Journal of University of Science and Technology Beijing
Volume 14, Number 4, August 2007, Page 361

Electrochemical determination of Gibbs free energy of formation of magnesium ferrite

Ling Wang[1)], *Huizhu Zhou*[1)], *Yanruo Hong*[2)], *and Girish M Kale*[3)]

1) School of Chemical Engineering and Biotechnology, Hebei Polytechnic University, Tangshan 063009, China
2) Materials Science and Engineering School, University of Science and Technology Beijing, Beijing 100083, China
3) School of Process, Environmental and Materials Engineering, Department of Mining and Mineral Engineering, University of Leeds, Leeds, LS2 9JT, UK

(Received 2006-08-15)

Abstract: The standard Gibbs free energy of formation of magnesium ferrite was determined by means of two types of solid state electrochemical cells: one using $MgZr_4(PO_4)_6$ (MZP) as the solid electrolyte and the other using CaF_2 as the solid electrolyte. The first cell was operated in the range of 950 to 1100 K. The second cell was operated in the range of 1125 to 1200 K. The reversibility of the cell EMFs was confirmed by microcoulometric titration. The Gibbs energy changes of magnesium ferrite relative to component oxides were calculated based on EMF measurements and are given by following expressions, respectively: $\Delta G_{\mathrm{I}}^{\ominus} = -3579-15\,T$ (J/mol) and $\Delta G_{\mathrm{II}}^{\ominus} = 6258-24.3\,T$ (J/mol). The results obtained from two different cells are consistent with each other. The results also are in agreement with Rao's and Tretjakov's data in the measured temperature range. When the Gibbs free energies of formation of MgO and Fe_2O_3 were substituted in the reaction, the Gibbs free energies of formation of $MgFe_2O_4$ was obtained in two temperature ranges and the formations are shown as follows: $\Delta G_{\mathrm{I\,Formation}}^{\ominus} = -1427394+360.5\,T$ (J/mol) and $\Delta G_{\mathrm{II\,Formation}}^{\ominus} = -1417557+351.2\,T$ (J/mol).

Key words: magnesium ferrite; electrochemical cell; Gibbs free energy of formation; solid electrolyte

[*This study was financially supported by the National Natural Science Foundation of China (No.50572024) and the Education Ministry Foundation for Returning Overseas Scholar of China.*]

1. Introduction

$MgFe_2O_4$ is of spinel structure and is one of typical magnetic materials [1-2]. In steel-making process it is an important product of the reaction of refractory with slag. It is also a potential reference electrode material in a high temperature electrochemical cell. Hong *et al.* [3-4] has used it as the auxiliary electrode material for Fe sensors. The thermodynamic data of $MgFe_2O_4$ is required for predicting the reaction possibility of refractory-slag in the pyrometallurgical process and for determining the reaction mechanism. If $MgFe_2O_4$ is used as sensing materials for sensors, its thermodynamic data is crucial to calculate the theoretical EMF of a sensor. Unfortunately, only a few data were reported and big discrepancies exist among them.

Tretjako and Schmalzried [5] determined the Gibbs free energy change of $MgFe_2O_4$ relative to the component oxides employing a CaO-ZrO_2 solid state electrolyte cell. They employed an air reference electrode and $MgFe_2O_4$+MgO+Fe as the working electrode in their cells. Rao [6] gave the data of Gibbs free energy change of $MgFe_2O_4$ from the component oxides in a certain temperature range. Barin [7-8] measured the data using calorimetry. The data obtained by Tretjako and Schmalzried [5] was found to be 16 to 20 kJ/mol more negative than that of Barin [7-8], and the entropy change value was opposite. However, Rao's data is very close to Tretjako's (the difference is about 1 kJ/mol). So it is not very clear which data is more accurate. An electrochemical cell has been widely used to determine the Gibbs free energy of formation [9]. Hence, the aim of the present investigation is to determine accurately the Gibbs free energy of the formation of $MgFe_2O_4$ relative to component oxides using a solid state cell incorporating $MgZr_4(PO_4)_6$ and a single crystal of CaF_2 as solid electrolytes.

2. Experimental

2.1. Materials

$MgZr_4(PO_4)_6$ tube as Mg^{2+} conducting electrolyte was made from MgO, ZrO_2 and $NH_4H_2PO_4$ according to the method used by Ref. [10]. $MgFe_2O_4$ was synthe-

Corresponding author: Yanruo Hong, **E-mail:** hongyanruo@mater.ustb.edu.cn

sized for 1 h by intimately mixing the powders MgO and Fe_2O_3 at an equimolar ratio under acetone in a ball mill with alumina balls and drying the slurry in air, finally firing the mixing powder at 1623 K for 10 h in a high-density crucible. After the first cycle of mixing and firing, the powder was again mixed and fired following the same procedure. The powder was subjected to XRD analysis, which indicated the complete formation of single phase $MgFe_2O_4$. The high purity O_2 gas was used to provide atmosphere during the EMF measurements.

