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GIBBS FREE ENERGY OF FORMATION OF SOLID $SnFe_2O_4$

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ABSTRACT

Employing the electrochemical cell with the solid oxide electrolyte

$Sn, SnO_2|O^{2-}|air\ (p_{O_2} = 0.21\ atm)$

The Gibbs free energy of formation of solid SnO_2 was determined over the temperature range 923–1173 K

$\Delta G^0_{f,SnO_2} = -578\,500 + 205.64\ T\ J\ mol^{-1}$

Next, using the cell

$Sn, FeO, SnFe_2O_4|O^{2-}|Fe, FeO$

The Gibbs free energy of formation of solid $SnFe_2O_4$ from the respective oxides was established over the temperature range 873–1123 K

$\Delta G^0_{f,SnFe_2O_4} = -51\,040 + 44.01\ T\ J\ mol^{-1}$

The presented results are applied to determine the phase relations in the Fe–Sn–O system at 1073 K, which are confirmed by the phase equilibrium investigations.

INTRODUCTION

The possibility of selective reduction of SnO_2 in preference to iron oxides has long been recognized [1]. A gas having suitable oxygen potential can reduce SnO or SnO_2 without affecting FeO, provided that tin and iron oxides are not in contact with each other. This process can be achieved by roasting followed by magnetic separation and the proper treatment below 1273 K with reducing gases. However, complex high-iron content ores are not suitable for this procedure as reduction followed by liquation of the crude metal gives poor metal recoveries because of the Fe–Sn hardhead alloy formation. Recently, Tshumarev et al. [2] reported the formation of the spinel-type compound $SnFe_2O_4$ in the SnO_2–Fe system. Consequently, the Fe–Sn–O phase diagram should be revised and the conditions of equilibrium between Fe–Sn alloys and solid oxides should be re-evaluated.

Therefore, an attempt was made to determine the stability of solid $SnFe_2O_4$ using galvanic cells with solid oxide electrolyte.

EXPERIMENTAL

Materials

SnO_2 and Fe powders were obtained from SERVA International (W. Germany) and Johnson Matthey Chemicals Ltd. (Gt. Britain), and were 99.9 and 99.99% pure, respectively. Fe_2O_3 powder was obtained from Merck (W. Germany) and was 99.95% pure. Solid electrolyte tubes 12-mm OD were obtained from Degussa (W. Germany) while the $ZrO_2 + CaO$ crucible was supplied by Yamari Trading Co. (Japan).

Phase diagram investigations

Three samples of SnO_2 + Fe powder mixtures characterized by the molar ratios: $X_{Fe}/X_{Sn} = 0.25/0.25$; $0.33/0.22$; and $0.51/0.16$ were prepared. Compositions of these samples labeled from 1 to 3, respectively, are shown on the Fe–Sn–O phase diagram in Fig. 1a. Next, powders were pelletized, sealed in silica capsules under vacuum, sintered at 1073 K for 4 h, and finally quenched in water. The visual observation showed heavy SnO attack on quartz in the case of the sample No. 1, and no evidence of such a process in the case of the two other samples. In all three cases metallic tin appeared at the bottom of the capsule. An X-ray investigation showed:

(1) in the case of sample No. 1 lines of tin, SnO_2 and $SnFe_2O_4$ were observed;

(2) in the case of sample No. 2 lines of tin, $SnFe_2O_4$ and FeO were

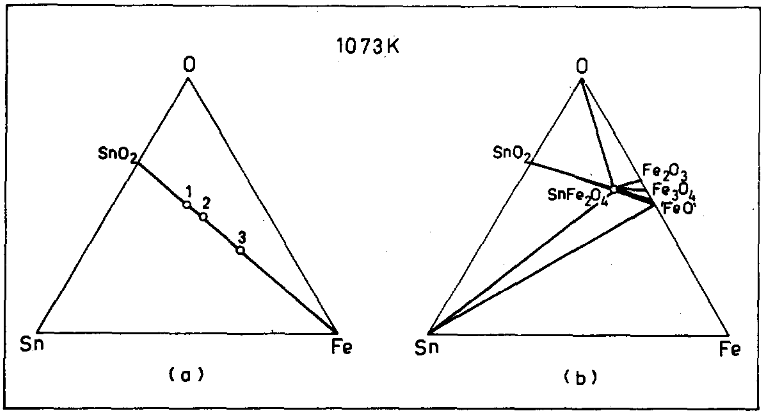

Fig. 1. Suggested phase relations in the system Fe–Sn–O at 1073 K.

observed. This sample was repeated three times, increasing the time of sintering up to 8 h.

