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DETERMINATION OF ENTHALPY OF FORMATION OF A SOLID SOLUTION IN THE Ti–S SYSTEM BY COMBUSTION CALORIMETRY *

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ABSTRACT

Combustion calorimetry of the Ti–S system has been carried out under a mixed oxygen–air atmosphere ($P_{O_2} = 4 \times 10^4$ Pa) at 406°C using a Calvet-type twin calorimeter. The enthalpies of formation of solid solutions for 4H′-Ti_2S_3, 4H-Ti_2S_3 and 2H-TiS_2 phases in the Ti–S system have been determined. The results are compared with the heat of combustion estimated from the literature.

INTRODUCTION

Transition metal sulfides have much potential as new materials. Among them, TiS_2 is used as a cathode material for high energy secondary batteries.

Phase equilibria and structure of the Ti–S system are rather complicated, and in the Ti_2S_3–TiS_2 range, three hexagonal types of crystal structures appear, i.e. 4H′-Ti_2S_3, 4H-Ti_2S_3 and 2H-TiS_2 phases [1–5], with rather wide ranges of solid solution in each phase. Unfortunately, there is still an insufficient supply of reliable thermodynamic information on the non-stoichiometry of these sulfides. Previously, some authors determined the isotherms of titanium sulfides at high temperatures [1], and also reported a similar combustion study on the Nb–S system [6].

The purpose of the work reported in this paper is mainly to determine the enthalpy of formation of a solid solution in the Ti–S system by combustion calorimetry. Also, the enthalpy of combustion is compared with values estimated from published thermodynamic data.

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* Dedicated to Professor Syûzô Seki in honor of his contribution to Calorimetry and Thermal Analysis.

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EXPERIMENTAL

Sample preparation

Sulfur powder (reagent grade) and titanium powder (99.9%) were purchased from Yoneyama Chemical Industries Ltd. and Soekawa Chemicals Co., Ltd., respectively. In order to make samples with composition x, from 1.65 to 2.00 in TiS_x, the elements were mixed directly, and 3 g of mixtures of various compositions were sealed in separate evacuated quartz ampoules. They were held in a furnace at 400°C for 1 day and then at 900°C for 3 or 4 days. Sulfur-rich samples (TiS_x, $1.95 < x < 2.00$) were further annealed at 500°C for 1 or 2 days. The samples with composition x from 1.50 to 1.63 in TiS_x were prepared by varying the partial pressure of sulfur using H_2S/H_2 gas mixtures on the basis of the equilibrium sulfur pressure–composition isotherm [1]. The phase of each sample prepared was identified by the X-ray powder diffraction method. The chemical composition of TiS_x was determined by oxidizing the samples completely to TiO_2 (rutile) in air for 16 h at 950°C.

Apparatus and procedure

The Calvet-type twin calorimeter designed for operation at temperatures up to 650°C, reported elsewhere [6], was used for the combustion of the titanium sulfides. The thermal effect is detected as electrical output with a thermocouple.

After combustion, a small amount of small black particles of TiS_x was observed in the matrix of TiO_2 (anatase) with an optical microscope, although they could not be identified from the X-ray powder diffraction pattern. In order to decide the optimum experimental conditions for combustion of titanium sulfides, five factors were altered: temperature of the calorimeter, oxygen partial pressure (P_{O_2}) of the reaction gas, its flow rate, amount of titanium sulfide and its particle size. Temperature and P_{O_2} were more important factors than the others. At higher temperatures, the amount of unreacted residual TiS_x was increased compared to that at lower temperatures. P_{O_2} was changed from 2.0×10^4 to 5.6×10^4 Pa by mixing air and oxygen at each temperature. Unreacted TiS_x tended to increase with increasing P_{O_2}, but when P_{O_2} was extremely low, it was difficult to estimate the

TABLE 1

Conditions for the combustion experiment

Temperature of calorimeter	406°C
Oxygen partial pressure	4×10^4 Pa
Flow rate of reaction gas	2 cm^3 s^{-1}
Particle size of samples	150–250 mesh
Amount of samples	9.00–10.00 mg

