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DETERMINATION OF THE ENTHALPIES OF FORMATION OF SOLID SOLUTIONS IN THE Ta–S SYSTEM BY COMBUSTION CALORIMETRY

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ABSTRACT

Combustion calorimetry of the Ta–S system was carried out under a mixed oxygen–air atmosphere ($Po_2 = 7 \times 10^4$ Pa) at 611° C using a Calvet-type twin calorimeter. The enthalpies of formation of solid solutions of 2S–TaS_x, 3S–TaS_x and 6S–TaS_x phases in the Ta–S system were determined. The enthalpies of phase transformation from 2S–TaS_x to 3S–TaS_x, from 3S–TaS_x to 6S–TaS_x and from 6S–TaS_x to 1S–TaS_2 were estimated to be −114, 32, and 65 kJ mol^{-1}, respectively.

INTRODUCTION

Tantalum sulphides belong to the group of NiAs type layered structures [1]. Recently, our research group determined the isotherms of tantalum sulphides at high temperatures [2]. It became clear that the structural changes in the Ta–S system were rather complicated, and in the range $TaS_{1.500}$–TaS_2 four types of crystal structures, 2S–TaS_x, 3S–TaS_x, 6S–TaS_x and 1S–TaS_2, were observed [1,3]. 2S–, 3S–, and 6S–TaS_x in these phases had rather wide ranges of solid solution. Unfortunately, there is still insufficient reliable thermodynamic information on the non-stoichiometry of these sulphides.

In general, since sulphides with a layered-type structure are easily oxidized at high temperatures, combustion calorimetry is effective in evaluating the enthalpies of formation of a solid solution of phase transformation. The combustion calorimetry on the Nb–S [4] and Ti–S systems [5] have been reported previously.

Through similar combustion studies, new data on the enthalpies of formation of the solid solution and the enthalpies of phase transformation of phases existing in the Ta–S system were obtained and are reported here.

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EXPERIMENTAL

Sample preparation

Sulphur powder (reagent grade) and tantalum plate (0.2 × 100 × 200 mm, 99.9%) were purchased from Yoneyama Chemical Industries Ltd. and Soekawa Chemical Co., Ltd., respectively. In order to make the stoichiometric TaS_2, tantalum plate was cut into needle form and mixed with excess sulphur powder. The mixture was sealed in an evacuated long quartz tube. The quartz tube was held in a furnace under a temperature gradient (low temperature, 300 °C; high temperature, 1000 °C) for two weeks. The tube was quenched in cold water. The formed powder was ground and mixed with excess sulphur, and then held in a furnace for a further week. On the basis of the isotherm curves obtained previously for the Ta–S system [2], the samples with composition x from 1.500 to 1.963 were prepared in the furnace by varying the partial pressure of sulphur (P_{S_2}) which was controlled by passing sulphur vapour/hydrogen mixtures (Fig. 1). The phase of each sample prepared was identified by using the X-ray powder diffraction method. The chemical composition of TaS_x was determined by oxidizing the samples completely to Ta_2O_5 in air for 48 h at 950 °C.

Apparatus and procedure

The Calvet-type twin calorimeter designed for operation at temperatures up to 650 °C [4,5] was used for the combustion of the tantalum sulphides. In

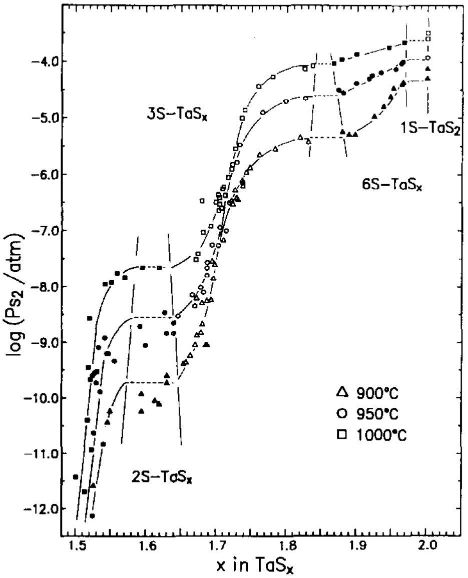

Fig. 1. Equilibrium sulphur vapour pressure/composition isotherms for the Ta–S system at certain temperatures.