(3) in the case of sample No. 3 lines of tin, FeO and Fe were detected.

Additional dim lines of SnO_2 and SnO detected in the case of sample No. 2 can be attributed to the short time of sintering (intensity of SnO_2 lines decreases with time of sintering) and to the process of quenching (SnO lines). An electron microprobe analysis revealed traces of iron in precipitated tin.

Following these results the suggested phase relations in the Fe–Sn–O system at 1073 K are shown in Fig. 1b. In the Sn–$SnFe_2O_4$–FeO three-phase field the oxygen chemical potential is fixed at a constant temperature by the reaction

$$Sn_{(l)} + 2\ FeO_{(s)} + O_{2(g)} \rightarrow SnFe_2O_{4(s)} \qquad (1)$$

which means it can be determined by EMF measurements using the galvanic cell with the solid oxide electrolyte.

Oxygen potential measurements

Solid oxide galvanic cells of the following types were used

$$Sn, SnO_2|O^{2-}|air\ (p_{O_2} = 0.21\ atm) \qquad (I)$$

$$Sn, FeO, SnFe_2O_4|O^{2-}|Fe, FeO \qquad (II)$$

for oxygen potential measurements corresponding to Sn, SnO_2 and three-phase field equilibria. The arrangement of cells is schematically shown in Fig. 2. Cell I was nearly identical to that used for the Sn–O dilute solution investigations [3]. It was kept in a vertical VS2 furnace of Metals Research Ltd. (Gt. Britain) within the constant temperature zone. The closed end of the electrolyte tube contained the metal sample together with SnO_2 powder. The upper end of the electrolyte tube was closed with a rubber stopper, which supported inside a small alumina tube with platinum wire with a piece of chromium cermet attached to its end. The cermet was preoxidized at 1473 K. Purified argon circulated inside the tube while dry air was flushed outside to maintain the constant oxygen partial pressure around the reference electrode. The platinum wire of the reference electrode was tightly wound around the electrolyte tube and then covered with platinum paste.

After the equilibrium state was reached at the desired temperature the cermet rod was inserted into the melt and the EMF was recorded. Then the temperature was changed and a new EMF value was obtained.

Cell II was similar to that used for sulfur activity measurements in liquid indium [4]. A zirconia crucible filled with FeO + $SnFe_2O_4$ powder mixed with tin was pressed together with the Fe, FeO reference electrode between two boron nitride discs. The investigated electrode was actually sample No. 2 taken after X-ray analysis. The Fe, FeO reference electrode was prepared by

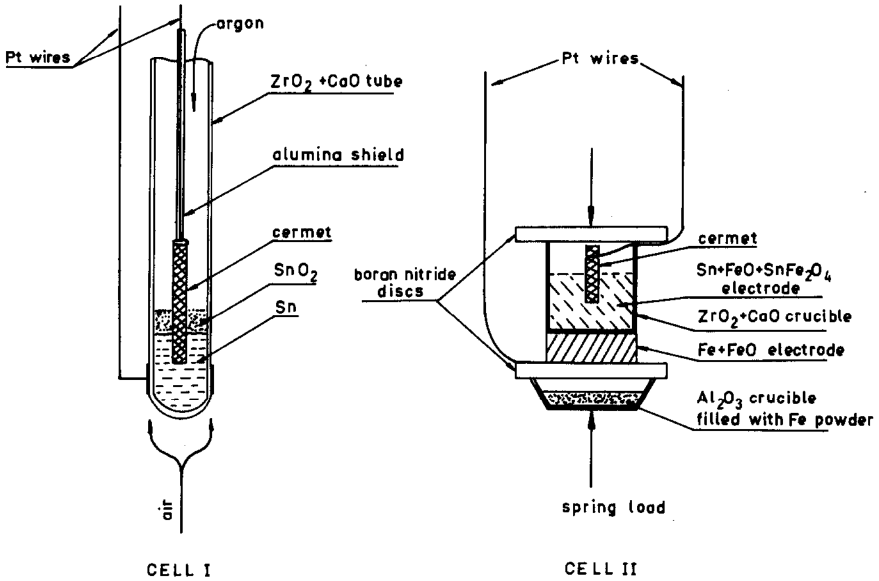

Fig. 2. Schematic diagram of the assembly of the cells.

