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PARTIAL MOLAR ENTHALPHY OF FORMATION OF SOLID SOLUTION IN TRANSITION METAL SULFIDES BY A COMBUSTION CALORIMETRY

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ABSTRACT

The combustion calorimetry on the Nb-S system has been carried out under an oxygen atmosphere at 453°C using a Calvet-type twin calorimeter. The partial molar enthalphies of the formation of solid solution for both 2S-NbS_x and 3S-NbS_x phase on the Nb-S system has been determined.

INTRODUCTION

A number of transition metal sulfides with nonstoichiometric composition form layer structures, and these structures can be derived from the NiAs type structure when the metal atoms were partially removed from every second metal layer. Accordingly, the nonstoichiometry of these sulfides originates from the number of metal vacancies involved in the metal layers of the structure. Unfortunatery, there is still a great insufficiency of reliable thermodynamic information on the nonstoichiometry of these sulfides. Previously, same authors determined the isotherms of the niobium sulfides at high temperatures (ref.1). The system has two types of crystal structures, 2S-NbS_x and 3S-NbS_x, according to Jellinek (ref.2), and the structures for rather wide homogeneous composition ranges.

The object of the present study is mainly to determine the partial molar enthalpy of formation of solid solution on the Nb-S system by a combustion calorimetry, since the differentiation of combustion enthalpy of the niobium sulfides by small change in composition give the partial molar enthalpy.

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EXPERIMENTAL

Sample preparation

Regent grade Nb_2O_5 was heated in a ceramic boat at about 700°C in a current of H_2S gas for 24h. After cooling rapidly to room temperature, the sample was ground in an agete mortar and the same heat treatment was repeated. Niobium sulfide with a composition near $NbS_{1.8}$ was always obtained. This was used as the starting material. No residual oxide was found in the sulfides by X-ray powder diffraction method.

The sample with desired composition was prepared by varying the partial pressure of sulfur using H_2S / H_2 gas high temperature sulfidation method on the basis of the equilibrium sulfur pressure· composition isotherm (ref.1). The phase of each sample was identified by X-ray powder diffraction method. The chemical composition of the sample was determined by oxidizing the sulfide completely to Nb_2O_5 in air for 48h at 700°C.

The particle size of the sulfides used in this study is 100-150 mesh.

Apparatus and Procedure

All the calorimetric experiments were performed at 453°C under an oxygen atmosphere using a Calvet-type twin calorimeter designed for operation at temperatures up to 650°C.

The cell, isothermal jacket and other metallic parts are made of stainless steel (SUS 304), and supporting parts of the cell are made of sintered zirconia. Thermal effects were detected by use of a platinel thermopile made of 128 thermocouples. Two cells are arranged in a differential and symmetrical way in order to eliminate thermal effects other than the intended one. The calorimeter is suspended in the furnace. A constant direct current generated by TAKASAGO POWER SUPPLY (GP 0200-10) is supplied to the furnace to keep the temperature of the calorimeter constant (453 ± 0.2°C). The output signal of the thermopile is fed to a recorder through a high impedance microvoltmeter. The detailes of this calorimeter will be described elsewhere soon.

The calibration was performed by measuring the thermal effects on dropping platinum chips, and also the known molar enthalpies of oxidation of NbO_2 to Nb_2O_5 was measured for the sake of comparison

For the estimation of thermal effect, 14 points (4 points from START to MAXIMUM, and 10 from MAXIMUM to END in Fig. 1) are selected and their coordinate values (X_i, Y_i) were determined from an e.m.f vs. time curve. By substituting these values into Lagrange's interpolation equation (eq. 1), we get 3-order function Fa(X) fitted for the curve from START to MAXIMUM and 9-order function Fb(X) for MAXIMUM to END (Fig. 1).

$$f(x) = \sum_{i=0}^{n} y_i \frac{(x-x_1)(x-x_2)\cdots(x-x_n)}{(x_i-x_1)(x_i-x_2)\cdots(x_i-x_n)} \qquad (1)$$

Peak area under this curve can be calculated from the sum of integration of Fa(X) and Fb(X). The Simpson's rule was applied for the integration and an NEC PC-9801F, personal computer, was used for the calculation.

