SHORT COMMUNICATION

Thermodynamic stability of magnesium chromite from e.m.f. measurements

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1. Introduction

Tretjakov and Schmalzried [1] employed a ZrO_2–CaO solid electrolyte cell to determine the Gibbs' energy of formation of $MgCr_2O_4$ from the component oxides. Jacob [2] determined the Gibbs' energy of formation of $MgCr_2O_4$ from the component oxides in the temperature range 1073–1473 K from the e.m.f. of a galvanic cell incorporating ThO_2–Y_2O_3 solid electrolyte. These authors employed a Cr/Cr_2O_3 reference electrode and $MgCr_2O_4$ + MgO + Cr as the working electrode in their cells. At a mean temperature of 1273 K, the Gibbs' energy of formation of $MgCr_2O_4$ from the component oxides obtained by Tretjakov and Schmalzried [1] was found to be 4 to 5 kJ more positive than that of Jacob [2], who attributed this difference to electronic conduction in the ZrO_2–CaO electrolyte at the low oxygen potentials associated with the $MgCr_2O_4$ + MgO + Cr electrode. In the present work, a galvanic cell with MgF_2 as the solid electrolyte was used to determine the Gibbs' energy of formation of $MgCr_2O_4$ in the temperature range 1220–1280 K. The suitability and reliability of this technique to measure activities of MgO in solid solutions and compounds containing MgO are well documented [3–5].

2. Experimental procedure

2.1. Materials

Magnesium fluoride for making the solid-electrolyte and electrodes was made according to the method of Taylor and Schmalzried [3]. The electrolyte was prepared by pressing the powder to a pressure of 235 MPa in a cylindrical die. The green pellet was then sintered in an atmosphere of CO_2-free dry argon gas at 1323 K for 4 h. The magnesium chromite ($MgCr_2O_4$) was synthesized from fine powders of dried reagent grade Cr_2O_3 and MgO. These starting materials were mixed in the correct ratio under acetone. $MgCr_2O_4$ was prepared by sintering the oxide mixture pellet at 1623 K in a platinum boat under air for 48 h with intermittent grinding. The formation of $MgCr_2O_4$ was confirmed by X-ray diffraction.

2.2. Cell operation

The apparatus used in the present work was similar to that described in earlier work [6]. The performance of the polycrystalline MgF_2 as a solid electrolyte was checked by operating the cell:

$$O_2(g), Pt|MgO, MgF_2|MgF_2|MgO \cdot 2TiO_2,$$

$$TiO_2, MgF_2|Pt, O_2(g)$$
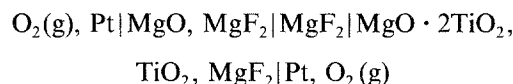
in the temperature range 1173–1273 K. The e.m.f.s obtained for this cell agreed with those reported by Shah *et al.* [7] within ± 2 mV. The Gibb's energy of formation of $MgO \cdot 2TiO_2$ from the component binary oxides calculated from the e.m.f. is also in reasonably good agreement with the results of Barin *et al.* [8] when the error limits are taken into account.

The cell employed in the investigation of $MgCr_2O_4$ was of the type

$$O_2(g), Pt|MgO, MgF_2|MgF_2|MgCr_2O_4,$$

$$Cr_2O_3, MgF_2|Pt, O_2(g)$$
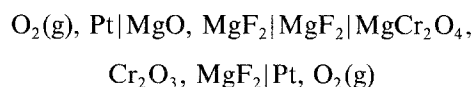
The chromite working electrode was prepared by mixing $MgCr_2O_4$ and Cr_2O_3 in roughly equimolar proportions. About 10 to 15 wt % of MgF_2 was then added to this mixture. The overall reaction is

$$MgO(rs) + Cr_2O_3(cor) = MgCr_2O_4(spinel) \quad (1)$$
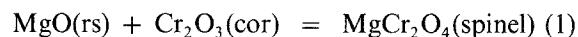
in which the crystal structure of each phase was identified by X-ray diffraction. The two half-cell reactions of this cell reaction can be represented as follows in accordance with Benz and Wagner [9]. At the reference electrode (anode) where pure MgO is in contact with MgF_2 electrolyte:

