Properties and Applications of Polycrystalline Calcium-Beta''-Alumina

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CONTENTS

Abstract

Polycrystalline β''-alumina samples conducting calcium ions were prepared. Both the ionic and electronic conductivities of the samples at 570 K were measured. Then they were used as solid electrolytes in solid-state galvanic cells. In this way, thermodynamic properties of CaO-MnO and $CaO-Al_2O_3$ systems at 1100 K were determined.

1. Introduction

It is now well documented that the nominally sodium ion conducting solid electrolyte β''-alumina can be readily ion exchanged with divalent conducting cations upon their immersion in an appropriate molten salt /1,2/. Divalent β''-aluminas form the first family of high conductivity solid electrolytes of divalent cations.

Measurements on Ca^{2+}-β''-aluminas indicated that their conductivities were in the range of $10^{-1}\Omega^{-1}cm^{-1}$ to $10^{-4}\Omega^{-1}cm^{-1}$ at 570 K, depending on the thermal history of the sample preparation /2-4/. Due to its high calcium ionic conductivity, this material could be used as an electrolyte in solid galvanic cells designed to measure the thermodynamic properties of compounds, alloys and slags containing calcium.

In our earlier studies, divalent cation β''-aluminas (where the divalent cation was Zn^{2+}, Ni^{2+}, Mn^{2+} and Hg^{2+}, respectively) were prepared and successfully applied to galvanic cells for the study of high temperature thermodynamic equilibria in oxide systems /5-7/. In the present study, calcium-β''-alumina was prepared; its conduction properties were found; and then the galvanic cells were built in order to determine the thermodynamic functions characterising both CaO-MnO and $CaO-Al_2O_3$ oxide systems.

2. Experimental Procedures

Calcium-β''-alumina was prepared from MgO-stabilized sodium-β''-alumina by ion exchange in the molten salt condition. The method of Na-β''-alumina preparation is available in the literature /5/. Ion exchange experiments with Ca^{2+} ions were performed in an α-alumina crucible with a $Ca(NO_3)_2$-$CaCl_2$ eutectic mixture. Na-β''-alumina pellets (3 mm thick and 12 mm in diameter) were dipped in fused salt at 850 K in air and held there over 24 hours. The exchange surfaces of the samples were then cleaned of solidified eutectic salt by immersion in a molten $CaCl_2$ bath. Then the samples were treated with anhydrous ethyl alcohol to remove salt residue. The extent of ion exchange, as determined by weighing the pellets before and after exchange, was greater than 96%. All samples prepared were X-ray controlled. They consisted of pure β''-Al_2O_3 phase.

Ionic conductivity measurements were made using an impedance analyser (TESLA 507) over the frequency range of 500 Hz to 500 kHz. Each calcium-β''-alumina pellet was contacted with two sputtered platinum electrodes over which platinum paste was applied to ensure satisfactory electrical contact. The sample was held between platinum net electrodes under slight spring tension in an alumina holder. All measurements were carried out at 570 K in a stream of dry argon. Samples were initially heated at 750 K for 3 hours to remove residual moisture. They were equilibrated for 15 minutes at the temperature of measurement, 570 K.

Electronic conductivity measurements of the samples were performed using the Wagner polarization method /8/. Platinum was used as a blocking electrode. A reversible electrode consisted of CaO particles dispersed in Ca-β''-alumina pellet. A similar reversible Na^+ ion electrode, containing Na_2O as a separate phase, was successfully applied by us to determine the thermodynamic properties of sodium-β''-alumina /9/.

Calcium-β''-alumina was used as a solid electrolyte in oxide galvanic cells. The first series of the cells served in determining the free enthalpy of mixing in $Ca_xMn_{1-x}O$ solid solutions. The cells employed were of the type:

$$Pt|O_2|CaO|\text{Ca-β''-alumina}|Ca_xMn_{1-x}O|O_2|Pt \qquad (1)$$

Half-cells were prepared as described in a recent study by Róg et al. /10/. The measurements were performed for x = 0.14, 0.34, 0.50, 0.68 and 0.76.