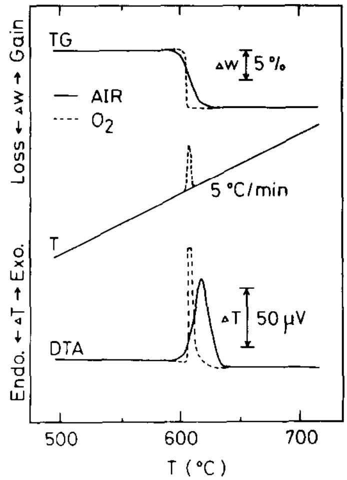

Fig. 2. TG–DTA curves for the oxidation of TaS_2 in air and oxygen flow.

this calorimeter the thermal effect is detected as electrical output with a thermocouple. In order to determine the optimum experimental condition for the combustion of tantalum sulphides, five factors were altered: the temperature of the calorimeter, the oxygen partial pressure (P_{O_2}) of the reaction gas, its flow rate, the amount of tantalum sulphide and its particle size. The temperature and P_{O_2} were more important factors than the others. Since the TG–DTA curves of the oxidation of the stoichiometric TaS_2 showed that the oxidation starts at about 600 °C in air and in O_2 (Fig. 2), the temperature of the calorimeter was set at 611 °C. P_{O_2} was changed from 6.0×10^4 to 9.0×10^4 Pa by mixing air and oxygen. Unreacted TaS_2 tended to increase with increasing P_{O_2}, but when P_{O_2} was extremely low, it was difficult to estimate the enthalpy of combustion because of the broadened peak due to slow combustion. Considering these two contrary phenomena, P_{O_2} was fixed at 7×10^4 Pa. The other factors were fixed, taking account of factors such as good reproducibility, minimizing unreacted residual TaS_x and small heat loss. The values of these factors as fixed for the present study are summarized in Table 1. Electron probe micro-analysis (EPMA) was used to find the amount of unreacted TaS_x. Since the trace of unreacted TaS_x in the matrix of Ta_2O_5 was less than 1 mol%, no correction was made for the

TABLE 1

The conditions for the combustion experiment on the Ta–S system

Temperature of calorimeter (°C)	611
Partial pressure of oxygen (Pa)	7×10^4
Flow rate of reaction gas ($cm^3\ s^{-1}$)	2
Particle size of sample (μm)	53–104
Amount of sample (mg)	9.00–10.00

TABLE 2

The enthalpies of combustion for the Ta–S system

x in TaS_x	w (mg)	$-\Delta H_c$ (kJ mol^{-1})	
			Mean ± SD
2S–TaS_x			
1.500	9.84	1217	1215 ± 11.1
	9.31	1228	
	10.22	1201	
1.517	9.69	1226	1224 ± 6.2
	9.30	1231	
	9.52	1216	
1.529	11.00	1228	1228 ± 0.5
	11.09	1227	
1.551	8.81	1249	1239 ± 10.0
	9.48	1234	
	10.07	1248	
	9.27	1225	
1.595	9.05	1240	1243 ± 2.1
	10.43	1245	
	10.33	1243	
3S–TaS_x			
1.646	9.74	1121	1129 ± 6.6
	10.07	1128	
	9.86	1137	
1.678	9.31	1122	1126 ± 2.5
	9.69	1124	
	9.40	1132	
1.683	9.41	1127	1132 ± 3.5
	9.55	1137	
1.693	9.54	1174	1177 ± 1.5
	9.51	1176	
	9.26	1180	
1.710	9.77	1196	1202 ± 7.4
	10.10	1199	
	9.78	1213	
3S–TaS_x			
1.728	9.83	1245	1249 ± 3.5
	9.24	1246	
	9.48	1256	
1.737	9.51	1250	1255 ± 2.6
	9.33	1255	
	9.15	1259	
1.760	9.48	1251	1258 ± 4.1
	9.41	1257	
	9.16	1265	
1.780	11.47	1253	1262 ± 3.7
	9.61	1261	
	9.00	1262	
	9.75	1271	

