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GIBBS FREE ENERGY OF FORMATION OF In_2O_3 AND $CaIn_2O_4$

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ABSTRACT

Employing the following solid oxide galvanic cells with a zirconia electrolyte

$Ni, NiO|O^{2-}|In, In_2O_3$

and

$Ni, NiO|O^{2-}|In, CaO, CaIn_2O_4$

the Gibbs free energies of formation of solid In_2O_3 and $CaIn_2O_4$ were determined in the form

$\Delta G^0_{f,In_2O_3} = -909425 + 307.49T$ J mol^{-1}

and

$\Delta G^0_{f,CaIn_2O_4} = -952550 + 342.79T$ J mol^{-1}

Consequently, the Gibbs free energy change for the formation of $CaIn_2O_4$ from the respective oxides

$CaO + In_2O_3 \rightarrow CaIn_2O_4$

was established as

$\Delta G^0_{f,oxides} = -43126 + 35.3T$ J mol^{-1}

over the temperature range 923–1123 K.

INTRODUCTION

Indium oxide, In_2O_3, and its compounds have been applied in electrooptical devices in technology. As an example, In_2O_3–SnO_2 films can be made which are used as transparent electrical contacts in a photoconductor [1]. Similarly, ternary phases with spinel structures based on In_2O_3 are of interest due to the possible substitution of α Fe_2O_4 compounds (α = Er, Ho, Yb, Lu, Y) and the elimination of the influence of their non-stoichiometry on electrical transport phenomena [2]. In any case, a knowledge of the stability of In_2O_3-based phases at elevated temperatures is important. Although thermodynamic properties have already been established for a number of mixed oxide systems, there is virtually no information on the Gibbs

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free energy of formation of In_2O_3-based compounds of this kind. The formation of one of these compounds, $CaIn_2O_4$ oxide, was reported by Schwartz and Bommert [3], and has recently been confirmed by Porotnikov et al. [4]. Since no thermodynamic information was available in the literature about this particular compound, it was decided to determine $\Delta G^0_{f,CaIn_2O_4}$ using a solid oxide galvanic cell with $ZrO_2 + CaO$ as electrolyte.

EXPERIMENTAL

Materials

Indium metal (99.999%) was obtained from Zakład Doświadczalny Skawina, Poland. Indium sesquioxide and calcium oxide (both 99.9%) were obtained from Polskie Odczynniki Chemiczne, Poland. The $CaIn_2O_4$ compound was synthesized by heating pressed pellets containing an equimolar mixture of CaO and In_2O_3 for 24 h in air at 1273 K, followed by grinding, pressing into pellets again and heating at 1273 K for one week. The formation of the compound was confirmed by X-ray diffraction. Nickel and nickel oxide (both 99.95%) used for the reference electrode were obtained from International Nickel Ltd. and BDH, respectively. CSZ tubes closed at one end were supplied by Degussa, W. Germany.

Oxygen potential measurements

EMF cells of the type

$$\text{Ni, NiO}\,|\,ZrO_2 + CaO\,|\,\text{In}, In_2O_3 \qquad (I)$$

and

$$\text{Ni, NiO}\,|\,ZrO_2 + CaO\,|\,\text{In} + CaO + CaIn_2O_4 \qquad (II)$$

were used for oxygen potential measurements of $In + In_2O_3$ and $In + CaO + CaIn_2O_4$ phase equilibria. Oxygen potential, either over two- or three-phase field, is related to the measured EMF by the relationship

$$E = \frac{RT}{4F} \ln\left(\frac{p'_{O_2}}{p''_{O_2}}\right) \qquad (1)$$

where $F = 96580$ J V^{-1} mol^{-1}, E is the EMF (V), R is the gas constant, and T is the absolute temperature (K). The oxygen partial pressure, p''_{O_2}, over the Ni + NiO reference electrode was calculated from the standard free energy of formation of nickel oxide given by Steele [5].

A schematic diagram of the cell assembly is shown in Fig. 1. A solid electrolyte tube was inserted into an alumina crucible filled with Ni + NiO powder. Indium metal was sealed, together with either In_2O_3 or $CaO + CaIn_2O_4$ powder, inside the CSZ tube by use of an alumina cement.