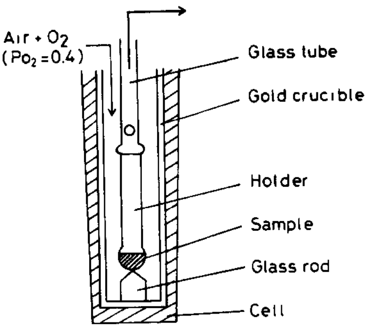

Fig. 1. Combustion arrangement in the calorimeter cell.

enthalpy of combustion because of the broadened peak due to slow combustion. Considering these two contrary phenomena, P_{O_2} was fixed at 4×10^4 Pa. The other factors were fixed taking account of points such as good reproducibility, minimizing unreacted residual TiS_x and small heat loss. These factors fixed for the present study are summarized in Table 1. Both EPMA (electron probe micro analysis) and chemical analysis were used to find the amount of unreacted TiS_x. There was 5.0 mol% titanium sulfides existing in the oxides when using $TiS_{1.5}$ as a starting sample, and 2.4 mol% when using $TiS_{2.0}$. Consequently, the experimental results were corrected by linear approximation.

The cell used for the combustion experiment is shown schematically in Fig. 1. The sample, accurately weighed to 10 ± 0.01 mg, was put in a small pyrex holder (ID = 4 mm) and sealed under vacuum. Then the holder was joined to another long pyrex tube. Oxygen–air mixed gas ($P_{O_2} = 4 \times 10^4$ Pa), purified by passing it over P_2O_5, was passed through this cell at a flow rate of 2 cm^3 s^{-1}. The cell was pre-heated for about 15 min in an electric furnace at 350°C and inserted into the calorimeter. After thermal equilibration (~ 1 h), the combustion experiment was initiated by breaking the bottom of the pyrex ampoule by means of a glass manipulation tube. It took about 50 min to complete the combustion reaction.

Calibration of the calorimeter was performed by measuring the thermal effects on the known molar enthalpies [7] of oxidation of the stoichiometric NbO_2 to stoichiometric Nb_2O_5 phase:

$$NbO_2 + \tfrac{1}{4}\ O_2 \rightarrow NbO_{5/2}\ (Nb_2O_5\ \text{phase})\ \Delta H^0 = -154.3\ \text{kJ mol}^{-1}$$

under the same conditions as used for the combustion experiments.

RESULTS AND DISCUSSION

Heat of transformation

The enthalpies of combustion (ΔH_c) of 4H′-TiS_x, 4H-TiS_x and 2H-TiS_x obtained in the present study are summarized in Table 2 and are plotted graphically in Fig. 2. The curves show two sets of profiles, and the mean deviation is also shown as error bars at each point in Fig. 2.

The isotherms of the Ti–S system previously reported [1] are shown in

TABLE 2

Enthalpies of combustion

x in TiS_x	w (mg)	$-\Delta H_c$ (observed) (kJ mol^{-1})		$-\Delta H_c$ (calculated) (kJ mol^{-1})
4H′-TiS_x phase				
1.498	9.30	1037		
	9.71	1012	mean = 1025 ± 8.7 [a]	1027
	9.50	1026		
1.513	9.42	1062		
	10.05	1107	mean = 1080 ± 17.7	1082
	10.09	1072		
1.542	9.48	1104		
	10.08	1092	mean = 1092 ± 8.3	1093
	9.19	1079		
1.575	10.11	1093		
	9.66	1095	mean = 1103 ± 12.3	1099
	9.96	1122		
1.634	9.67	1087		
	9.99	1114	mean = 1110 ± 15.0	1105
	9.40	1128		
4H-TiS_x phase				
1.656	9.33	1107		
	9.92	1106	mean = 1102 ± 5.7	1107
	9.95	1094		
1.687	9.69	1120		
	9.73	1105	mean = 1110 ± 6.7	1109
	9.94	1105		
1.710	9.95	1094		
	9.66	1117		
	9.93	1120	mean = 1108 ± 11.6	1110
	9.66	1116		
	9.88	1093		
1.739	9.67	1108	mean = 1109 ± 0.5	1111
	9.69	1109		
1.765	9.99	1122	mean = 1111 ± 11.0	1112
	10.16	1099		
1.801	10.09	1147		
	9.75	1082	mean = 1119 ± 18.8	1114
	10.03	1122		
	9.69	1126		