The cell used for the combustion experiment is shown schematically in Fig. 2. About 30mg of the niobium sulfide sample was precisely measured and was placed in a small pyrex ampoule, and sealed in vacuum. The ampoule was joined to a long glass tube. To ensure complete combustion, about 40mg V_2O_5 powder was placed in the bottom part of the tube as a catalyst. Dried oxygen (over P_2O_5) with a flow rate of 120 cc/min was passed through this cell. The cell was then pre-heated for about 10 minutes in an electric furnace at 450°C before it was inserted into the calorimeter. It took about one hour to attain a thermal equilibrium. After the equilibration, the combustion experiment was initiated by breaking the bottom of the pyrex ampoule by means of the glass manipulation tube.

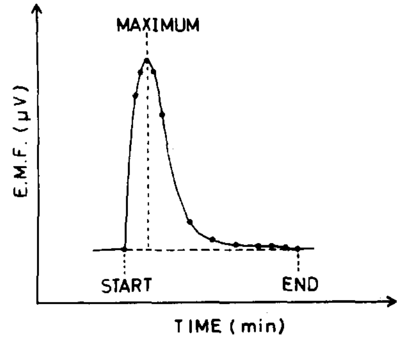

Fig. 1 An e.m.f. vs. time curve.

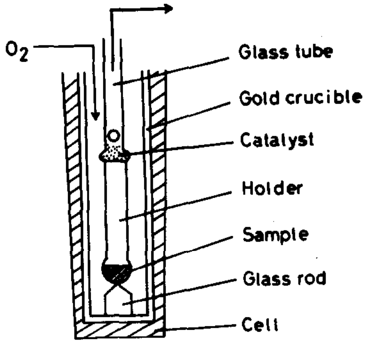

Fig. 2 Combustion arrangment in the calorimeter cell.

Following combustion reaction is considered for the niobium sulfides oxidation.

$$NbS_x + \left(\frac{5+6x}{4}\right) O_2 \longrightarrow \frac{1}{2} Nb_2O_5 + x\,SO_3 \qquad (2)$$

After the combustion we could not find any other phases beside Nb_2O_5 by the X-ray powder diffraction pattern. About 40 minutes were needed to complete the combution reaction. If the above reaction proceeds under equilibrium condition, the existance of SO_2 would be negligible, because the equilibrium constant for the reaction $SO_2 + 1/2\,O_2 = SO_3$, $Kp = Pso_3 / Pso_2 \cdot Po_2^{1/2} = Pso_3 / Pso_2$, estimated at 453°C by using J A N A F Thermochemical Tables (ref.3), is 153.

RESULT AND DISCUSSION

Estimation of heat pick-up correction on dropping platinum chips

The heat pick-up during the drop of the Pt chip was evaluated to be 6.9% at 453°C by the following way.

$$(\text{Effect of heat pick-up}) = \frac{Qobs - Qcal}{Qcal} \qquad (3)$$

where, Qcal is the calculated heat by using literature (ref.3) and Qobs is the observed heat.

$$Qcal = \int_{T1}^{T2} Cp\,dT \qquad (4)$$

$$Qobs = \int_{T1'}^{T2} Cp\,dT \qquad (5)$$

where, C is the specific heat of Pt, and T2 is the calorimeter temperature. The temperature of the Pt chip increases from the room temperature T1 to T1' by heat pich-up. Accordingly, Qobs is always smaller than Qcal. Since Qcal is proportional to the peak area A of the e.m.f. vs. time curve, it can be expressed as

$$Qobs = \beta A \qquad (6)$$

where, β is a constant. Substitution of eqn.6 into eqn.3 gives the following equation,

$$(\text{Effect of heat pick-up}) = \frac{\beta A - Qcal}{Qcal} \qquad (7)$$

If we assume that the heat pick-up is proportional to the surface area S of the Pt chip, we will get the following relationship from eqn.7,

$$\alpha S = \frac{\beta A - Qcal}{Qcal} \qquad (8)$$

where α is a constant, and rearrangement of eqn.8 gives

$$\frac{A}{Qcal} = \frac{\alpha}{\beta}S + \frac{1}{\beta} \qquad (9)$$

Therefore using the value of β, calculated from intercept of the plot of A / Qcal against S, the effect of the heat pick-up can be evaluated from eqn.3.

