ELSEVIER

Journal of Alloys and Compounds 228 (1995) 1–5

Journal of
ALLOYS
AND COMPOUNDS

An electrochemical investigation of the thermodynamic properties of cerium stannide ($CeSn_3$) and liquid tin–cerium alloys

Tom Mathews, H.N. Jena, T. Subramanian, P.R. Vasudeva Rao*, C.K. Mathews

Fuel Chemistry Division, Chemical Group, Indira Gandhi Centre For Atomic Research, Kalpakkam 603 102, India

Received 9 December 1994; in final form 21 February 1995

Abstract

The thermodynamic properties of the intermetallic compound $CeSn_3$ and the tin-rich liquid tin–cerium alloys in equilibrium with $CeSn_3$ were studied by a high-temperature galvanic cell technique using the reversible concentration cell

Ta, Ce‖$CeCl_3$, LiCl–KCl (eutectic)‖Ce–Sn (two-phase alloy), Ta

in the temperature range 723–873 K. The standard Gibbs energy of formation of $CeSn_3$ from pure solid cerium and pure liquid tin varies with temperature according to the equation

$$\Delta G^0_{f(CeSn_3)} = -260.08 + 0.0476T \ (\pm 2) \text{ kJ mol}^{-1}$$

The activity coefficients, excess partial molar free energies, enthalpies and entropies of cerium in the saturated liquid alloys have been computed from the e.m.f. data obtained in this study and the data for the solubility of cerium in liquid tin. The activity coefficients of cerium in liquid tin with reference to solid cerium can be expressed as

$$\bar{G}^{xs}_{Ce} = RT \ln \tau_{Ce} = -249 + 0.059T \ (\pm 2) \text{ kJ mol}^{-1}$$

Keywords: Formation enthalpy; Galvanic cell technique

1. Introduction

Phase relations in the system Ce–Sn are given in the literature [1]. In the tin-rich region of the phase diagram, the liquidus line rises with a high slope from a eutectic close to the melting point of tin. Accordingly the solubility of cerium in tin is small ($X_{Ce} = 0.045$–0.067) over the temperature range of measurement (723–873 K). The intermetallic phase in equilibrium with the liquidus has the fixed stoichiometry $CeSn_3$. The enthalpy of formation of the intermetallic compound $CeSn_3$ has been determined by high-temperature calorimetry [2–4]. The enthalpy of solution of cerium in liquid tin was obtained by Colinet and co-workers [2,5] by solution calorimetry in liquid tin. The purpose of the present investigation is to determine the thermodynamic properties of the intermetallic phase $CeSn_3$ and liquid cerium–tin alloys in equilibrium with $CeSn_3$ by using a molten-salt galvanic-cell technique.

2. Experimental techniques

2.1. Materials

Analytical grade KCl, LiCl and $CeCl_3$ were obtained from Aldrich Chemicals (USA). Pure cerium (99.99%) and tin (99.9%) metals were obtained from Alpha Chemicals (USA).

2.2. Electrolyte

The electrolyte was prepared by dissolving $CeCl_3$ in

---

* Corresponding author.

SSDI 0925-8388(95)01608-2

dried and purified KCl–LiCl eutectic in a recrystallized alumina crucible. The KCl–LiCl eutectic mixture was prepared and purified by using the method described by Laitinen et al. [6]. The KCl–LiCl mixture contained in a recrystallized alumina crucible was slowly heated to 673 K in a stream of dried HCl gas until a homogeneous melt was obtained. The dried HCl gas was then bubbled through the melt for 1 h. The melt saturated with HCl was then sparged with ultra-pure helium gas and filtered. The dried salt was then stored in an inert and moisture-free atmosphere until use.

2.3. Electrodes

Cerium metal and cerium–tin alloy electrodes were prepared by melting pure cerium and cerium–tin mixtures in separate tantalum crucibles (6 mm diameter by 10 mm high) welded to tantalum wire of 1/16 inch diameter, under inert atmosphere in a vacuum induction melting unit (Leybold, Germany). The alloy electrodes contained approximately 15 mol.% cerium. The alloys were held in the molten state at 1473 K for 1 h for homogenization and then cooled to room temperature. Proper electrical contacts between the leads and the respective electrode materials were ensured prior to the assembly of the cell.