TABLE 2 (continued)

x in TiS_x	w (mg)	$-\Delta H_c$ (observed) (kJ mol^{-1})		$-\Delta H_c$ (calculated) (kJ mol^{-1})
2H-TiS_x phase				
1.826	9.67	1051	mean = 1045 ± 17.2	1048
	10.00	1019		
	9.55	1060		
	9.82	1029		
	10.25	1068		
1.866	9.70	1079	mean = 1077 ± 6.3	1068
	10.49	1062		
	9.74	1074		
	9.87	1076		
	9.47	1080		
	10.00	1091		
1.917	9.67	1091	mean = 1102 ± 15.3	1117
	9.56	1082		
	9.79	1112		
	9.82	1122		
1.928	9.21	1151	mean = 1131 ± 16.5	1131
	9.80	1115		
	8.14	1114		
	9.62	1144		
1.956	9.40	1196	mean = 1184 ± 20.5	1173
	9.53	1143		
	10.34	1199		
	9.35	1198		
1.998	9.47	1239	mean = 1249 ± 7.0	1252
	9.52	1251		
	9.78	1258		

[a] Mean deviation.

Fig. 3. The profiles of the isotherms are not continuous at the phase transformation from 4H-TiS_x to 2H-TiS_x, since this phase transformation is first order. In contrast, the phase transformation from 4H′-TiS_x to 4H-TiS_x is the second or a highly ordered transformation, because the isotherms are continuous. In the present study, $-\Delta H_c$ also changes continuously from 4H′ to 4H-TiS_x phase within the limits of the experiment.

In the region of 4H′ and 4H phases, $-\Delta H_c$ can be fitted smoothly by the following analytical equation which was derived by the trial-and-error method:

$$-\Delta H_c = 10.86 \times \ln(-20X_1 + 20.084) + 1087 \qquad (1)$$

where X_1 is the mole fraction of $TiS_{1.5}$ in the $TiS_{1.5}$(Ti_2S_3 phase)–TiS_2 system. While $-\Delta H_c$ in the 2H-TiS_x phase can be expressed by the

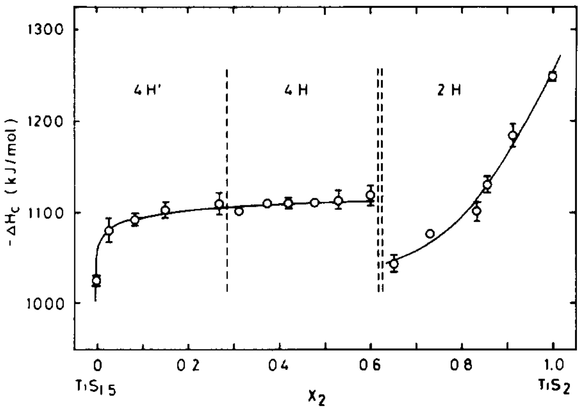

Fig. 2. Heat of combustion for 4H′, 4H and 2H phases.

following equation which was derived by the method of least squares:

$$-\Delta H_c = 1368 - 1008X_2 + 602.3X_2^2 + 294.5X_2^3 \qquad (2)$$

where X_2 is the mole fraction of TiS_2 in the $TiS_{1.5}$(Ti_2S_3 phase)–TiS_2 system. $-\Delta H_c$ calculated by eqns. (1) and (2) are tabulated in Table 2 and the curves are shown in Fig. 2.

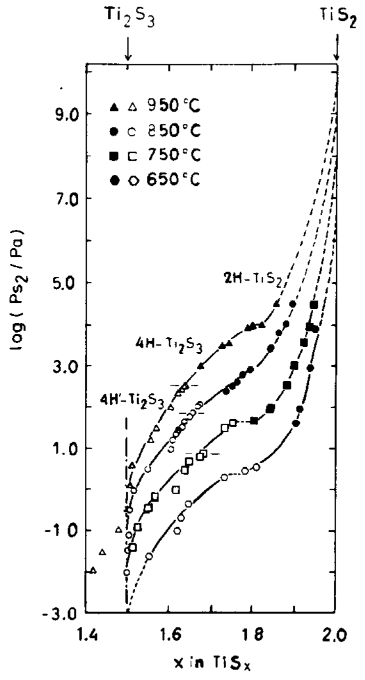

Fig. 3. Equilibrium sulfur vapor pressure–composition isotherms in Ti–S system at certain temperatures.

