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Abstract

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INVESTIGATION OF THE THERMODYNAMIC PROPERTIES OF COBALT ANTIMONIDES BY THE METHOD OF ELECTROMOTIVE FORCES

Cobalt forms three antimonides: $CoSb_3$ with the skutterudite structure ([1,2]), $CoSb_2$ with the marcasite structure ([1,3]), and CoSb with the nickel arsenide structure ([3,4]).

The phase diagram of the Co–Sb system is given in ([5]). The compound CoSb has no substantial deviations from stoichiometry. According to Rosenqvist ([1]), the compound $CoSb_2$ exists with some excess of cobalt (cobalt atoms replace antimony atoms in the crystal lattice of the compound). In ([6]), Rosenqvist assigns this compound the composition $CoSb_{1\cdot 9}$. On the phase diagram of the Co–Sb system in ([5]), the homogeneity range of $CoSb_2$ is marked by a dashed line within 64–66.7 at. % Sb. Other authors (including ([2])) give no indication of nonstoichiometry of $CoSb_2$. According to Ageev and Makarov ([7]), the CoSb phase exists in the concentration interval 43.4–49.2 at. % Sb, with the excess cobalt atoms occupying paired tetrahedral voids of the antimony sublattice.

Integral thermodynamic quantities were calculated by us for the compositions $CoSb_3$, $CoSb_2$, and CoSb, although in fact $CoSb_2$ deviates from the stoichiometric composition, and the antimony-rich boundary of the homogeneity range based on CoSb is at the composition 49.2 at. % Sb (experimental data were obtained for this composition). The errors introduced by such a calculation are smaller than the experimental errors.

The thermodynamic properties of cobalt-antimony alloys were investigated by the electromotive-force (e.m.f.) method. The method used has been described by us previously in its main features ([8,9]). The equation for the dependence of the e.m.f. on the absolute temperature (in the form of a straight-line equation) was found by treating, by the method of least squares, the experimental data relating to all experiments with all alloys of the given heterogeneous region of the phase diagram. By the formulas of the method of least squares ([10]), the errors in the e.m.f. and in the coefficients of the equation $E = f(T)$ were also calculated.

For preparing the alloys, the following metals were used: zone-melted antimony of purity 99.999% Sb and cobalt prepared from $Co(NO_3)_2$ of the grade "chemically pure, nickel-free."

The reaction

$$\mathrm{Co} + 3\mathrm{Sb} = \mathrm{CoSb_3} \tag{1}$$

is the potential-forming process of the electrochemical cell:

$$(-)\ \mathrm{Co} \mid \mathrm{CoCl_2} + \mathrm{KCl} + \mathrm{LiCl} \mid \mathrm{CoSb_3} + \mathrm{Sb}\ (+). \tag{I}$$

melt solid heterogeneous alloy

The change in the isobaric-isothermal potential in reaction (1) can be expressed through the e.m.f. of cell (I):

$$\Delta G_1 = -zFE_1, \tag{A}$$

where $z = 2$ is the charge of the cobalt ion, F is the Faraday number, and E_I is the emf of element (I). For the temperature interval investigated (790–890°K), the experimental data are described by the following equation:

$$E_I = (302.2 + 1.45 \cdot 10^{-3}T)\ \mathrm{mV} \pm 9.6\ \mathrm{mV}.$$

Then

$$\Delta G_1 = (-13.94 - 0.067 \cdot 10^{-3}T)\ \mathrm{kcal/mol\ CoSb_3}.$$

The reaction

$$\mathrm{Co} + 2\mathrm{CoSb_3} = 3\mathrm{CoSb_2} \tag{2}$$

is the potential-forming process of the element:

$$(-)\ \mathrm{Co} \mid \mathrm{CoCl_2} + \mathrm{KCl} + \mathrm{LiCl} \mid \mathrm{CoSb_2} + \mathrm{CoSb_3}\ (+). \tag{II}$$

melt solid heterogeneous alloy

For the temperature interval 800–990°K:

$$E_{\mathrm{II}} = (136.3 + 30.4 \cdot 10^{-3}T)\ \mathrm{mV} \pm 15.0\ \mathrm{mV}.$$

According to equation (A),

$$\Delta G_2 = (-6.29 - 1.40 \cdot 10^{-3} T) \text{ kcal/g-at. Co.}$$

The formation of $CoSb_2$ from the elements by the reaction

$$\mathrm{Co} + 2\mathrm{Sb} = \mathrm{CoSb_2} \tag{3}$$

can be represented as a combination of reactions (1) and (2):

$$\Delta G_3 = \frac{2\Delta G_1 + \Delta G_2}{3} = (-11.39 - 0.51 \cdot 10^{-3} T) \text{ kcal/mol CoSb}_2.$$

The reaction

$$\mathrm{Co} + \mathrm{CoSb_2} = 2\mathrm{CoSb} \tag{4}$$

is the potential-forming process of the element:

$$(-)\ \mathrm{Co} \mid \mathrm{CoCl_2} + \mathrm{KCl} + \mathrm{LiCl} \mid \mathrm{CoSb} + \mathrm{CoSb_2}\ (+). \tag{III}$$

melt solid heterogeneous alloy

For the temperature interval 770–980°K:

$$E_{\mathrm{III}} = (98.8 + 35.5 \cdot 10^{-3} T) \text{ mV} \pm 4.2 \text{ mV},$$

$$\Delta G_4 = (-4.56 - 1.55 \cdot 10^{-3} T) \text{ kcal/g-at. Co.}$$

The formation of CoSb from the elements by the reaction

$$\mathrm{Co} + \mathrm{Sb} = \mathrm{CoSb} \tag{5}$$

can be represented as a combination of reactions (3) and (4), then

$$\Delta G_5 = \frac{\Delta G_3 + \Delta G_4}{2} = (-7.98 - 1.03 \cdot 10^{-3} T) \text{ kcal/mol CoSb.}$$

The heats and entropies of formation of the cobalt antimonides were obtained from the expressions for ΔG_1, ΔG_3, and ΔG_5, according to the relations

$$\Delta S = -\left(\frac{\partial \Delta G}{\partial T}\right)_p \quad \text{and} \quad \Delta H = \Delta G + T\Delta S.$$

The magnitudes of the changes in thermodynamic functions upon the formation of solid cobalt antimonides from the elements, calculated per 1 g-at. of cobalt antimonide, are given in Table 1.

Table 1

	$\Delta G = f(T)$, kcal	$\Delta G_{850^\circ\mathrm{K}}$, kcal	ΔH, kcal	ΔS, e.u.
$CoSb_3$	$-3.48 - 0.02 \cdot 10^{-3}T$	-3.50 ± 0.11	-3.5 ± 0.6	0.0 ± 0.7
$CoSb_2$	$-3.80 - 0.17 \cdot 10^{-3}T$	-3.94 ± 0.17	-3.8 ± 0.7	$+0.2 \pm 0.8$
CoSb	$-3.99 - 0.52 \cdot 10^{-3}T$	-4.43 ± 0.18	-4.0 ± 0.6	$+0.5 \pm 0.7$

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Note: Figure translations are in progress. See original paper for figures.