

Thermogravimetric Study of the $\text{Ln}_2\text{O}_3\text{-Co-Co}_2\text{O}_3$ System Ln = Sm at 1000 °C

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Phase equilibrium is established in a system Sm-Co-O at 1000°C by changing the oxygen partial pressure from 0 to 13.00 in $-\log(P_{\text{O}_2}/\text{atm})$, and a phase diagram is represented for a $\text{Sm}_2\text{O}_3\text{-Co-Co}_2\text{O}_3$ system. Under the experimental conditions, Sm_2O_3 , CoO, Co, and SmCoO_3 phases are present. But Sm_2CoO_4 and $\text{Sm}_4\text{Co}_3\text{O}_{10}$ phases are not stable in the system.

A slight nonstoichiometry is found in CoO and SmCoO_3 phases, and the nonstoichiometry of SmCoO_3 is discussed with respect to the oxygen partial pressure, and the activities of the components in the solid solutions are calculated using the composition-oxygen partial pressure relations obtained. Lattice constants of SmCoO_3 , made in different oxygen partial pressures, are determined and compared with those values prepared at 1200°C. Standard Gibbs energy changes of the reactions in the phase diagram are calculated with the oxygen partial pressure in equilibrium with solids, and these are compared with previous values.

Key word: Thermogravimetry, phase equilibrium, Sm-Co oxide, Standard Gibbs energy change of reaction.

INTRODUCTION

The phase equilibrium on the lanthanoid(Ln)-Co-O system has been established at 1200°C by an author(1-3). These earlier works revealed the stability of Ln_2O_3 , Co, CoO, Ln_2CoO_4 , $\text{Ln}_4\text{Co}_3\text{O}_{10}$, and LnCoO_3 phases, and the ternary stable compounds depend on the lanthanoid used. Consequently, the patterns of the system were different one another depending on the ternary compounds which are stable in the systems.

Moreover, standard Gibbs energy changes of reactions were determined based on the phase diagram, and lattice constants of quenched Ln_2CoO_4 , $\text{Ln}_4\text{Co}_3\text{O}_{10}$ and LnCoO_3 were determined.

The structures, lattice parameters, and the method of preparation of these compounds

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were reported previously(4~7).

The objectives of the present study are 1) to establish detailed phase equilibria in the system at 1000 °C as a function of the oxygen partial pressure, 2) to determine the thermochemical properties based on the phase equilibrium at different temperatures, and 3) to ascertain whether the isothermal pattern of the phase diagram of Sm-Co-O system at 1000°C is different from that at 1200°C or not.

EXPERIMENTALS

Analytical grade Sm₂O₃(99.9%) and CoO(99.9%) were used as starting materials. The CoO and Sm₂O₃ were dried by heating at 1000°C in air. Mixtures with desired ratios of Sm₂O₃/CoO were prepared by mixing thoroughly in an agate mortar and then were calcined several times during the intermediate mixing, and treated by the same procedures as described previously(8).

Mixed gases of CO₂ and H₂ and of CO₂ and O₂, and one atmosphere of CO₂ and O₂ were used to obtain the oxygen partial pressures in the present experiment, respectively.

The apparatus and procedures for controlling the oxygen partial pressures and keeping a constant temperature, the method of thermogravimetry, and the criterion for the establishment of equilibrium were the same as those described in the previous paper(8). The method of establishment of equilibrium is briefly written as follows. To ensure equilibrium, the equilibrated point of each sample at an oxygen partial pressure was established from both sides of reaction, that is, from low oxygen partial pressures to high oxygen partial pressures and vice versa. The balance, furnace, and gas mixer are schematically shown(8). The furnace is used vertically, which has a mullite tube wound with Pt 60%-Rh 40% alloy wire as its heating element. Mixed gases, which ensure the desired oxygen partial pressures, pass from the bottom of the furnace to top.

The identification of phases and the determination of lattice constants were performed with Rigaku X-ray diffractometer Rint 2500 apparatus, employing Ni-filtered CuK_α radiation.

RESULTS AND DISCUSSIONS

(1) Phase equilibrium

1)Co-O system at 1000°C.

The Co-O system was reinvestigated at 1000 °C by using the present apparatus and procedures. Fig. 1 shows the relationship between the oxygen partial pressure, $-\log(P_{O_2}/\text{atm})$ and O/Co mole ratio. The oxygen partial pressure in equilibrium with

CoO and Co metal at 1000°C is 11.35 ± 0.03 in $-\log(\text{Po}_2/\text{atm})$. And the value is tabulated together with those values at 1100° , 1150° , and 1200°C in Table 4. The CoO has slight nonstoichiometric composition as shown in Fig. 1. A x in CoO_x was 1.000, 1.008, 1.011, 1.013, and 1.021 at 11.35, 11.00, 10.00, 8.00, and 0 in $-\log \text{Po}_2$, respectively and an empirical equation, $x = 1.294 \times \log \text{Po}_2 + 1.021$, was obtained for the CoO solid solution.

