1.475)/2)\ \mathrm{S}_2(\mathrm{g}) = \mathrm{TiS}_{1.483}((4\mathrm{H})_{\mathrm{super}})$$

$$\Delta G^\circ = (1/2)(1.483-1.475)RT\ln P_{\mathrm{S}_2} = -600(\mathrm{J/mol})$$

$$\mathrm{Tis}_{1.535}((4\mathrm{H})_{\mathrm{super}}) + ((1.550-1.535)/2)\ \mathrm{S}_2(\mathrm{g}) = \mathrm{TiS}_{1.550}(4\mathrm{H})$$

$$\Delta G^\circ = (1/2)(1.550-1.535)RT\ln P_{\mathrm{S}_2} = -700(\mathrm{J/mol})$$

$$\mathrm{Tis}_{1.730}(4\mathrm{H}) + (1/2)(1.810-1.730)\mathrm{S}_2(\mathrm{g}) = \mathrm{TiS}_{1.810}(2\mathrm{H})$$

$$\Delta G^\circ = (1/2)(1.810-1.730)RT\ln P_{\mathrm{S}_2} = -1500(\mathrm{J/mol})$$

Although the existence of Ti_5S_8 (12R) has been reported in some papers,[3,14,15] it was not detected in the present experiments.

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