TABLE 2 (continued)

x in TaS_x	w (mg)	$-\Delta H_c$ (kJ mol^{-1})	
			Mean ± SD
1.798	9.11	1258	1263 ± 2.7
	9.21	1265	
	9.70	1267	
1.817	9.72	1255	1265 ± 5.5
	9.12	1266	
	9.30	1274	
1.825	10.05	1257	1269 ± 4.3
	9.52	1267	
	9.26	1273	
	9.05	1277	
6S–TaS_x			
1.879	9.14	1294	1301 ± 6.5
	9.98	1307	
1.898	9.90	1296	1310 ± 4.8
	10.54	1309	
	9.33	1316	
	9.66	1317	
1.934	9.71	1304	1314 ± 3.6
	9.44	1312	
	9.86	1318	
	9.40	1320	
1.945	9.27	1302	1316 ± 5.1
	9.48	1314	
	9.29	1323	
	9.75	1324	
6S–TaS_x			
1.963	9.09	1309	1324 ± 5.7
	10.28	1319	
	9.48	1320	
	9.37	1328	
	9.42	1343	
1S–TaS_2			
2.000	10.02	1384	1389 ± 2.1
	9.21	1386	
	9.82	1429	
	10.25	1368	
(2S + 6S)–TaS_2			
1.994	9.31	1361	1366 ± 3.1
	9.48	1367	
	9.78	1258	

experimental results. The sample, accurately weighed to 10 ± 0.01 mg, was put in a small quartz holder (i.d. = 4 mm) and sealed under vacuum. The details of the procedure have been described previously [4,5].

Calibration of the calorimeter was performed by measuring the thermal effect on the known molar enthalpies [6] of the oxidation of the stoichiometric NbO_2 to the stoichiometric Nb_2O_5 phase

$$NbO_2 + 0.25O_2 \rightarrow NbO_{2.5}\ (Nb_2O_5 \text{ phase})\ \Delta H = -155.3 \text{ kJ mol}^{-1}\ (611°C)$$

RESULTS AND DISCUSSION

Heat of transformation

The enthalpies of combustion ΔH_c of 2S–TaS_x, 3S–TaS_x, 6S–TaS_x and 1S–TaS_2 obtained in the present study are summarized in Table 2 and are plotted graphically in Fig. 3. The curves in Fig. 3 show three different profiles and the deviation is shown as error bars at each point.

The isotherms of the Ta–S system are shown in Fig. 1. The profiles of the isotherms are not continuous at the phase transformations from 2S–TaS_x to 3S–TaS_x, from 3S–TaS_x to 6S–TaS_x and from 6S–TaS_x to 1S–TaS_2, since these transformations are of first order.

In the region of the 2S–TaS_x phase, $-\Delta H_c$ can be fitted smoothly by following the analytical equation derived by the least-squares method

$$-\Delta H_c = -1116x^3 + 1259x^2 + 4426x + 4493\ (1.500 \leqslant x \leqslant 1.595) \qquad (1)$$

where x is the composition of sulphur in TaS_x. While $-\Delta H_c$ in the 3S–TaS_x phase can be expressed by the following equations, which were derived by

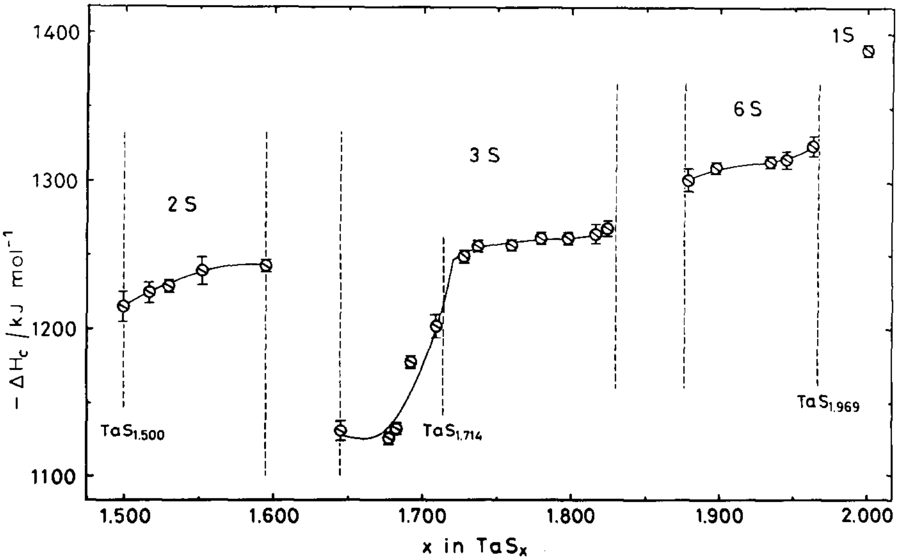

Fig. 3. The heat of combustion for the Ta–S system.