sintering pressed pellets containing a 2:1 molar ratio of Fe and FeO powders. Pellets were sintered in evacuated silica capsules at a temperature of 1273 K. FeO powder was obtained by mixing Fe and Fe_2O_3 powders containing a 3:1 molar ratio of Fe and Fe_2O_3. Pressed pellets were sintered in evacuated silica capsules at a temperature of 1273 K. A piece of molybdenum cermet attached to a platinum wire was used as an electric lead. The cell was placed within the constant temperature zone of the VS 2 furnace. The tube of the furnace was flushed with purified argon. In order to equalize the oxygen pressures between the gas phase and the cell a flat alumina crucible filled with iron powder was held below the cell. After a constant temperature was reached, the cell was left overnight to attain an equilibrium state, and then the EMF was recorded with the digital voltmeter V 534 (Elwro, Poland).

RESULTS

The electromotive forces produced by cells I and II are shown in Fig. 3. Using the least-squares method one can obtain for cell I

$$E_{\mathrm{I}} = 1497.5 - 0.5659\,T\,(\mathrm{mV}) \tag{2}$$

Using the above equation the oxygen equilibrium pressure over the Sn-SnO_2 mixture can be calculated form the well-known relation

$$E_{\mathrm{I}} = \frac{RT}{4F}\ln\left[\frac{p_{O_2}(\mathrm{air})}{p_{O_2}(\mathrm{Sn,SnO_2})}\right] \tag{3}$$

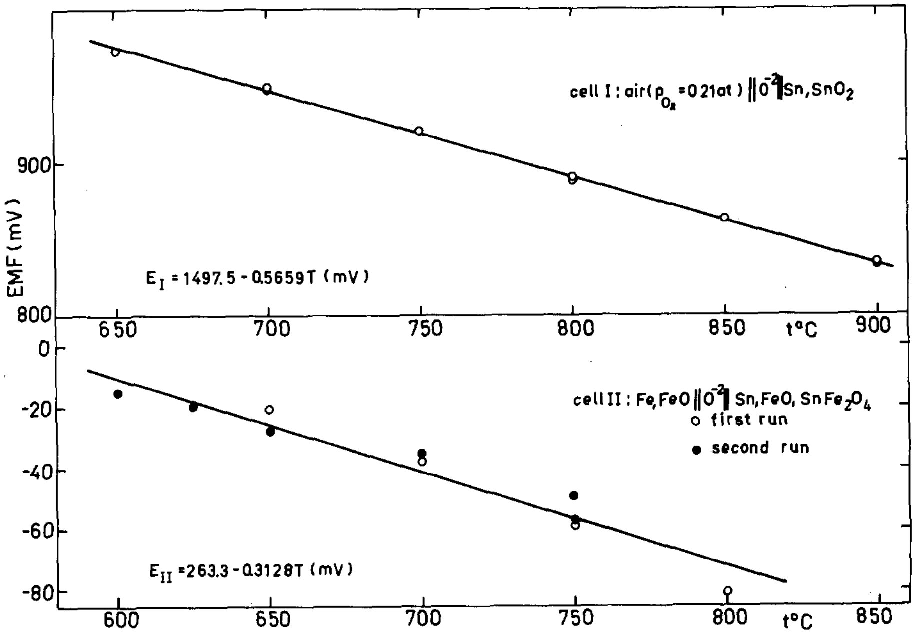

Fig. 3. Temperature dependence of the electromotive force of cells I and II.

After rearrangement of eqn. (3), and using eqn. (2) the following is obtained

$$\log p_{O_2(Sn,SnO_2)} = -\frac{30\,200}{T} + 10.735 \qquad (4)$$

A plot of $\log p_{O_2}$ vs. temperature is shown in Fig. 4, and compared with

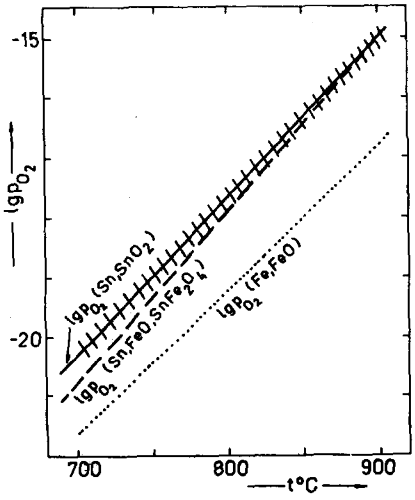

Fig. 4. Oxygen equilibrium pressure in the Sn–SnO₂, Sn–FeO–SnFe₂O₄ and Fe–FeO systems.

results of other investigations. Results reported by Petot-Ervas et al. [5] Seetharaman and Staffansson [6], Ramanarayanan and Bar [7], and Kammel et al. [8] are almost identical. Log p_{O_2} values resulting from their investigations are represented in Fig. 4 by the shaded area. Results of Palamutcu [9], and Belford and Alcock [10] differ insignificantly from these data.