The measurements of oxidation enthalphies from NbO_2 to Nb_2O_5 was performed under the same condition of the combustion measurement on Nb-S system mentioned above to compare with the result obtained from the Pt chip dropping method. The enthalpy of the above mentioned oxidation reaction was evaluated as 154.30 kJ / mol from Barin and Knacke's data (ref.4). The results of calibration by two different methods showed good agreement (within 2%).

Results of combustion experiment

We measured the enthalphies of combustion of 2S-NbS_x (x = 1.457, 1.487, 1.515 and 1.535) and 3S-NbS_x (x = 1.657, 1.666, 1.710, 1.736 and 1.751). The results are shown in Table 1. The net amount of enthalpy change $-\Delta H$ in the calorimeter, and molar enthalpy of reaction $-\Delta H_m$ for eqn.2 are also shown in Table 1. Fig. 3 represents the average value of $-\Delta H_m$ of each sample against their composition x in NbS_x, and the results can be fitted smoothly by the following analytical expressions which were derived from a least-square treatment.

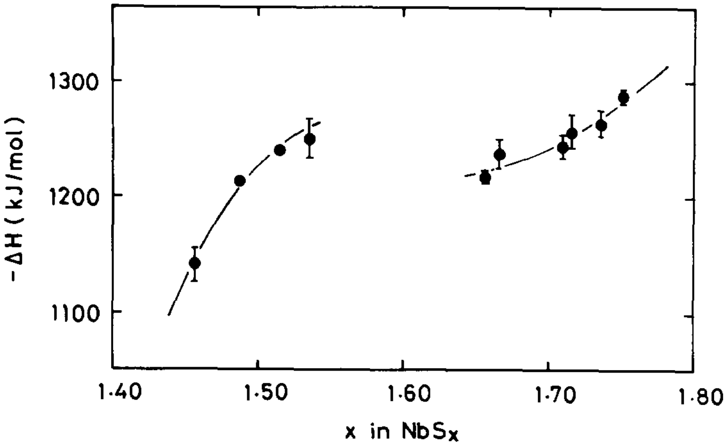

Fig. 3 Heat of combustion for 2S-NbS_x and 3S-NbS_x phases.

$$2S\text{-}NbS_x \;;\; -\Delta H_m = -2583\,x^4 + 5581\,x^3 - 1978\,x^2 + 4528\,x - 6876 \qquad (10)$$

$$3S\text{-}NbS_x \;;\; -\Delta H_m = 475\,x^4 - 433\,x^3 - 2126\,x^2 + 2237\,x + 1746 \qquad (11)$$

Although the equilibrium sulfur vapor pressure-composition isotherm at a tempeature of about 450°C has not yet been established, it can be estimated approximately from our previous isotherms (ref.1) for high temperature. We could not synthesize a single phase niobium sulfide between $NbS_{1.55}$ - $NbS_{1.64}$, and as a result it was not possible to determine the exact phase region, 2S-NbS_x and 3S-NbS_x. However, the difference of $-\Delta H_m$ value 33 kJ / mol between $NbS_{1.535}$ and

TABLE 1

Calorimetric results of the combustion of the niobium sulfides.