From the difference of combustion enthalpies between 4H-TiS_x and 2H-TiS_x, the enthalpy of phase transformation, ΔH_t,

$$\Delta H_t = 75 \text{ kJ mol}^{-1} \qquad (3)$$

was evaluated.

Enthalpy of formation of solid solution

The enthalpy of formation of a solid solution could be estimated by the following method.

When stoichiometric Ti_2S_3 was chosen as standard state 1 for 4H′ and 4H phases, it was considered that nonstoichiometric Ti_2S_3 was formed by solvating S_2 in the stoichiometric Ti_2S_3 as follows:

$$TiS_{1.5} + a/2\ S_2 \rightarrow TiS_{1.5+a} \qquad (4)$$

Then the net enthalpy change between standard state 1 and nonstoichiometric Ti_2S_3 is given by

$$-\Delta H_1 = -\Delta H_c - (-\Delta H_{c1}) \qquad (5)$$

where $-\Delta H_{c1}$ is the enthalpy of combustion at standard state 1. $-\Delta H_{c1}$ is obtained when $X_1 = 1$ in eqn. (1), and the value is 1060 kJ mol^{-1} (cf. $TiS_{1.498}$; $-\Delta H_c = 1025$ kJ mol^{-1}).

From eqn. (4), the mole fraction of $TiS_{1.5}$, N_1, in the $TiS_{1.5}$(Ti_2S_3 phase)–S_2 system is given by

$$N_1 = 1/(1 + a/2) \qquad (6)$$

In terms of N_1, $-\Delta H_1$ can also be expressed by the following equation which was derived by the trial-and-error method:

$$-\Delta H_1 = 11.29 \times \ln(-30N_1 + 30.032) + 39 \qquad (7)$$

$-\Delta H_1$ is the change in enthalpy of the solid solution from standard state 1. Consequently the partial molal enthalpy of $-\Delta H_1$ represents the enthalpy of formation of a solid solution of $TiS_{1.5+a}$, $-\Delta H_{f1}^{ss}$, corresponding to eqn. (4). According to the thermodynamic treatment [8] involving the Gibbs–Duhem equation,

$$-\Delta H_{f1}^{ss} = -\Delta \overline{H}_1 = -\Delta H_1 + (1 - N_1)[d(-\Delta H_1)/dN_1] \qquad (8)$$

Hence, combination of eqns. (7) and (8) yields

$$-\Delta H_{f1}^{ss} = 11.29 \times \ln(-30N_1 + 30.032) + 39 - (1 - N_1) \times 338.7/(-30N_1 + 30.032) \qquad (9)$$

When stoichiometric TiS_2 was chosen as the standard state for the 2H phase, it was considered that nonstoichiometric TiS_2 was formed by solvating Ti in stoichiometric TiS_2 as follows:

$$TiS_2 + b\ Ti \rightarrow Ti_{1+b}S_2 \qquad (10)$$

Then the net combustion enthalpy change between standard state 2 and nonstoichiometric TiS_2 is given by

$$-\Delta H_2 = -\Delta H_c - (-\Delta H_{c2}) \tag{11}$$

where $-\Delta H_{c2}$ is the enthalpy of combustion at standard state 2. $-\Delta H_{c2}$ is obtained when $X_2 = 1$ in eqn. (2), and the value is 1257 kJ mol^{-1} (cf. $TiS_{1.998}$; $-\Delta H_c = 1249$ kJ mol^{-1}).

From eqn. (10), the mole fraction of TiS_2, N_2, in the TiS_2–Ti system is given by

$$N_2 = 1/(1+b) \tag{12}$$

In terms of N_2, $-\Delta H_2$ can also be expressed by the following equation which was derived by the method of least squares:

$$-\Delta H_2 = 7469 - 8229N_2 - 10240N_2^2 + 11000N_2^3 \tag{13}$$

In the same way as $-\Delta H_{f1}^{ss}$, the partial molal enthalpy of $-\Delta H_2$ represents the enthalpy of formation of a solid solution of $Ti_{1+b}S_2$, $-\Delta H_{f2}^{ss}$, corresponding to eqn. (10) and is expressed by

$$\begin{aligned} -\Delta H_{f2}^{ss} &= -\Delta \overline{H}_2 = -\Delta H_2 + (1 - N_2)[\mathrm{d}(-\Delta H_2)/\mathrm{d}N_2] \\ &= 7469 - 8229N_2 - 10240N_2^2 + 11000N_2^3 \\ &\quad + (1 - N_2)(-8229 - 20480N_2 + 33000N_2^2) \end{aligned} \tag{14}$$