the least-squares method ($1.646 \leqslant x < 1.720$) and the trial-and-error method ($1.720 \leqslant x \leqslant 1.825$), respectively

$$-\Delta H_c = 3.402 \times 10^4 x^2 - 1.129 \times 10^5 x + 9.483 \times 10^4 \quad (1.646 \leqslant x < 1.720) \tag{2}$$

$$-\Delta H_c = 10.35 \times \ln(30x - 51.13) + 1254 \quad (1.720 \leqslant x \leqslant 1.825) \tag{3}$$

$-\Delta H_c$ in the 6S–TaS$_x$ phase can be calculated using the following equation which was derived by the least-squares method

$$-\Delta H_c = 24.80x^4 - 34.24x^3 - 74.64x^2 + 202.9x + 1103 \quad (1.879 \leqslant x \leqslant 1.969) \tag{4}$$

The solid lines in Fig. 3 correspond to the curves which stand for these functions.

From the difference of the combustion enthalpies at adjacent compositions of 2S–TaS$_x$ and 3S–TaS$_x$, the enthalpy of the phase transformation (ΔH_t^1) from 2S–TaS$_x$ to 3S–TaS$_x$ was evaluated ($\Delta H_t^1 = -114$ kJ mol^{-1}). In the same way, the enthalpy of the phase transformation (ΔH_t^2) from 3S–TaS$_x$ to 6S–TaS$_x$ was evaluated as $\Delta H_t^2 = 32$ kJ mol^{-1} and that for 6S–TaS$_x$ to 1S–TaS$_2$ (ΔH_t^3) as $\Delta H_t^3 = 65$ kJ mol^{-1}.

Relation between $-\Delta H_c$ and crystal structure

The crystal structure of the Ta–S system is layered in nature and the metal environment is octahedral or trigonal-prismatic. 1S–TaS$_2$ has a structure of the CdI$_2$ type with the octahedral surroundings of the metal. Every slab formed (sulphur–tantalum–sulphur layers) is bonded by weak van der Waals forces. The structure in the $(11\bar{2}0)$ sectional view is shown in Fig. 4a. The structure of 2S–TaS$_x$ is shown in Fig. 4b and that of 3S–TaS$_x$ in Fig. 4c. Tantalum atoms within the slabs in both structures are in a trigonal-prismatic environment, and those between the slabs are octahedrally surrounded. In the 6S–TaS$_x$ phase, slabs with trigonal-prismatically coordinated Ta and those with octahedrally surrounded Ta are stacked alternately, as shown in Fig. 4d.

The cohesion energy U_0 of transition-metal sulphides is based on Coulomb's force, the intermolecular force, the covalent bond, the metallic bond, etc. Intrinsically, U_0 is a function of the ionic radii and the number of charges