(2) $\text{Sm}_2\text{O}_3\text{-Co-Co}_2\text{O}_3$ system

Four samples with $\text{Sm}_2\text{O}_3/\text{CoO}$ mole ratios of 6/4, 4/6, 3/7, and 15/85 were prepared for thermogravimetry. In Fig. 2, the relationship between the oxygen partial pressure, $-\log(\text{Po}_2/\text{atm})$, on the ordinate and the weight change, $W_{\text{O}_2}/W_{\text{T}}$, on the abscissa are shown with three representative samples, 6/4 (Fig. 1a), 4/6 (Fig. 1b), and 15/85 (Fig. 1c). Here, W_{O_2} is the weight increase of the samples from the reference weight at $\log \text{Po}_2 = -13.00$, at which Sm_2O_3 and Co metal are stable, and W_{T} is the total weight gain from the reference state to the weight at 1 atm O_2 . Break points are found at 11.35 and 3.70 in $-\log \text{Po}_2$ in equilibrium with solid phase regions. The value 11.35 corresponds to the oxygen partial pressure in equilibrium with Co and CoO, and the value 3.70 to the oxygen partial pressure in equilibrium with three solids, Sm_2O_3 , Co, and SmCoO_3 , respectively.

Samples of about 500 mg were made by the quenching method for the identification

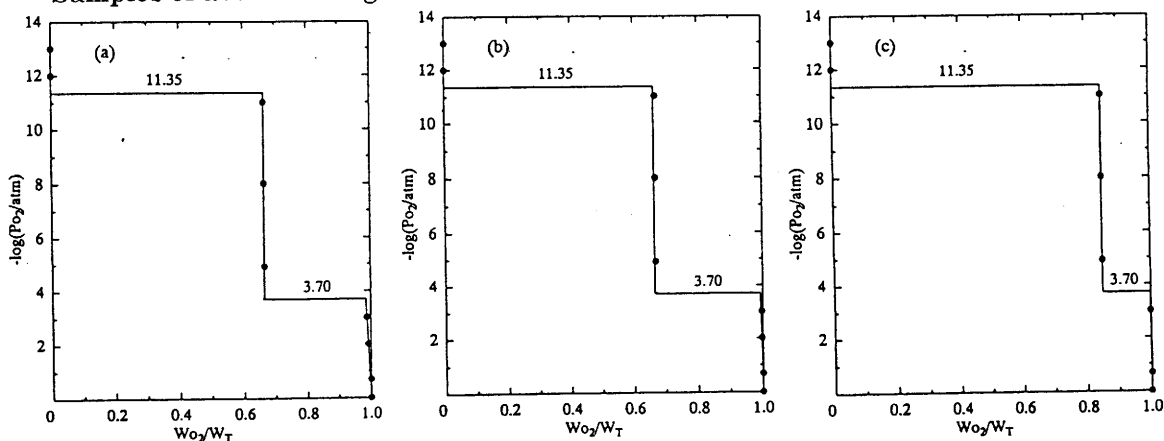


Fig. 2. Relationship between the oxygen partial pressure, $\log(\text{Po}_2/\text{atm})$, and the weight change of the samples, $W_{\text{O}_2}/W_{\text{T}}$. (a) $\text{Sm}_2\text{O}_3/\text{CoO} = 6/4$, (b) $\text{Sm}_2\text{O}_3/\text{CoO} = 4/6$, and (c) $\text{Sm}_2\text{O}_3/\text{CoO} = 15/85$.

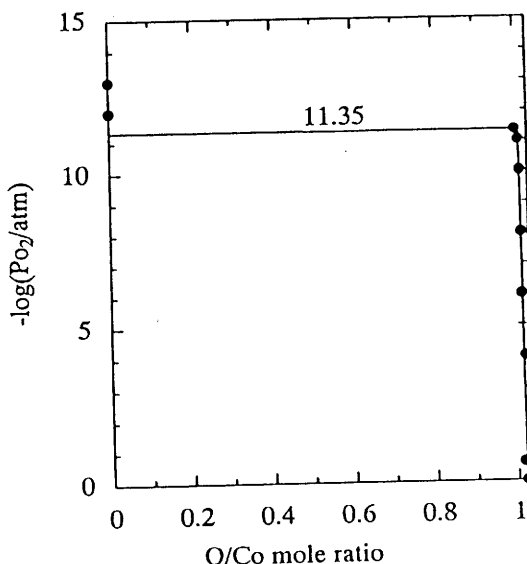


Fig. 1. Relationship between the oxygen partial pressure, $\log(\text{Po}_2/\text{atm})$, and O/Co mole ratio at 1000°C .

of phases. In Table 1 results of the identification of phases are shown at 1000°C. Four phases, Sm_2O_3 , Co, CoO, and SmCoO_3 are stable under the present experimental conditions. However, Co_3O_4 and Co_2O_3 are not stable.

