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Letter

Thermodynamics of formation of tetramagnesium niobate from e.m.f. measurements

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1. Introduction

The phase diagram [1] of the system $MgO–Nb_2O_5$ shows the existence of only two compounds below 1473 K, namely $MgO \cdot Nb_2O_5$ and $4MgO \cdot Nb_2O_5$. The Gibbs energy of formation of monomagnesium niobate has been determined [2] in the temperature range 1172–1278 K using an MgF_2 solid electrolyte galvanic cell. From the data so obtained and from e.m.f. measurements using a similar galvanic cell in the present work, the Gibbs energy of formation of $4MgO \cdot Nb_2O_5$ from the component oxides has been determined in the temperature range 1245–1292 K. The suitability and reliability of this technique for the determination of the thermodynamic properties of solid solutions and compounds involving MgO are well documented [3–5]. It is possible to determine the Gibbs energy of formation of $4MgO \cdot Nb_2O_5$ by setting up the following cell incorporating MgF_2 as the solid electrolyte:

$$O_2(g),Pt/MgO,MgF_2//MgF_2//4MgO \cdot Nb_2O_5,MgO \cdot Nb_2O_5,MgF_2/Pt,O_2(g)$$

The reaction at the $MgO–MgF_2$ interface is

$$3MgO + 6F^- \longrightarrow 3MgF_2 + \tfrac{3}{2}O_2(g) + 6e^-$$

The reaction at the $MgF_2–MgO \cdot Nb_2O_5,4MgO \cdot Nb_2O_5,MgF_2$ interface is

$$3MgF_2 + \tfrac{3}{2}O_2(g) + MgO \cdot Nb_2O_5 + 6e^- \longrightarrow 4MgO \cdot Nb_2O_5 + 6F^-$$

Therefore the net cell reaction is

$$3MgO + MgO \cdot Nb_2O_5 \longrightarrow 4MgO \cdot Nb_2O_5 \qquad (1)$$

The Gibbs energy change of reaction (1) is given by

$$\Delta G^\circ = -6FE$$

where E is the e.m.f. of the cell and F the Faraday.

The Gibbs energy of formation of $4MgO \cdot Nb_2O_5$ from the component oxides can be calculated from the Gibbs energy change involved in reaction

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(1) and that of the formation of $MgO \cdot Nb_2O_5$ determined in previous work [2].

The electrode reactions at the interfaces of MgF_2 indicate that the cell would require an atmosphere of oxygen for the development of its e.m.f. and an atmosphere of dry, carbon-dioxide-free oxygen was provided throughout the working period of the cell.

2. Materials

Magnesium fluoride, for use as the solid electrolyte and as an additive to improve the conductivity of the electrodes, was prepared 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 dry, CO_2-free argon gas at 1323 K for 4 h. The tetramagnesium niobate was prepared from dried reagent grade MgO and Nb_2O_5 by mixing in stoichiometric proportions and sintering the oxide mixture pellets at 1623 K under air for 48 h with intermittent grinding. The formation of the niobate was confirmed by X-ray diffraction. The appropriate compounds, prepared earlier, were mixed in roughly equimolar proportions to make the electrode pellets. About 10–15 wt.% of magnesium fluoride was then added to the mixture which was pressed into a pellet at 235 MPa and finally sintered at 1273 K in dry CO_2-free oxygen gas before use.

3. Experimental details

The apparatus used in the present work was similar to that described earlier [6]. In the cell the magnesium fluoride solid electrolyte pellet was sandwiched between the reference electrode and working electrode pellets. The cell was electrically connected to a Keithley 617 electrometer by means of platinum leads connected to platinum foils pressing against the outer pellets. The pellets and the platinum foils rested on an inverted alumina crucible supported on a closed alumina tube. The pellets were kept pressed from the top by an alumina tube which also functioned as an inlet for dry, CO_2-free oxygen gas. The whole cell assembly was enclosed inside a sillimanite reaction tube and kept in the even temperature zone of the furnace.