$$U_0 = f(r_+, r_-, Z_+, Z_-) \tag{5}$$

The enthalpy is defined as

$$\Delta H = \Delta U + p\Delta V \tag{6}$$

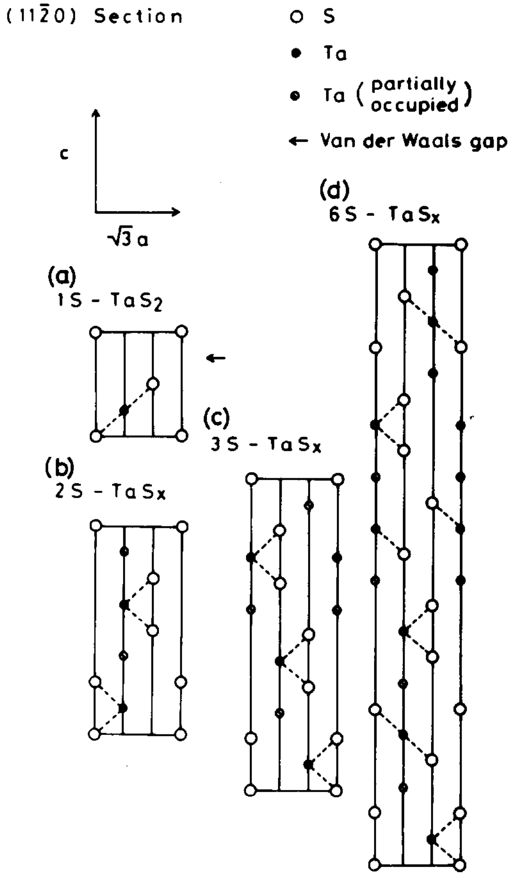

Fig. 4. Crystal structure of the Ta–S system (11$\bar{2}$0 plane). (a) 1S–TaS_2; (b) 2S–TaS_x; (c) 3S–TaS_x; (d) 6S–TaS_x.

In the present study, since the sulphides are solid, ΔV in eqn. (6) is almost zero. The internal energy ΔU is approximately equal to U_0 and, accordingly, the relation $\Delta H \simeq U_0$ is obtained.

The energy levels of the oxidation of sulphides can be estimated from a diagram of energy states as shown in Fig. 5. A transition-metal sulphide MS_x separates into a metal atom M(g) and a sulphur atom S(g), which both react with oxygen. The term U_0 for TaS_x corresponds to the following reaction

$$TaS_x \rightarrow Ta(g) + xS(g) \tag{7}$$

Then, Ta(g) + xS(g) react with oxygen and form $TaO_{5/2}$ (Ta_2O_5 phase). Therefore, $-\Delta H_c$ can be expressed as

$$-\Delta H_c = U_0 - \left(\Delta H_c^M + \Delta H_c^S\right) \tag{8}$$

where $-\Delta H_c^M$ and $-\Delta H_c^S$ are the enthalpies of oxidation of the tantalum and sulphur atoms, respectively. These schematic energy levels are shown in Fig. 5. If U_0 is large (sulphide is stable) the observed $-\Delta H_c$ will be small.

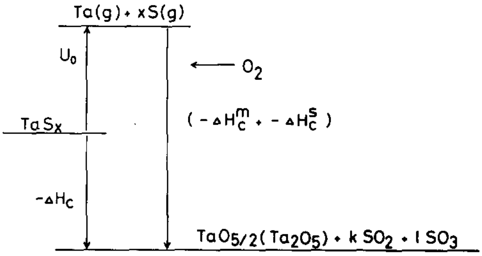

Fig. 5. A schematic diagram of the energy states.

Huisman et al. [7] suggested that the covalency of the *d* electron in transition metal atoms stabilizes trigonal-prismatic coordination rather than octahedral coordination. In the present experiment, when trigonal-prismatic coordination in the slab increased (1S → 6S → 3S), the values of $-\Delta H_c$ became progressively smaller. This means that a sulphide with trigonal-prismatic coordination would be the more stable. From these considerations, it is concluded that 3S–TaS_x with lower sulphur compositions ($x \simeq 1.65$) will be the most stable structurally in the present Ta–S system.

Enthalpy of formation of solid solution

The enthalpies of formation of solid solutions were estimated in the same way as described previously [5]. For the 3S–TaS_x phase region, $TaS_{1.714}$ was chosen as standard state 1 because the isotherm curves (Fig. 1) had an inflection point at this composition. For the $TaS_{1.714}$, one-sixth of the total metal sites in the partially occupied layer are occupied by tantalum atoms.

It was considered that the sulphur rich phase 3S–TaS_x ($1.714 \leqslant x \leqslant 1.825$) is formed by dissolving S_2 in the stoichiometric $TaS_{1.714}$ as follows

$$TaS_{1.714} + a/2S_2 \rightarrow TaS_{1.714+a} \tag{9}$$

Then the net enthalpy change of the sulphur rich 3S–TaS_x is given by

$$\Delta H_1 = -\Delta H_c - (-\Delta H_{c_1}) \tag{10}$$

where $-\Delta H_{c_1}$ is the enthalpy of combustion at standard state 1 in eqn. (2), and its value is 1222 kJ mol^{-1}.