x in NbS_x	m (mg)	$-\Delta H$ (J)	$-\Delta H_m$ (kJ/mol)	
2S-NbS_x phase				
1.457	28.70	239.3	1164	mean = 1142 ± 14.9 $\Delta\overline{H}_{f.ss}$ = 2354
	28.53	228.9	1120	
	29.94	244.7	1141	
1.487	28.90	249.3	1213	mean = 1214 ± 1.0 $\Delta\overline{H}_{f.ss}$ = 1700
	29.76	257.2	1215	
1.515	30.89	271.0	1241	mean = 1241 ± 0 $\Delta\overline{H}_{f.ss}$ = 1041
	30.05	263.6	1241	
1.535	29.14	259.8	1267	mean = 1251 ± 17.6 $\Delta\overline{H}_{f.ss}$ = 542
	29.19	251.6	1225	
	29.23	259.6	1262	
3S-NbS_x phase				
1.657	29.18	242.4	1213	mean = 1219 ± 5.5 $\Delta\overline{H}_{f.ss}$ = 267
	31.33	262.4	1224	
1.666	28.93	246.4	1246	mean = 1238 ± 12.7 $\Delta\overline{H}_{f.ss}$ = 332
	30.99	264.6	1249	
	31.00	258.3	1219	
1.710	29.79	251.1	1245	mean = 1245 ± 10.8 $\Delta\overline{H}_{f.ss}$ = 666
	29.81	246.8	1223	
	33.93	285.3	1242	
	29.58	254.7	1272	
	28.84	242.7	1243	
1.716	30.20	258.1	1264	mean = 1258 ± 15.1 $\Delta\overline{H}_{f.ss}$ = 714
	29.54	246.6	1235	
	30.11	259.3	1274	
1.736	28.68	246.3	1276	mean = 1265 ± 11.0 $\Delta\overline{H}_{f.ss}$ = 879
	28.24	238.4	1254	
1.756	27.27	237.5	1298	mean = 1288 ± 6.4 $\Delta\overline{H}_{f.ss}$ = 1008
	28.22	249.3	1288	
	29.21	250.7	1279	

$NbS_{1.657}$ is approximately considered to be the enthalpy of phase transition from 2S-NbS_x to 3S-NbS_x (2S-$NbS_x \rightarrow$ 3S-NbS_x : Endothermic)

The partial molar enthalpy of formation of solid solution $\Delta\bar{H}_{f.ss}$ in the Nb-S system could be estimated from the differentiation of eqns.10 and 11. The $\Delta\bar{H}_{f.ss}$ for the variation of x in NbS_x is shown in Fig. 4. The $\Delta\bar{H}_{f.ss}$ values can be calculated from the isotherms, determined by us (ref.1), by using the equation $\Delta\bar{H}_{f.ss} = R\,d(\ln a_s) / d(1/T)$, and these values are plotted as broken line in the same figure (Fig. 4) for comparison. The maximum value of $\Delta\bar{H}_{f.ss}$ is found around $x = 1.60$ from this figure. This result consists with the phase transition of the niobium sulfide.

Beside the Nb-S system, we tried the combustion calorimetry for the V-S and Ti-S systems, but owing to various experimental difficulties, we have not yet succeeded to determine the $\Delta\bar{H}_{f.ss}$ for these system under oxygen atmosphere. However, the values can be determined by controlling the oxygen partial pressure, which will be discussed later.

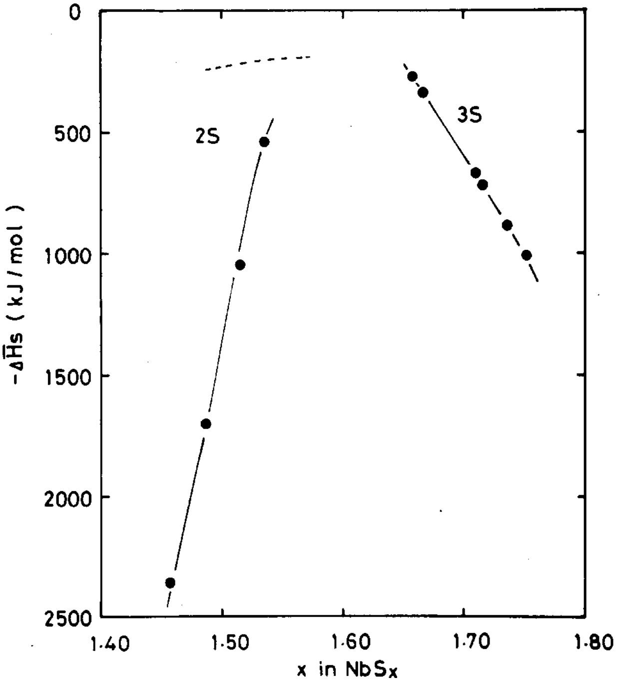

Fig. 4 Partial molar enthalphy estimated by 4-order equation for 2S-NbS_x and 3S-NbS_x phases.

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