Table 1. The Identification of Phase

Sample $\text{Sm}_2\text{O}_3/\text{CoO}$	$-\log P_{\text{O}_2}$ (atm)	Time (h)	Phases
6/4	12.00	9	$\text{Sm}_2\text{O}_3 + \text{Co}$
	11.00	7	$\text{Sm}_2\text{O}_3 + \text{CoO}$
	5.60	22	$\text{Sm}_2\text{O}_3 + \text{CoO}$
	3.00	24	$\text{Sm}_2\text{O}_3 + \text{SmCoO}_3$
	0.68	14	$\text{Sm}_2\text{O}_3 + \text{SmCoO}_3$
4/6	12.00	9	$\text{Sm}_2\text{O}_3 + \text{Co}$
	11.00	7	$\text{Sm}_2\text{O}_3 + \text{CoO}$
	5.60	22	$\text{Sm}_2\text{O}_3 + \text{CoO}$
	3.00	24	$\text{Sm}_2\text{O}_3 + \text{SmCoO}_3$
	0.68	14	$\text{Sm}_2\text{O}_3 + \text{SmCoO}_3$
3/7	12.00	9	$\text{Sm}_2\text{O}_3 + \text{Co}$
	11.00	7	$\text{Sm}_2\text{O}_3 + \text{CoO}$
	5.60	22	$\text{Sm}_2\text{O}_3 + \text{CoO}$
	3.00	24	$\text{CoO} + \text{SmCoO}_3$
	0.68	14	$\text{CoO} + \text{SmCoO}_3$
15/85	12.00	9	$\text{Sm}_2\text{O}_3 + \text{Co}$
	11.00	7	$\text{Sm}_2\text{O}_3 + \text{CoO}$
	5.60	22	$\text{Sm}_2\text{O}_3 + \text{CoO}$
	3.00	24	$\text{CoO} + \text{SmCoO}_3$
	0.68	14	$\text{CoO} + \text{SmCoO}_3$

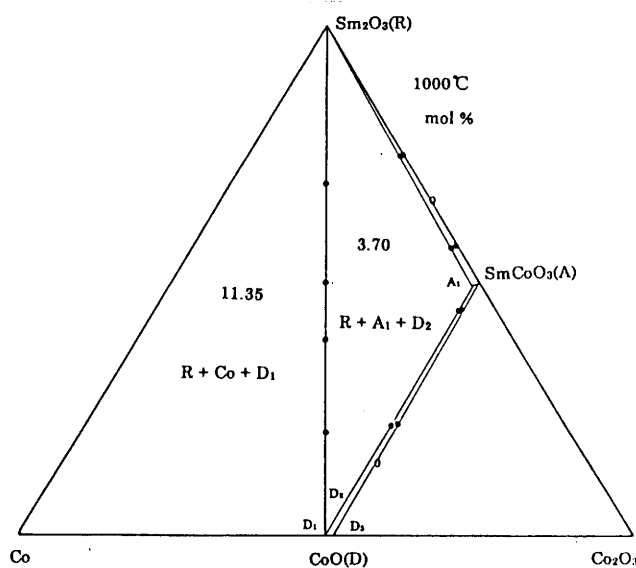


Fig. 3. Phase equilibrium in the Sm_2O_3 -Co- Co_2O_3 system at 1000°C. Numerical values in the three phase regions are the oxygen partial pressures in $-\log(P_{\text{O}_2}/\text{atm})$. Abbreviations are the same as those in Table 2.

Based on the above results of thermogravimetry and of identification of phases, a phase diagram is drawn and is illustrated in Fig. 3 as an Sm_2O_3 -Co- Co_2O_3 , although Co_2O_3 is not stable under the experimental conditions. The numerical values in the three solid phases in Fig. 3 are two values in $-\log P_{\text{O}_2}$ described above, and the Ln_2CoO_4 -type and $\text{Ln}_4\text{Co}_3\text{O}_{10}$ -type compounds are not stable in the Fig. 3 in contrast to La-Co-O system at 1200°C(1). But the Fig. 3 shows the same pattern as that of the same system at 1200°C(3) except for the oxygen partial pressures in equilibrium with solid phases. That is, -9.30 and -1.82 in $\log(P_{\text{O}_2}/\text{atm})$ at 1200°C change to the lower oxygen partial pressure, -11.35 and -3.70 at 1000°C, respectively. The SmCoO_3 has nonstoichiometric composition in the range from 3.70 to 0 in $-\log(P_{\text{O}_2}/\text{atm})$. However, its range is narrow.