From eqn. (9), the mole fraction of $TaS_{1.714}$ (N_1) in the $TaS_{1.714}$–S_2 system is given by

$$N_1 = 1/(1 + a/2) \tag{11}$$

In terms of N_1, ΔH_1 can also be expressed by the following equation which was derived by using the trial-and-error method

$$\Delta H_1 = 10.5 \times \ln(-10N_1 + 10.048) + 31.9 \tag{12}$$

ΔH_1 corresponds to the change in enthalpy of the solid solution from standard state 1. Consequently, the partial molal enthalpy of ΔH_1 represents the enthalpy of formation of a solid solution of $TaS_{1.714+a}$ (ΔH_{f1}^{ss}) corresponding to eqn. (9). According to the thermodynamic treatment [8] involving the Gibbs–Duhem equation

$$\begin{aligned}\Delta H_{f1}^{ss} &= \Delta \overline{H}_1 = \Delta H_1 + (1 - N_1)[d(\Delta H_1)/dN_1] \\ &= 10.5 \times \ln(-10N_1 + 10.048) + 31.9 \\ &\quad -(1 - N_1) \times 105/(-10N_1 + 10.048) \qquad (13)\end{aligned}$$

On the other hand, it was considered that the tantalum rich 3S–TaS_x ($1.646 \leqslant x \leqslant 1.714$) is formed by dissolving Ta in $TaS_{1.714}$ as follows

$$TaS_{1.714} + bTa \rightarrow Ta_{1+b}S_{1.714} \qquad (14)$$

Then the net combustion enthalpy change of the tantalum rich 3S–TaS_x is given by

$$\Delta H_1' = -\Delta H_c - (-\Delta H_{c_1}) \qquad (15)$$

From eqn. (14), the mole fraction of $TaS_{1.714}$ (N_1) in the $TaS_{1.714}$–Ta system is given by

$$N_1' = 1/(1 + b) \qquad (16)$$

In terms of N_1', $\Delta H_1'$ can also be expressed by the following equation which was derived by using the least-squares method

$$\Delta H_1' = 9.426 \times 10^5 N_1'^2 - 1.825 \times 10^5 N_1' + 8.821 \times 10^4 \qquad (17)$$

In the same way as for $-\Delta H_{f1}^{ss}$, the partial molal enthalpy of $-\Delta H_1'$ represents the enthalpy of formation of a solid solution of $Ta_{1+b}S_{1.714}$ ($-\Delta H_{f1'}^{ss}$) corresponding to eqn. (14) and is expressed by

$$\begin{aligned}\Delta H_{f1'}^{ss} &= \Delta \overline{H}_1' = \Delta H_1' + (1 - N_1')[d(\Delta H_1')/dN_1'] \\ &= -9.426 \times 10^4 N_1'^2 + 1.885 \times 10^5 N_1' - 9.426 \times 10^4 \qquad (18)\end{aligned}$$

For 6S–TaS_x, $TaS_{1.969}$ was chosen as standard state 2 because this composition was an end point in the 6S–TaS_x phase (see isotherms in Fig. 1). At $TaS_{1.969}$, the Ta atoms in the partially occupied layer occupy 1/64 of the Ta sites. It was considered that the tantalum rich 6S–TaS_x ($1.879 \leqslant x \leqslant 1.969$) was formed by dissolving Ta in $TaS_{1.969}$ as follows

$$TaS_{1.969} + cTa \rightarrow Ta_{1+c}S_{1.969} \qquad (19)$$

Then the net combustion enthalpy change (ΔH_2) between standard state 2 and the tantalum rich 6S–TaS_x is given by

$$\Delta H_2 = -\Delta H_c - (-\Delta H_{c_2}) \qquad (20)$$

where ΔH_{c_2} is the enthalpy of combustion at standard state 2. The term $-\Delta H_{c_2}$ is obtained when $x = 1.969$ in eqn. (4), and the value is 1325 kJ mol^{-1}.