The second series of cells was applied to determine the standard free enthalpies of compounds formed in the $CaO-Al_2O_3$ system. The cell arrangement can be represented as:

$Pt|O_2|Al_2O_3,CaO.6Al_2O_3|Ca\text{-}\beta''\text{-}Al_2O_3|CaO.6Al_2O_3,CaO.2Al_2O_3|O_2|Pt$ (2)

$Pt|O_2|CaO.6Al_2O_3,CaO.2Al_2O_3|Ca\text{-}\beta''\text{-}Al_2O_3|CaO.2Al_2O_3,CaO.Al_2O_3|O_2|Pt$ (3)

$Pt|O_2|CaO.2Al_2O_3,CaO.Al_2O_3|Ca\text{-}\beta''\text{-}Al_2O_3|CaO.Al_2O_3,3CaO.2Al_2O_3|O_2|Pt$ (4)

$Pt|O_2|CaO.Al_2O_3,3CaO.Al_2O_3|Ca\text{-}\beta''\text{-}Al_2O_3|3CaO.Al_2O_3,CaO|O_2|Pt$ (5)

Calcium aluminates were prepared following the method developed by Kumar and Kay /11/. The half-cells and electrolyte pellets were assembled in a simple spring-loaded alumina holder according to the respective cell scheme. The cell was placed in the furnace and heated to the measurement temperature. The emf was monitored with a high resistance digital voltmeter.

A purified dry argon flow was passed through the furnace during emf measurements of cell (1). In cells (2) - (5), the oxygen partial pressure was fixed as 0.21 atm. Five independent series of emf measurements for each cell were performed at a temperature of 1100 K.

3. Results and Discussion

Ionic conductivity data were analysed on the complex impedance plane. The frequency plot had the characteristic shape of a partial semicircle. In such a case, the overall impedance of a polycrystalline sample may be modelled by the bulk resistivity of individual crystallites in-series with impedance due to parallel resistance-capacitance effects associated with crystallite grain boundaries /12/. In this model, the high frequency intersection with the real axis of the impedance can be attributed to the bulk resistivity, and the low frequency intersection of the semicircle is the sum of bulk and grain boundary resistivity. According to our measurements, the high frequency intercept with the real axis passed through the origin; the resistivity of a sample obtained by extrapolating low frequency impedance data to the real axis was due to the predominance of a grain boundary resistivity. The mean value of the ionic conductivity calculated on the basis of the impedance plots of our samples was $3.84 \times 10^{-4}\Omega^{-1}cm^{-1}$ at 570 K.

Electronic conductivity values were obtained from current-potential curves and was $4.20 \times 10^{-7}\Omega^{-1}cm^{-1}$ at the same temperature. As a result of comparing the values of ionic and electronic conductivities, the samples of Ca-β''-alumina were shown to be practically pure ionic conductors.

The emf of cells (1) - (5) was a result of a difference in the activity of Ca^{2+} ions at the electrodes. The overall reaction for cell (1) consisted in transferring CaO to the solid solution. From the values of emf (E) at 1100 K, the partial molar free enthalpy of CaO (G^{-}_{CaO}) in the solid solution and then the activity of CaO (a_{CaO}) and the activity coefficient (f_{CaO}) of CaO could be calculated as:

$$G^{-}_{CaO} = -2FE = RT \ln a_{CaO} = RT \ln f_{CaO}x \quad (6)$$

(F is Faraday constant)

Knowing the activity coefficient, f_{CaO}, to be a function of the molar fraction of CaO (x) in the solid solution, the activity coefficients of MnO (f_{MnO}) for all compositions of solid solution were determined using the method proposed by Darken and Gurry /13/.