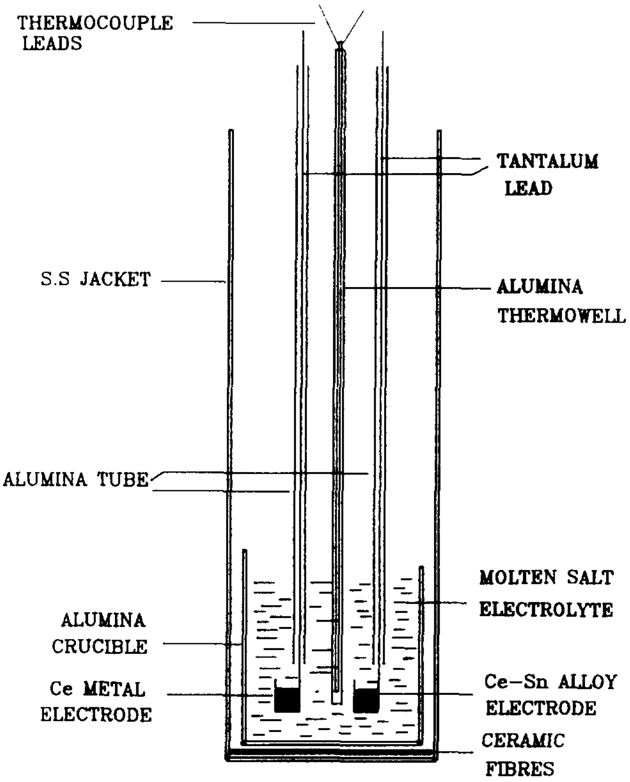

Fig. 1. Schematic diagram of the high-temperature galvanic cell.

2.4. E.m.f. measurements

The thermodynamic properties of the tin-rich region of the cerium–tin system were determined from e.m.f. measurements of the cells of the type

Ta, Ce||$CeCl_3$, LiCl–KCl (eutectic)||Ce–Sn (two-phase alloy), Ta

in which the two-phase alloy was a mixture of saturated liquid and the solid intermetallic phase $CeSn_3$. A schematic representation of the cell is shown in Fig. 1.

The electrochemical cell consisted of pure metallic cerium and cerium–tin alloy electrodes immersed in the molten electrolyte ($CeCl_3$ + KCl–LiCl(eutectic)) contained in a recrystallized alumina crucible. The cell assembly was enclosed in a stainless steel jacket with provisions for gas inlet and exit, electrode leads and thermocouple wires. The cell was assembled inside an argon glove-box with continuous argon purification. The argon gas was purified by passing it over a mixture of copper-based catalyst and molecular sieves to remove traces of oxygen and moisture respectively. The oxygen and moisture content of the box was less than 10 ppm. The cell was evacuated and flushed with pre-purified helium gas. The helium gas used to provide an inert blanket over the cell was 99.999% pure. It was further purified by passing it over a mixture of copper catalyst and molecular sieves, and anhydrous P_2O_5 to remove residual oxygen and moisture. The entire assembly was suspended in the even temperature zone of a Kanthal wire wound vertical tube furnace. The temperature of the furnace was controlled within ± 1 K using a PID temperature controller.

The cell temperature was measured with a chromel–alumel thermocouple kept inside the alumina thermowell, well immersed in the electrolyte with its tip in level with the electrodes. The stainless steel jacket was earthed to minimize induced e.m.f. on the measuring leads. The cell was heated to the desired temperature, and e.m.f. measurements were carried out under flowing helium gas. The e.m.f. was measured by using a high-impedance electrometer. At each temperature the cell voltage was monitored for at least 4 h. The cell e.m.f. was found to be reproducible on thermal cycling. The reversibility of the cell was verified by microcoulometric titration in both directions. The open-circuit e.m.f. was monitored after each titration. Reversibility was established when the e.m.f. returned to the same value after forward and reverse titrations at the same temperature.