$$MgO(s) + 2F^- = MgF_2(s) + \tfrac{1}{2}O_2(g) + 2e^- \quad (2)$$
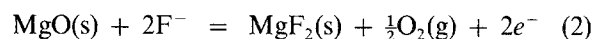
At the working electrode (cathode) where ($MgCr_2O_4$ + Cr_2O_3) is in contact with the MgF_2 electrolyte:

$$MgF_2(s) + \tfrac{1}{2}O_2(g) + Cr_2O_3(s) + 2e^-$$
$$= MgCr_2O_4(s) + 2F^- \quad (3)$$
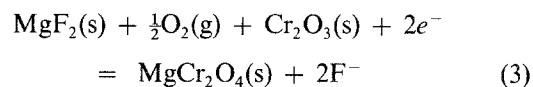
The measured e.m.f. (mV) is related to the Gibbs' energy change of Reaction (1) by the expression

$$-2EF = \Delta G^0 \quad (4)$$

where *F* is the Faraday constant. The half-cell reactions clearly indicate that oxygen is necessary at the electrodes. An atmosphere of CO_2-free, dry oxygen gas was provided throughout the working period of the cell. The half-cell reactions given assume that the electrolyte is reversible only to fluoride ions. Measurement of the *in situ* temperature of the cell was made with a Pt/Pt–13% Rh thermocouple welded to the platinum foil in contact with the reference electrode. The platinum wire of the couple also served as the lead wire for measuring the cell e.m.f.. The temperature of the furnace was controlled using another thermocouple to within
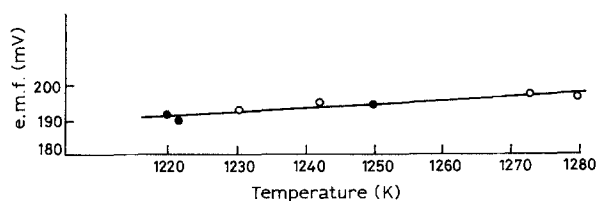
Fig. 1. Plot of e.m.f. (mV) against temperature (K) for the cell $O_2(g)$, $Pt|MgO$, $MgF_2|MgF_2|MgCr_2O_4$, Cr_2O_3, $MgF_2|Pt$, $O_2(g)$. (O) Heating; (●) cooling.

± 3 K. The cell e.m.f. was measured using a potentiometer correct to ± 0.2 mV. The reversible e.m.f.'s of the cells, measured in the temperature range 1220–1280 K, were reproducible on temperature cycling and the time for equilibration varied from 6 to 7 h at each temperature.

3. Results and discussion

Figure 1 shows the e.m.f. as a function of temperature of the cell on heating and cooling. A cell with pure MgO on both sides gave e.m.f.'s close to zero (± 0.5 mV). Changes in gas flow rate also did not affect the cell e.m.f.. Reproducible e.m.f.s were obtained even after an initial polarization of the cell by passing an external current. The least-mean-square analysis of the data shown in Fig. 1 gives the following equation for the cell e.m.f.:

$$E = 79.2 + 0.0918T \ (\pm 1.2)\,\text{mV}$$

$$(1220\text{–}1280\,\text{K})$$

This e.m.f. is directly related to the standard energy

change of Reaction 1

$$\Delta G^0 = -2FE$$

$$= -15.287 - 0.0177T \pm (0.8)\,\text{kJ mol}^{-1}$$

This equation for the Gibbs' energy change of cell Reaction 1 corresponds to a value of $-37.82 (\pm 0.8)$ kJ for the Gibbs' energy of formation of $MgCr_2O_4$ from the component oxides at 1273 K. This compares with values of $-38.5 (\pm 0.4)$ kJ mol^{-1} and -33.89 kJ mol^{-1} at the same temperature obtained by Jacob [2] and Tretjakov and Schmalzried [1], respectively. While the present results are not in agreement with those of Tretjakov and Schmalzried [1], there is reasonably good agreement with the data reported by Jacob [2] considering the different experimental techniques and the error limits of the measurements.

References

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