From eqn. (16), the mole fraction of $TaS_{1.969}$ (N_2) in the $TaS_{1.969}$–Ta system is given by

$$N_2 = 1/(1 + c) \qquad (21)$$

In terms of N_2, ΔH_2 can also be expressed by the following equation which was derived by using the least-squares method

$$\Delta H_2 = 196.0N_2^4\text{-}136.3N_2^3 + 172.6N_2^2 - 202.1N_2 - 30.20 \qquad (22)$$

In the same way as for ΔH_{f1}^{ss}, the partial molal enthalpy of ΔH_2 is the enthalpy of formation of a solid solution of $Ta_{1+c}S_{1.969}$ (ΔH_{f2}^{ss}) corresponding to eqn. (16) and is expressed by

$$\begin{aligned}\Delta H_{f2}^{ss} = \Delta \overline{H}_2 &= \Delta H_2 + (1 - N_2)[d(\Delta H_2)/dN_2] \\ &= -30.20 - 202.1N_2 + 172.6N_2^2 - 136.3N_2^3 + 196.0N_2^4 \\ &\quad + (1 - N_2) \times (-202.1 + 345.2N_2 - 408.9N_2^2 + 784N_2^3) \qquad (23)\end{aligned}$$

Furthermore, for 2S–TaS_x, $TaS_{1.500}$ was chosen as standard state 3 for the same reason as in the case of 3S–TaS_x, i.e. at $TaS_{1.500}$ the tantalum atoms in the partially occupied layer occupy one-third of Ta sites. It was considered

TABLE 3

Enthalpy of formation of the solid solution for the 3S phase: standard state $TaS_{1.714}$

x in TaS_x	N_1	ΔH_1 (kJ mol^{-1})	ΔH_{f1}^{ss} (kJ mol^{-1})
1.728	0.993	28.46	22.23
1.737	0.989	31.79	24.40
1.760	0.978	37.31	28.61
1.780	0.968	40.48	31.25
1.798	0.960	42.69	33.16
1.817	0.951	44.61	34.83
1.825	0.947	45.32	35.45

TABLE 4

Enthalpy of formation of the solid solution for the 3S phase: standard state $TaS_{1.714}$

x in TaS_x	N_1'	$\Delta H_1'$ (kJ mol^{-1})	$\Delta H_{f1'}^{ss}$ (kJ mol^{-1})
1.646	0.960	−93.11	(−154.7)
1.678	0.979	−95.78	−45.46
1.683	0.982	−89.78	−34.44
1.693	0.988	−45.11	−17.46
1.710	0.999	−19.12	−0.990

that the sulphur rich 2S–TaS$_x$ ($1.500 \leqslant x \leqslant 1.595$) was formed by dissolving S$_2$ in the stoichiometric TaS$_{1.500}$ as follows

$$\mathrm{TaS}_{1.500} + d/2\mathrm{S}_2 \rightarrow \mathrm{TaS}_{1.500+d} \tag{24}$$

After the same treatments in 3S– or 6S–TaS$_x$, the following equations were obtained

$$\Delta H_3 = -1.355 \times 10^4 N_3^2 + 2.586 \times 10^4 N_3 - 1.231 \times 10^4 \tag{25}$$

$$\Delta H_{f3}^{ss} = 1.355 \times 10^4 N_3^2 - 2.710 \times 10^4 N_3 + 1.355 \times 10^4 \tag{26}$$