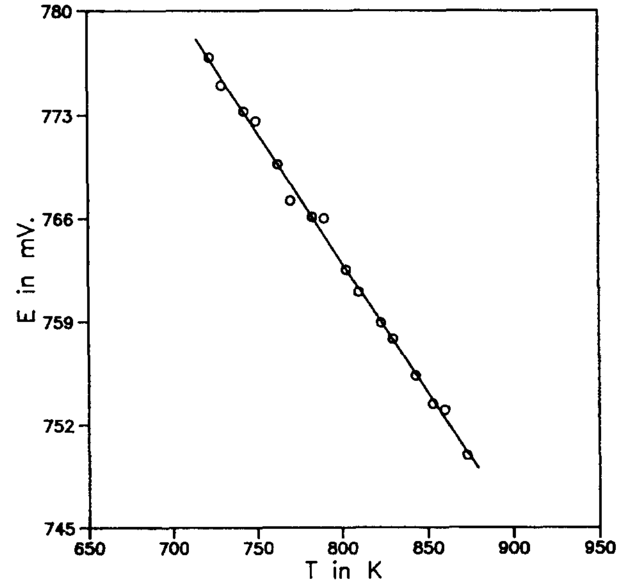

Fig. 2. Temperature dependence of the e.m.f. of cell 1.

3. Results and discussion

The variation of the e.m.f. of cell 1 with temperature is shown in Fig. 2. The least-squares regression analysis of the e.m.f. data yields

$$E = 907 - 0.18\ T(\pm 2)\ \text{mV} \tag{1}$$

The e.m.f. between the electrodes is a measure of the difference in the chemical potential of cerium in pure solid cerium and in a saturated solution in liquid tin. The thermodynamic properties of dilute solution of cerium in liquid tin and of the solid intermetallic compound, $CeSn_3$, that was in equilibrium with the tin-rich liquid phase were computed from the e.m.f. data.

The galvanic cell reaction consists of the transfer of cerium from pure solid metal to the liquid alloy, where the reaction with tin occurs to precipitate the solid intermetallic compound as follows;

$$\text{Ce(s)} \Rightarrow \text{Ce (soln.)} \tag{2}$$

and

$$\text{Ce (soln.)} + 3\text{Sn (soln.)} \Rightarrow \text{CeSn}_3\text{(s)} \tag{3}$$

The overall cell reaction may be written as

$$\text{Ce(s)} + 3\text{Sn (soln.)} \Rightarrow \text{CeSn}_3\text{(s)} \tag{4}$$

Therefore the cell e.m.f., E, the partial molar free energy of cerium, $\overline{G}_{Ce}$, and the standard Gibbs energy of formation of $CeSn_3$, $\Delta G^0_{f(CeSn_3)}$, from pure solid cerium and pure liquid tin are related by the equations

$$\overline{G}_{Ce} - G^0_{Ce} = -zFE \tag{5}$$

and

$$\Delta G^0_{f(CeSn_3)} = -zFE + 3RT \ln a_{Sn} \tag{6}$$

where G^0_{Ce} is the free energy of cerium in the reference state (pure solid cerium), $z = 3$ is the number of electrons participating in the electrode reaction, F is the Faraday constant and a_{Sn} is the activity of tin.

In the cerium–tin system the saturated solutions were sufficiently dilute that the term $RT\ln a_{Sn}$ could be estimated to the required accuracy by assuming that the solutions were ideal with respect to tin. The standard Gibbs energy of formation of $CeSn_3$, $\Delta G^0_{f(CeSn_3)}$ obtained from Eq. (6) is expressed as

$$\Delta G^0_{f(CeSn_3)} = -260.08 + 0.0476T\ (\pm 2)\ \text{kJ mol}^{-1} \tag{7}$$

The enthalpy and entropy of formation are thus $-260.08(\pm 1)$ kJ mol^{-1} and $-47.6(\pm 2)$ J mol^{-1} K^{-1} respectively. The enthalpy of formation obtained in this study is compared with those obtained from high-temperature calorimetry [2–4] in Table 1. The stan-

Table 1
Values of the enthalpy of formation of $CeSn_3$ and partial enthalpy of Ce in liquid Sn