The free enthalpy (G^M) of mixing was then obtained:

$$G^M = RT [x \ln a_{CaO} + (1-x) \ln a_{MnO}] \quad (7)$$

In Table 1, G^M values for $Ca_xMn_{1-x}O$ solutions are compared with those calculated for ideal solution, (G^M_{id}). In order to demonstrate the deviations of the solution from the ideal behaviour, the excess free enthalpy (G^E) are also calculated. The G^M_{id} and G^E values at 1100 K are also given in Table 1. As seen in the table, the $Ca_xMn_{1-x}O$ solid solution exhibited a significant nonideal behaviour in contrast to the results published by other authors /14,15/. The strong positive deviations from ideal can be related to a tendency towards immiscibility in the solid solution at lower temperatures.

Overall cell reactions for cells (2) - (5) can be written as:

$$CaO.2Al_2O_3 + 4Al_2O_3 = CaO.6Al_2O_3 \quad (8)$$

$$\Delta G^o_I = -\frac{4}{3} FE_I \quad (8a)$$

$$4(CaO.Al_2O_3) + CaO.6Al_2O_3 = 5(CaO.2Al_2O_3) \quad (9)$$

$$\Delta G^o_{II} = -4FE_{II} \quad (9a)$$

$$3CaO.Al_2O_3 + 2(CaO.2Al_2O_3) = 5(CaO.Al_2O_3) \quad (10)$$

$$\Delta G^o_{III} = -4\,FE_{III} \quad (10a)$$

$$2CaO + CaO.Al_2O_3 = 3CaO.Al_2O_3 \quad (11)$$

$$\Delta G^o_{IV} = -4FE_{IV} \quad (11a)$$

Eqs. 8a - 11a show the relation between the standard free enthalpies of reactions 8 - 11 (ΔG^o_i) and the emf (E_i) of cells (2) - (5). Based on Eqs. 8 - 11 and 8a - 11a, the standard free enthalpies of formation (from oxides) for all calcium aluminates under study can be derived as:

$$\Delta G^o_f(CaO.6Al_2O_3) = \frac{3}{2}\Delta G^o_I + \frac{1}{2}\Delta G^o_{II} + \frac{1}{2}\Delta G^o_{III} + \frac{1}{2}\Delta G^o_{IV} \quad (12)$$

$$\Delta G^o_f(CaO.2Al_2O_3) = \frac{1}{2}\Delta G^o_I + \frac{1}{2}\Delta G^o_{II} + \frac{1}{2}\Delta G^o_{III} + \frac{1}{2}\Delta G^o_{IV} \quad (13)$$

$$\Delta G^o_f(CaO.Al_2O_3) = \frac{1}{4}\Delta G^o_I + \frac{1}{4}\Delta G^o_{II} + \frac{1}{2}\Delta G^o_{III} + \frac{1}{2}\Delta G^o_{IV} \quad (14)$$

$$\Delta G^o_f(3CaO.Al_2O_3) = \frac{1}{4}\Delta G^o_I + \frac{1}{4}\Delta G^o_{II} + \frac{1}{2}\Delta G^o_{III} + \frac{3}{2}\Delta G^o_{IV} \quad (15)$$

In Table 2, ΔG^o_f values obtained by us at 1100 K are listed together with those obtained by other authors /11,16/. They do not differ significanty.

It can, therefore, be concluded from our investiga-

Table 1
Free Enthalpy of Mixing of $Ca_xMn_{1-x}O$ Solid Solutions at 1100 K

x	G^M, J/mol	G^M_{id}, J/mol	G^E, J/mol
0.14	- 1754	- 3704	1950
0.34	- 2166	- 5863	3697
0.50	- 2272	- 6339	4067
0.68	- 2242	- 5703	3461
0.76	- 2091	- 5040	2949

Table 2
Standard Free Enthalpy of Calcium Aluminates Formation (from Oxides) Values at 1100 K

Reference	$-\Delta G^o_f$, kJ/mol			
	$CaO.6Al_2O_3$	$CaO.2Al_2O_3$	$CaO.Al_2O_3$	$3CaO.Al_2O_3$
This work	58.62	41.12	34.26	39.66
Kumar, Kay	61.13	42.33	35.13	40.27
Allibert	58.35	44.34	38.59	–

tion that calcium-β''-alumina appears to be a promising electrolyte for various types of reversible solid-state galvanic cells and other electrochemical devices.

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