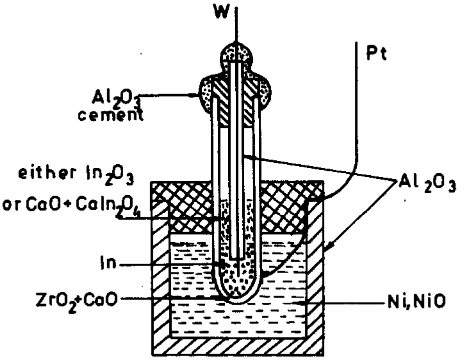

Fig. 1. Schematic diagram of the cell assembly.

Tungsten wire was used as the conductivity lead to provide electrical contact with the liquid indium. The cell was kept in the constant-temperature zone of a resistance furnace under a stream of pure argon.

After constant temperature had been reached, the cell was left for 24 h to attain equilibrium. The EMF was then recorded by means of a digital voltmeter (V 534, Elwro, Poland). The temperature was cycled in the range 873–1173 K, and the full run was completed after 3 days.

RESULTS

The proper operation of the cell assembly was checked by EMF measurements of the free energy change of the reaction

$$\mathrm{In}_{(l)} + 3/2\mathrm{O}_2 \rightarrow \mathrm{In}_2\mathrm{O}_{3(s)} \tag{2}$$

Electromotive force values obtained after the necessary Pt–W thermoelectric power corrections were treated by the least-squares method and are represented by the equation (Fig. 2)

$$E_\mathrm{I} = -355.3 + 0.09086T \text{ mV} \tag{3}$$

The Gibbs free energy of formation of solid In_2O_3 is related to the cell EMF (eqn. 1) through the equilibrium constant of reaction (2) in the following way

$$\begin{aligned}\Delta G^0_{\mathrm{f,In_2O_3}} &= 3/2\left(RT \ln p'_{\mathrm{O_2}}\right) = 3/2\left(4FE_\mathrm{I} + 2\Delta G^0_{\mathrm{f,NiO}}\right)\\ &= -909\,425 + 307.49T \text{ J mol}^{-1}\end{aligned} \tag{4}$$

A comparison of calculated $\Delta G^0_{\mathrm{f,In_2O_3}}$ values obtained in this study with those reported by Anderson and Donaghey [6], and Katayama et al. [7] shows good agreement over the temperature range investigated.

Next, using the least-squares method, results obtained for cell II can be represented by the equation (Fig. 2)

$$E_\mathrm{II} = -430.7 + 0.15167T \text{ mV} \tag{5}$$

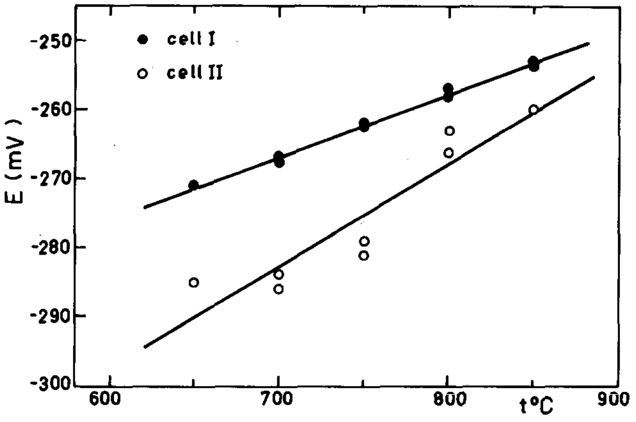

Fig. 2. Temperature dependence of the electromotive force of cells I and II (after Pt–W correction).

and, consequently, the equilibrium oxygen pressure for the three-phase field $In + CaO + CaIn_2O_4$ was determined from the relationship

$$RT \ln p'_{O_2} = 4FE_{II} + 2\Delta G^0_{f,NiO} \tag{6}$$

The Gibbs free energy of formation of solid $CaIn_2O_4$ was calculated from the equilibrium constant of the reaction

$$2\,In_{(l)} + 3/2 O_2 + CaO_{(s)} \rightarrow CaIn_2O_{4(s)} \tag{7}$$

in the following way

$$\Delta G^0_{f,CaIn_2O_4} = 3/2(RT \ln p'_{O_2})$$

$$= -952\,550 + 342.79T \text{ J mol}^{-1} \tag{8}$$

Combining reaction (7) and the reaction of formation of solid In_2O_3 (2) it was possible to derive the Gibbs free energy of formation of solid $CaIn_2O_4$ from the respective oxides

$$CaO + In_2O_3 \rightarrow CaIn_2O_4 \tag{9}$$

which is equal to

$$\Delta G^0_{f,oxides} = -43\,126 + 35.3T \text{ J mol}^{-1} \tag{10}$$

Contrary to entropy-stabilized compounds like $CaAl_2O_4$ and $CaGa_2O_4$ [8,9], $CaIn_2O_4$ should decompose at about 1220 K.