Compound	Method	T(K)	ΔH^0_f (kJ mol^{-1})	Ref.
$CeSn_3$	Sn solution calorimetry	298	−248	[2]
	Precipitation in Sn	939	−248	[2]
		298	−224	[2]
	Reaction calorimetry	300	−234	[3]
	Reaction calorimetry	510	−216	[4]
	e.m.f. technique	723-873	−260.08 (±1)	This work
	e.m.f. technique	298	−239.08 (±1)	This work

Element	Solvent	T(K)	$\Delta \bar{H}_{Ce}$ (kJ mol^{-1})	Ref.
Ce	Sn	930	−201	[2]
		999	−194	[5]
		723–873	−249 (±1)	This work

dard enthalpy of formation of $CeSn_3$ obtained by Colinet et al. [2] (-248 and -224 kJ mol^{-1}) and by Borzone et al. [3] (-234 kJ mol^{-1}) is in reasonable agreement with the value (-239 kJ mol^{-1}) obtained in this study. Palenzona [4] obtained a value of -216 kJ mol^{-1} at 510 K by using low-temperature reaction calorimetry. One of the limitations of low-temperature reaction calorimetry is that the intermetallic compound may not be in thermodynamic equilibrium at the temperature of measurement.

From the variation of the solubility of cerium in liquid tin [1] in the temperature range of measurement, and the data for e.m.f., the excess thermodynamic quantities of the saturated solutions could be computed using the equation

$$\begin{aligned}\bar{G}^{xs}_{Ce} &= \bar{G}_{Ce} - \bar{G}^{id}_{Ce} = RT \ln \tau_{Ce} \\ &= -3FE - RT \ln X_{Ce}(\text{satd.}) \qquad (8)\end{aligned}$$

where X_{Ce}(satd.) is the mole fraction of cerium in the saturated solution at temperature T. The computed values are given in Table 2. The data are reported for the first time. The extremely low value of activity coefficient of cerium, τ_{Ce}, indicates strong interaction between cerium and tin atoms in the liquid alloy. The computed excess partial molar free energy and activity coefficients are based on solid cerium as the reference state; consequently they differ from the values based on the supercooled liquid (s l) cerium as the standard state by the free energy for the reaction

$$\text{Ce(s)} \Rightarrow \text{Ce(s l)} \qquad (9)$$

The thermodynamic quantities with respect to pure supercooled liquid cerium can be obtained by correcting the measured e.m.f. values by using the relation

$$E_l = E_s + \Delta G_f / zF \qquad (10)$$

where E_l and E_s are the cell potentials relative to the liquid and solid cerium respectively and ΔG_f is the Gibbs free energy change corresponding to reaction (9). ΔG_f for reaction (9) can be calculated from the following relations

$$\Delta G_f = \Delta H_f - T\Delta S_f \qquad (11)$$

$$\begin{aligned}\Delta H_f = &\int_T^{T_{tr}} C'_p \mathrm{d}T + \Delta H_{tr} + \int_{T_{tr}}^{T_{mp}} C''_p \mathrm{d}T + \Delta H_m \\ &+ \int_{T_{mp}}^{T} C^l_p \mathrm{d}T \qquad (12)\end{aligned}$$

and

$$\begin{aligned}\Delta S_f = &\int_T^{T_{tr}} \frac{C'_p}{T} \mathrm{d}T + \frac{\Delta H_{tr}}{T_{tr}} + \int_{T_{tr}}^{T_{mp}} \frac{C''_p}{T} \mathrm{d}T + \frac{\Delta H_m}{T_{mp}} \\ &+ \int_{T_{mp}}^{T} \frac{C^l_p}{T} \mathrm{d}T \qquad (13)\end{aligned}$$

where ΔH_f and ΔS_f are the molar enthalpy and entropy change, respectively, from solid to liquid at temperature T. ΔH_m and ΔS_m, ΔH_{tr} and ΔS_{tr}, and T_{mp} and T_{tr} are enthalpy and entropy of melting, enthalpy and entropy of transformation, melting temperature and transformation temperature, respectively, and C'_p, C''_p and C^l_p are the heat capacities of pure α (solid), β (solid) and liquid cerium, respectively. The data of Kubaschewski and Alcock [7] were used in the calculations.