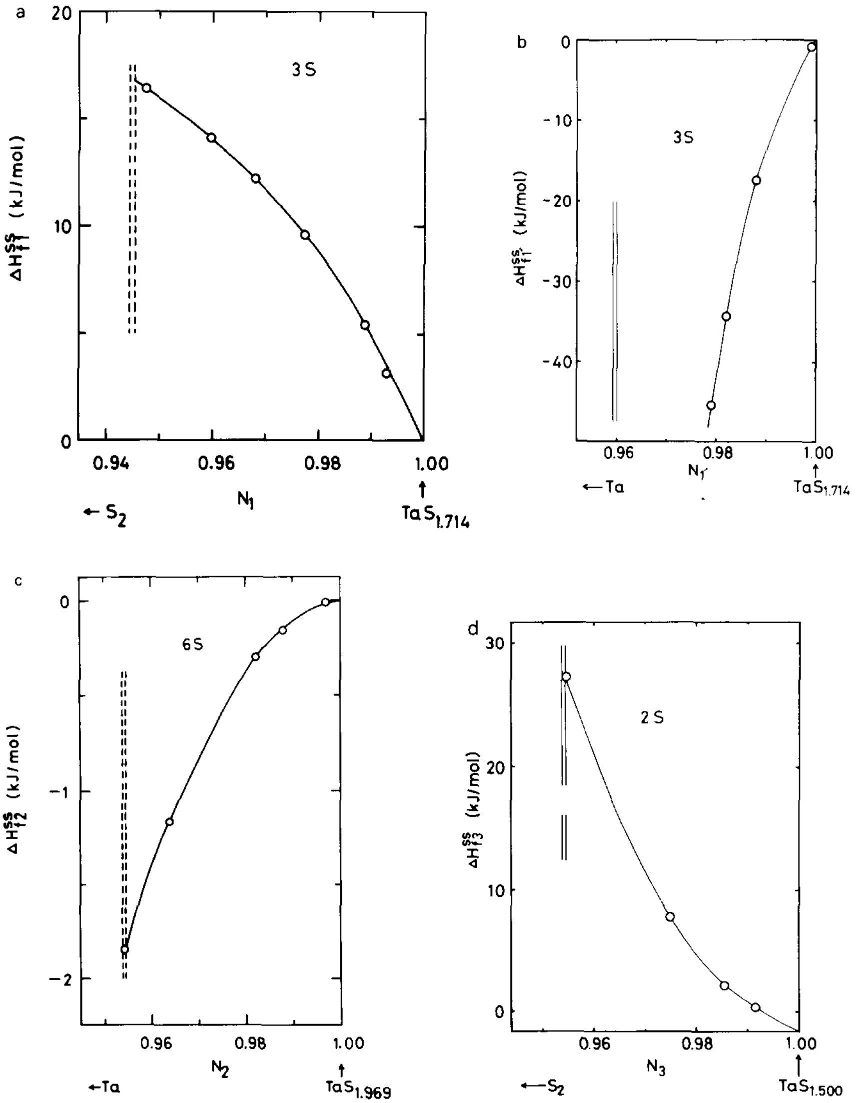

Fig. 6. The enthalpy of formation of the sulphur solid solutions: (a) 3S–TaS$_x$ ($1.714 \leqslant x \leqslant 1.825$); (b) 3S–TaS$_x$ ($1.646 \leqslant x \leqslant 1.714$); (c) 6S–TaS$_x$ ($1.879 \leqslant x \leqslant 1.969$); (d) 2S–TaS$_x$ ($1.500 \leqslant x \leqslant 1.595$).

TABLE 5

Enthalpy of formation of the solid solution for the 6S phase: standard state $TaS_{1.969}$

x in TaS_x	N_2	$-\Delta H_2$ (kJ mol^{-1})	$-\Delta H_{f2}^{ss}$ (kJ mol^{-1})
1.879	0.954	−21.79	−1.841
1.898	0.964	−17.75	−1.164
1.934	0.982	−9.000	-2.905×10^{-1}
1.945	0.988	−6.242	-1.375×10^{-1}
1.963	0.997	−1.578	-8.422×10^{-3}

TABLE 6

Enthalpy of formation of the solid solution for the 2S phase: standard state $TaS_{1.500}$

x in TaS_x	N_3	ΔH_3 (kJ mol^{-1})	ΔH_{f3}^{ss} (kJ mol^{-1})
1.500	1.000	–	–
1.517	0.9916	9.000	0.392
1.529	0.9857	12.17	2.207
1.551	0.9751	23.67	7.836
1.595	0.9547	27.34	27.24

where $N_3 = 1/(1 + d/2)$, and ΔH_{f1}^{ss}, $\Delta H_{f1'}^{ss}$, ΔH_{f2}^{ss} and ΔH_{f3}^{ss} are summarized in Tables 3–6. Figs. 6(a)–6(d) show ΔH_{f1}^{ss}, $\Delta H_{f1'}^{ss}$, ΔH_{f2}^{ss} and ΔH_{f3}^{ss} for the variation of N_1, N_1', N_2 and N_3, respectively.

ΔH_{f1}^{ss} and ΔH_{f3}^{ss} will indirectly correspond to the enthalpy of formation of a tantalum solid solution. The absolute magnitude in the tantalum rich region ($\Delta H_{f1'}^{ss}$ in 3S–TaS_x) is larger than that in the other phases. This suggests that the tantalum atoms in partially occupied metal layers in the region of the tantalum rich 3S–TaS_x ($TaS_{1.714} \approx TaS_{1.65}$) are strongly combining S–Ta–S slabs compared with those in the other regions.

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