The results of the compositions of the ternary compounds, symbols, stability ranges in $\log P_{\text{O}_2}$, and activities of the components in the solid solutions are shown in Table 2.

The relationship between the composition of SmCoO_3 solid solutions and the oxygen partial pressures is represented by an equation, $N_{\text{O}}/N_{\text{SmCoO}_3} = 5.86 \times 10^{-3} \log P_{\text{O}_2}$, which can be used in

Table 2. Compositions, Symbols, Stability Ranges in Oxygen Partial Pressure, and Activities of Components in Solid Solutions.

Component	Composition	Symbol	$-\log P_{\text{O}_2}$ (atm)	$\log a_i$
SmCoO ₃	SmCoO _{2.98}	A ₁	3.70	0
	SmCoO _{3.00}	A	0	0.0194
CoO	CoO _{1.00}	D ₁	11.35	0
	CoO _{1.00}	D ₂	3.70	~0
	CoO _{1.02}	D ₃	0	~0

 Table 3. Lattice Constants of SmCoO₃

Temp./°C	$-\log(P_{\text{O}_2})$ (atm)	Other phases	a/A	b/A	c/A	V/A ³	Ref.
1000	0.68	CoO	5.286(5)	5.357(2)	7.503(4)	212.5(2)	Present
	0.68	Sm ₂ O ₃	5.289(2)	5.356(2)	7.500(3)	212.4(1)	" "
	3.00	CoO	5.285(4)	5.358(2)	7.501(2)	212.4(2)	" "
	3.00	Sm ₂ O ₃	5.285(3)	5.359(2)	7.498(2)	212.4(1)	" "
1200	0.68	CoO	5.284(6)	5.343(6)	7.506(6)	211.9(4)	3)
	0.68	Sm ₂ O ₃	5.283(6)	5.344(5)	7.502(2)	211.8(3)	3)

Table 4. The Standard Gibbs Energy Change of Reactions.

Reaction	Temp. (°C)	$-\log P_{\text{O}_2}$ (atm)	$-\Delta G^\circ$ * (kJmol ⁻¹)
[1] $1/2 \text{Sm}_2\text{O}_3 + \text{CoO} + 1/4 \text{O}_2 = \text{SmCoO}_3$	1000	3.70	24.3
	1200	1.82	12.4
[2] $\text{Co} + 1/2 \text{O}_2 = \text{CoO}$	1000	11.35	149.2
	1100	10.33	135.8
	1150	9.70	132.2
	1200	9.30	131.1

 * $\pm 0.5 \text{ kJmol}^{-1}$

standard Gibbs energy changes of reactions, which appear in the phase diagram and are shown in Table 4, are determined with an equation, $\Delta G^\circ = -RT \ln K$. Here, R is the gas constant, T the absolute emperature, and K the equilibrium constant of the reaction. Activities of the components in the solid solutions, which are necessary to calculate K values, are tabulated in Table 2. The standard state of the components in the solid solution can be arbitrarily chosen for each solid solution and it is indicated as $\log a_i = 0$ in Table 2. ΔG° values for the reactions are tabulated in Table 4 together with those at 1200°C(3) for the reaction [1] and those at 1100° (10), 1150° (10), and 1200°C(3) for the reaction[2]. Compiled data of Ref. 11) and 12) of Gibbs energy change of reaction for the reaction [2] show $-142.6 \text{ kJmol}^{-1}$ and $-143.9 \text{ kJmol}^{-1}$ at 1000°C, -135.4 and -136.9 at 1100°C, -131.8 and -133.3 at 1150°C, and -128.1 and -129.8 at 1200°C, respectively. Present values are in fairly good agreement with the previous values.

Using the activity value, 0.0194 in Table 2, for the stoichiometric SmCoO₃, ΔG° value for the reaction [1] is -24.8 kJmol^{-1} . As the solid solution range is very small, the

calculation of activity of the components in the solid solutions with Gibbs-Duhem equation (9). Here, N_{O} and N_{SmCoO_3} denote the mole fraction of oxygen and component (cf. Table 2) in the solid solutions, respectively.

Lattice constants of SmCoO₃ are listed in Table 3.

The present values are in fairly good agreement with previous values prepared different temperatures except for b values.

Furthermore, the values do not depend on the oxygen partial pressure prepared.

(3) The Standard Gibbs Energy Changes of Reaction On the basis of the established phase diagram, the

difference is within an experimental error.

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