$-\Delta H_{f1}^{ss}$ and $-\Delta H_{f2}^{ss}$ are summarized in Tables 3 and 4 with related values. Figures 4 and 5 show $-\Delta H_{f1}^{ss}$ and $-\Delta H_{f2}^{ss}$ for the variation of N_1 and N_2, respectively.

The structure of the Ti–S system is layered in nature and can be derived from the original structure of the TiS (NiAs type) when the Ti atoms are

TABLE 3

Enthalpy of formation of a solid solution for 4H′ and 4H phases

x in TiS_x	N_1	$-\Delta H_1$ (kJ mol^{-1})	$-\Delta H_{f1}^{ss}$ (kJ mol^{-1})
Standard state Ti_2S_3			
1.513	0.994	21.49	11.90
1.542	0.979	34.34	23.60
1.575	0.964	40.20	29.23
1.634	0.937	46.38	35.27
1.656	0.928	47.86	36.74
1.687	0.914	49.84	38.69
1.710	0.905	50.95	39.79
1.739	0.893	52.28	41.10
1.765	0.883	53.28	42.09
1.801	0.869	54.54	43.34

TABLE 4

Enthalpy of formation of a solid solution for the 2H phase

x in TiS_x	N_2	$-\Delta H_2$ (kJ mol^{-1})	$-\Delta H_{f2}^{ss}$ (kJ mol^{-1})
Standard state TiS_2			
1.826	0.913	−208.3	−157.8
1.866	0.933	−188.6	−95.55
1.917	0.959	−138.4	−36.74
1.928	0.964	−125.5	−28.47
1.956	0.978	−83.50	−10.78
1.998	0.999	−4.286	−0.02273

partially removed from every second metal layer (see Fig. 6). Consequently TiS_2 has the CdI_2 type structure. Every slab formed (sulfur–titanium–sulfur layers) was bonded by weak Van der Waals forces. If a partially filled layer is filled by titanium atoms at the ratio of 33.3%, this titanium sulfide is stoichiometric $TiS_{1.5}$.

We consider that $-\Delta H_{f1}^{ss}$ will indirectly correspond to the enthalpy of formation of a titanium solid solution. In the 4H′ phase, $-\Delta H_{f1}^{ss}$ increases continuously with decreasing Ti_2S_3 content compared with the 4H phase as shown in Fig. 4. In other words, the energy of Ti atom distribution in the 4H phase is smaller than that in the 4H′ phase. In the 2H phase, the absolute magnitude of ΔH_{f2}^{ss} is larger than ΔH_{f1}^{ss} in the 4H and 4H′ phases. This

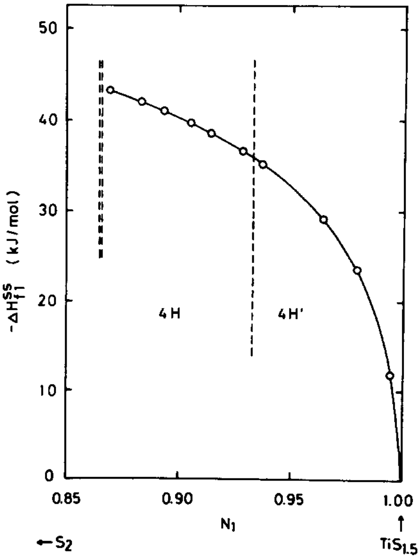

Fig. 4. Enthalpy of formation of a solid solution for 4H′ and 4H phases.