From the e.m.f. values relative to the supercooled liquid (s l) cerium, the excess partial molar free energy and activity coefficients, with respect to the same standard state, were computed by using the relation

$$\bar{G}^{xs}_{Ce}(\text{s l}) = RT \ln \tau_{Ce} = -3FE_l - RT \ln X_{Ce}(\text{satd.}) \qquad (14)$$

The computed values are given in Table 2.

The partial molar enthalpy of cerium in the saturated solutions with respect to pure solid cerium as

Table 2
Excess partial molar free energy of cerium in saturated solution with respect to pure solid and supercooled liquid cerium as reference state

T (K)	X_{Ce} (satd.)	$\bar{G}^{xs}_{Ce} = RT \ln \gamma_{Ce}$ (kJ mol^{-1})	
		With respect to solid cerium	With respect to supercooled liquid cerium
723	0.045	−206.3	−208.8
743	0.048	−205.0	−207.5
763	0.051	−203.8	−206.0
783	0.054	−202.7	−204.7
803	0.057	−201.6	−203.5
823	0.060	−199.4	−202.1
843	0.063	−198.7	−200.8
863	0.065	−198.0	−199.5
873	0.067	−197.5	−198.2

reference state is calculated from Eq. (8) using the relation

$$\frac{\mathrm{d}(\Delta\overline{G}/T)}{\mathrm{d}T} = \frac{\mathrm{d}(R\ln\tau)}{\mathrm{d}T} = -\frac{\Delta\overline{H}}{T^2} \qquad (15)$$

The results are compared with the calorimetric values of Colinet and co-workers [2,5] in Table 1. The partial molar enthalpy of cerium in liquid tin obtained in this study is significantly more negative than those reported in the literature. In the present study the partial molar enthalpy of cerium in liquid tin was computed from the e.m.f. data and the variation of solubility of cerium in liquid tin. Therefore any error in the solubility data will introduce a corresponding error in the computed partial molar enthalpy value.

From the results of this study, the variation of excess partial molar free energy of cerium, $\overline{G}^{\mathrm{xs}}_{\mathrm{Ce}}$, with respect to pure solid and supercooled liquid cerium are expressed as

$$\overline{G}^{\mathrm{xs}}_{\mathrm{Ce}}(\mathrm{solid}) = -249 + 0.059T \ (\pm 2)\ \mathrm{kJ\ mol^{-1}} \qquad (16)$$

$$\overline{G}^{\mathrm{xs}}_{\mathrm{Ce}}(\mathrm{s\ l}) = -257 + 0.067T \ (\pm 2)\ \mathrm{kJ\ mol^{-1}} \qquad (17)$$

respectively. The partial molar quantities pertain to the liquid alloy in equilibrium with the intermetallic compound $CeSn_3$.

4. Conclusion

The thermodynamic properties of saturated liquid tin–cerium alloys and the intermetallic compound, $CeSn_3$, in equilibrium with the liquid, have been investigated by an e.m.f. technique in the temperature range 723 to 873 K. The activity coefficients, excess free energies, enthalpies and entropies of cerium in liquid alloys were evaluated. The results agree satisfactorily with the available calorimetric data. The temperature dependence of the standard Gibbs energy of formation of $CeSn_3$ from elements is reported for the first time.

References

[1] T.B. Massalski, H. Okamoto, P.R. Subramanian and L. Kacprzak (eds.), *Binary Alloy Phase Diagrams, Vol. 2*, ASM International, 2nd edn., 1990.

[2] C. Colinet, A. Bessoud and A. Pasturel, *J. Less-Common Met., 143* (1988) 265.

[3] G. Borzone, A. Borsese and R. Ferro, *J. Less-Common Met., 85* (1982) 195.

[4] A. Palenzona, *Thermochim. Acta, 5* (1973) 473.

[5] C. Colinet, A. Pasturel and A. Percherow-Guegan and J.C. Achand, *J. Less-Common Met., 102* (1984) 167.

[6] H.A. Laitinen, W.S. Ferguson and R.A. Osteryoung, *J. Electrochem. Soc., 104* (1957) 516.

[7] O. Kubaschewski and C.B. Alcock, *Metallurgical Thermochemistry*, Pergamon Press, Oxford, 5th edn., 1989.