DISCUSSION

A schematic representation of phase equilibrium in the Ca + In + O system at 1073 K is shown in Fig. 3. At this temperature two intermetallic compounds in the Ca–In binary system, namely CaIn and $CaIn_2$, are solid

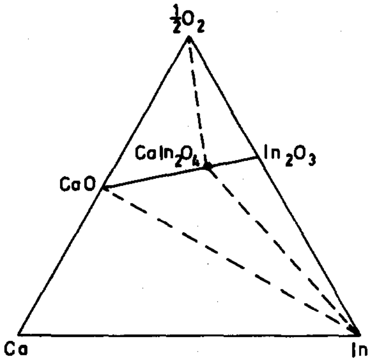

Fig. 3. Suggested phase relation in the system Ca + In + O at 1073 K.

[10]. However, due to the large difference in Gibbs free energy calculated for the displacement reaction

$$In_2O_{3(s)} + 3\ Ca_{(l)} \rightarrow 3\ CaO_{(s)} + 2\ In_{(l)} \tag{11}$$

(which is of the order of −980 kJ at 1073 K) it is unlikely that a range of alloy compositions exists which is not in equilibrium with CaO. Even a significant negative deviation from Raoult's Law, which may take place in the Ca–In liquid solution, should not change this situation.

No more information was found on the formation of other compounds in the $CaO + In_2O_3$ system. It seems that the small stability of the $CaIn_2O_4$ compound at high temperature makes the existence of other ternary oxides

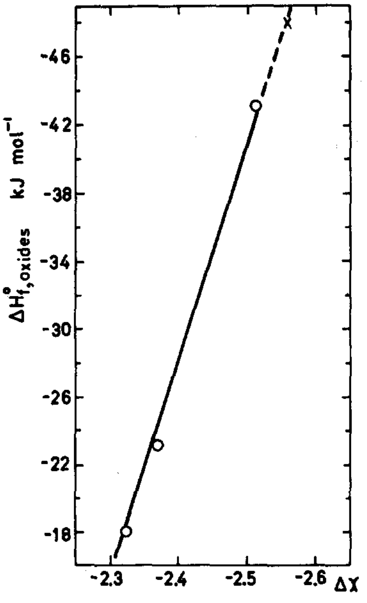

Fig. 4. The dependence of $\Delta H^0_{f,oxides}$ vs. Phillips electronegativity difference, $\Delta\chi$.

unlikely. It is interesting to compare the stability of the binary oxides $CaAl_2O_4$, $CaGa_2O_4$ and $CaIn_2O_4$.

The Gibbs free energy of formation of these compounds decreases significantly as Al and Ga atoms are substituted by indium atoms, which indicates that the stability depends on the properties of the M–O bond (M = Al, Ga, In). Al_2O_3 and Ga_2O_3 oxides exhibit a corundum structure related to fluorite, which in turn means the adoption of a structure in which the metal achieves a higher coordination. Assuming that the heat of formation of ternary oxides is a function of M–O electronegativity difference, values of the heat of formation (from oxides) were plotted (Fig. 4) against Phillips electronegativity difference, $\Delta\chi = \chi_0 - \chi_M$ [10].

A linear dependence of $\Delta H^0_{f,oxides}$ vs. $\Delta\chi$ was found, which means that the effect taking place is larger as the M–O bond becomes less directional. From the plot shown in Fig. 4 the heat of formation of $CaTl_2O_4$ from the respective oxides can be predicted (~ -48150 J mol^{-1}). However, no similar correlation for the entropy change can be suggested as long as the entropy of the α-corundum → Mn_2O_3-type structure transformation remains unknown.

One can only suggest that the increase in $\Delta H^0_{f,oxides}$ must be compensated by the respective entropy change in order to produce the observed decrease in the compounds stability.

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