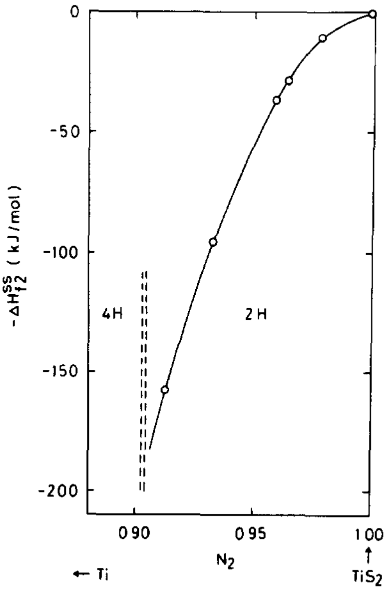

Fig. 5. Enthalpy of formation of a solid solution for the 2H phase.

suggests that the energy of Ti atom distribution in the 2H phase is larger than that in 4H and 4H′ phases.

Comparison of observed enthalpy of combustion with literature data

The enthalpy of combustion of stoichiometric TiS_2 at 406 °C (679 K) was calculated from literature data [7,9,10] and was compared with the present results. Mraw et al. [9] measured the heat capacity of TiS_2 (C_p) in the range

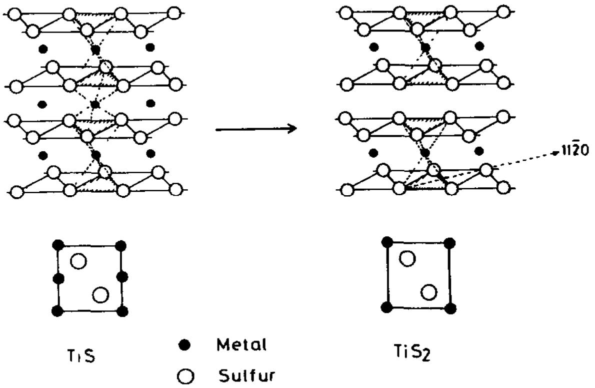

Fig. 6. Crystal structure of titanium sulfide.

105–700 K by differential scanning calorimetry. C_p as a function of temperature was evaluated as follows:

$$C_p = 17.13 + 1.662 \times 10^{-3}T - 1.291 \times 10^{5}T^{-2} \ (T = 298.15\text{–}700 \text{ K}) \qquad (15)$$

Equation (15) fits the data of Mraw et al. with a precision of ±0.2%. If TiS_2 is oxidized, and only SO_3 gas is formed, the reaction will be given by

$$TiS_2 + 4\ O_2 \rightarrow TiO_2 + 2\ SO_3 \qquad (16)$$

and the enthalpy of combustion is evaluated to be $-\Delta H_c = 1310$ kJ mol^{-1} [7] at 406°C. In the same way, if TiS_2 is burned, and only SO_2 gas is generated, the reaction can be written by

$$TiS_2 + 3\ O_2 \rightarrow TiO_2 + 2\ SO_2 \qquad (17)$$

and the enthalpy of combustion is calculated to be $-\Delta H_c = 1113$ kJ mol^{-1} [7] at 406°C. Since the enthalpy of combustion of TiS_2 was $-\Delta H_c = 1257$ kJ mol^{-1} in this investigation, we evaluated the reaction in the calorimeter by sharing eqns. (16) and (17). The estimated equation is given by

$$TiS_2 + 3.731\ O_2 \rightarrow TiO_2 + 1.462\ SO_3 + 0.538\ SO_2 \qquad (18)$$

When SO_2 is oxidized to SO_3 by the following reaction:

$$SO_2 + 0.5\ O_2 \rightleftarrows SO_3 \qquad (19)$$

the equilibrium constant, K_p, in eqn. (19) ($K_p = P_{SO_3}/(P_{SO_2} \times P_{O_2}^{0.5})$) is calculated to be 486 at 406°C from the data of JANAF Thermochemical Tables [10]. As the oxygen partial pressure is 0.4 atm (4.0×10^4 Pa) in this investigation, the ratio of P_{SO_3}/P_{SO_2} is evaluated to be 308. Accordingly, a small amount of SO_2 would exist at 406°C. Actually, when combustion starts in the calorimeter, the temperature in the cell suddenly increases. Therefore the SO_3/SO_2 ratio decreases in eqn. (18).

For all the discussion made in this paper it was considered that for the whole range of TiS_x, the SO_3/SO_2 ratio remains unchanged after combustion.

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