Using the dependence (4), the Gibbs free energy of formation of solid SnO_2 can be easily calculated

$$\Delta G^0_{f,SnO_2} = RT \ln p_{O_2(Sn,SnO_2)} = -578\,500 + 205{,}64\ T\ (\mathrm{J\ mol^{-1}}) \tag{5}$$

which is found to be in good agreement with the data reported previously [5–8].

Similarly, the Gibbs free energy of formation of solid $SnFe_2O_4$ can be calculated from reaction (1). Using the least-squares method the following can be obtained for cell II

$$E_{II} = 329.6 - 0.3811\ T\ (mV) \tag{6}$$

and consequently, the equilibrium oxygen pressure for reaction (1) can be determined from the relation analogical to (3)

$$RT \ln p_{O_2(Sn,FeO,SnFe_2O_4)} = RT \ln p_{O_2(Fe,FeO)} - 4FE \tag{7}$$

Accepting after Turkdogan [11] the values of $\Delta G^0_T = 263\,910 - 64.396\ T$ J for the reaction 'FeO' → Fe + 1/2 O_2, the Gibbs free energy change for reaction (1) can be calculated as follows

$$\Delta G^0_{f,SnFe_2O_4} = RT \ln p_{O_2(Sn,FeO,SnFe_2O_4)} = 2\Delta G^0_{f,FeO} - 4\ FE_{II}$$

$$= -629\,532 + 249.63\ T\ \mathrm{J\ mol^{-1}} \tag{8}$$

Combining reaction (1) and the reaction of formation of SnO_2 the Gibbs free energy of formation of solid $SnFe_2O_4$ can be derived from the respective oxides

$$SnO_2 + 2\ FeO \rightarrow SnFe_2O_4 \tag{9}$$

which is equal to

$$\Delta G^0_{f\,(\text{from oxides})} = -51\,040 + 44.01\ T\ \mathrm{J\ mol^{-1}} \tag{10}$$

Calculated from eqn. (7) log $p_{O_2(Sn,FeO,SnFe_2O_4)}$ vs. temperature is shown and compared with corresponding Fe(FeO and Sn)SnO_2 equilibrium oxygen pressures in Fig. 4.

DISCUSSION

The results obtained for Sn, SnO_2 equilibrium agree fairly well with those reported by other authors. As far as reaction (1) is concerned, the measured oxygen equilibrium pressure is lower than that corresponding to Sn, SnO_2 equilibrium. On the other hand, it is higher than the calculated pressure for Fe, FeO equilibrium. It seems that at higher temperatures $SnFe_2O_4$ may decompose. It results, from the ΔG_f^0 value obtained for reaction (9), that this temperature is about 1160 K. As the slope of dependence (8) is sensitive to experimental errors one should be careful, however, with this number. An X-ray examination of the Sn–FeO–$SnFe_2O_4$ electrode after electrochemical experiments confirmed the existence of $SnFe_2O_4$. Thus, the suggested Fe–Sn–O phase diagram (Fig. 1b) seems to have a firm basis, at least over the investigated temperature range.

There are still some problems to be solved with this system. At higher oxygen partial pressures FeO can be oxidized to Fe_3O_4 which can form a series of solid solutions with $SnFe_2O_4$ as other spinels usually do. However, the formation of this type of solid solution has not been reported so far.

The most interesting problem is to find out if the solubility of iron in liquid tin will decrease under the temperature and oxygen partial pressure corresponding to the equilibrium of the liquid alloy with solid $SnFe_2O_4$. The coulometric titration experiment should answer very precisely how the solubility and activity of oxygen vary with the alloy composition, and which alloy iron concentration corresponds to the Fe, $SnFe_2O_4$ equilibrium. If this concentration is lower than that characteristic for Fe, FeO equilibrium, the proper manipulation of temperature and oxygen partial pressure during the reduction process might decrease the extent of the hardhead formation.

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