2.2. Apparatus

The reversible EMFs of a solid state cell:

$$\text{Pt, } O_2\text{, Pt + MgO}|MgZr_4(PO_4)_6|\text{ Pt + } MgFe_2O_4 + Fe_2O_3\text{, } O_2\text{, Pt} \qquad \text{(I)}$$

and

$$\text{Pt, } O_2\text{, MgO + } MgF_2|CaF_2|MgFe_2O_4 + Fe_2O_3 + MgF_2\text{, } O_2\text{, Pt} \qquad \text{(II)}$$

were measured as a temperature function in the range of 950 to 1100 K and 1125 to 1200 K, respectively. The two-phase electrode containing MgO+Pt for cell (I) was prepared from an intimately mixed paste of Pt and MgO at 1:1 molar ratio and firing for 30 min at 1173 K. The electrode of Pt+$MgFe_2O_4$+Fe_2O_3 was prepared from a mixture of Pt, $MgFe_2O_4$, Fe_2O_3 at 1:1:1 molar ratio and firing for 30 min at 1173 K. As to cell (II), the positive electrode pellet of Fe_2O_3, $MgFe_2O_4$, and MgF_2 mixture (molar ratio 1:1:1) was prepared by mixing, isostatic pressing (200 MPa), and then sintering in a stream of prepurified oxygen at 1173 K. The negative electrode pellet of MgO and MgF_2 (molar ratio 1:1) mixture was prepared by the same procedure. Cell (I) was formed by placing MgO+Pt powder inside the $MgZr_4(PO_4)_6$ (MZP) solid electrolyte tube and spring loading Pt+$MgFe_2O_4$+ Fe_2O_3 powder against the outside of the closed-end solid electrolyte tube. The electrical contact was made by embedding the Pt wires into the compacted electrode mixture. A schematic diagram of the apparatus is shown in Fig. 1(b). Cell (II) was formed by series sandwiching of pellets. The contact surface of the electrolyte and references were polished. The three pellets were spring loaded against each other with the aid of an alumina support system. A schematic diagram of the apparatus is shown in Fig. 1(a). The cell was assembled in a closed-end quartz tube. The top open end of the quartz tube housing cells was fitted with a rubber bung. The atmosphere inside the cells was provided by flowing high purity O_2 that was further purified by passing over the pellets of NaOH and anhydrous P_2O_5 to remove any traces of CO_2 and moisture. Measurements of the *in situ* temperature of the cell was made with a Ni/Cr-Al/Cr thermocouple. The temperature of the furnace was controlled using another thermocouple within ±1 K.

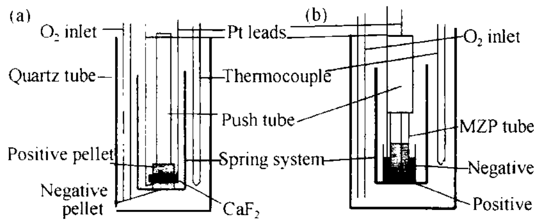

Fig. 1. A schematic diagram of construction of the measuring cell: (a) cell (II); (b) cell (I).

2.3. Procedure

The solid-state galvanic cell housed inside a quartz tube closed at one end was placed in a horizontal tube furnace. The cells were initially flushed with purified O_2 gas for 2 h, and then the temperature of the cells was raised to a required value. The cell EMF was measured using a Keithley digital electrometer with an input impedance $>10^{12}$ Ω. The analog output of the electrometer was connected to an *x-t* chart recorder for recording the EMF as a function of time. The reversibility of each cell was confirmed by microcoulometric titration. The microcoulometric titration was carried by applying about 100 μA current to the cell for a period of 30 s in both directions. In each case, the EMF was found to return its original value before the titration. The EMF of each cell was independent of the flowrate of O_2 gas over the electrodes between 120-200 mL/min. The reversible EMFs of the cells were reproducible on temperature cycling. The time to attain steady EMF varied from 0.5 to 3 h at each temperature, depending on the temperature.

3. Results and discussion

The reversible EMF of cell (I) is plotted as a function of absolute temperature in Fig. 2. The EMF of cell (I) is found to vary linearly with temperature. The half-cell reactions taking place at the left and right-hand electrode of cell (I) are

$$MgO-2e=Mg^{2+}+1/2O_2$$

and

$$Mg^{2+}+1/2O_2+2e+Fe_2O_3=MgFe_2O_4.$$

So the overall reaction is

$$Fe_2O_3+MgO=MgFe_2O_4$$

The measured EMF (mV) is related to the Gibbs free energy change of the above reaction by the following expression,

$$-nE_{\mathrm{I}}^{\ominus}F=\Delta G_{\mathrm{I}}^{\ominus}\text{ ,}$$