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. Shah *et al.* [7] have measured the Gibbs energies of formation of the magnesium titanates using this technique. The e.m.f.s obtained in the present work are in good agreement with those reported results, thereby confirming the suitability of MgF_2 as a solid electrolyte with $t(F^-)$ close to unity, in order to obtain reliable thermodynamic results on metal oxide systems.

A Pt–PtRh(13% Rh) thermocouple welded to the platinum foil in contact with the reference electrode served to measure the cell temperature. The platinum wire of the couple was also the lead wire for measuring the cell e.m.f. The temperature of the furnace was controlled by another thermocouple to within ±3 K. The cell e.m.f. and the temperature were measured using a Keithley 617 digital electrometer with an input impedance of about 10^{14} Ω. The reversible e.m.f.s of the cells were measured in the temperature range 1245–1292 K. The e.m.f.s were reproducible on temperature cycling. The time of equilibration was about 4 h. The e.m.f.s remained constant for several hours once the equilibrium was attained. The temperature dependence of the cell e.m.f. was found to be small and this is to be expected as the cell reaction involves solids and low entropy changes are expected.

4. Results and discussion

The experimental values of the e.m.f.s of the cell on heating and cooling are plotted as a function of temperature in Fig. 1. The e.m.f.s vary linearly with temperature within experimental error in the temperature range 1245–1292 K. The cell with pure MgO on both sides gave an e.m.f. close to zero. 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. It was found that the cell e.m.f. was reproducible to within ±1.5 mV when taken through a thermal cycle. The uncertainty of ±3 K in the temperature measurements is not likely to introduce any serious error since the variation in e.m.f. with temperature was quite small.

The least-mean-squares analysis of the e.m.f.s in Fig. 1 suggests the value of 153.85 ±1.5 mV for the cell at a mean temperature of 1272 K. This e.m.f. is directly related to the standard Gibbs energy change of -89.1 ± 0.9 kJ mol^{-1} for the reaction (1) at 1272 K. This value is combined with the standard Gibbs energy of formation of $MgO \cdot Nb_2O_5$ from the component

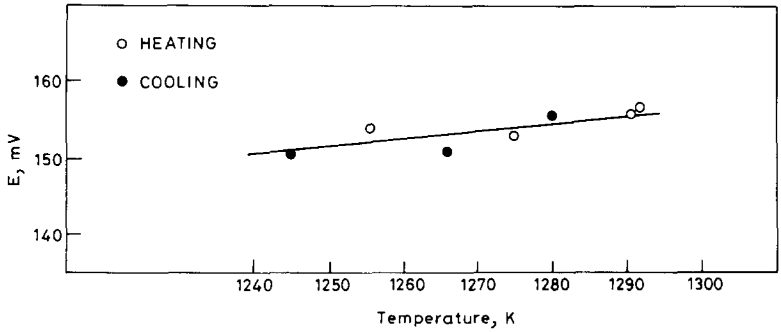

Fig. 1. E.m.f. E (mV) *vs.* temperature T (K) for the cell $O_2(g)$, Pt/MgO, MgF_2//MgF_2//$MgO \cdot Nb_2O_5$, $4MgO \cdot Nb_2O_5$,MgF_2/)Pt,$O_2(g)$.

oxides determined from previous work [2] to be

$$\Delta G^\circ - 0.016\,56T - (33.430 \pm 1.0)\ \mathrm{kJ\ mol^{-1}}$$

in the temperature range 1172–1278 K. The Gibbs energy of formation so obtained is -143.6 ± 1.4 kJ $\mathrm{mol^{-1}}$ at 1272 K for the reaction

$$4\mathrm{MgO} + \mathrm{Nb_2O_5} \longrightarrow 4\mathrm{MgO}\cdot\mathrm{Nb_2O_5}$$

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