Thermodynamics of the System $CaO–Al_2O_3$

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ABSTRACT

Thermodynamic properties of all compounds formed in the system $CaO-Al_2O_3$ were determined with the help of solid-state galvanic cells in the temperature range 1050 K – 1450 K. Calcium-β″-alumina containing 17 m/o $\alpha-Al_2O_3$ as a disperse phase was used as an electrolyte in the galvanic cells under study.

1. INTRODUCTION

The phase diagram of the $CaO-Al_2O_3$ system has been investigated in detail /1-3/. So far, six calcium aluminates: $(3CaO\cdot Al_2O_3)$, $(12CaO\cdot 7Al_2O_3)$, $(CaO\cdot Al_2O_3)$, $CaO\cdot 2Al_2O_3)$, $(CaO\cdot 6Al_2O_3)$ and $(CaO\cdot 10Al_2O_3)$ are formed in this system at atmospheric pressure. A knowledge of the thermodynamic properties of the compounds having high calcia content is important for many processes occurring in steel, cement and ceramic industries. Some of the calcium aluminates are good ionic conductors; they can be applied as solid electrolytes in modern electrochemical devices, e.g. solid-state batteries, gas sensors, etc. A study of the thermodynamics of the system is useful in understanding the interactions involving electrode and electrolyte in the galvanic cells.

The thermodynamic properties of calcium aluminates have been studied by several investigators. Systematic studies were performed first by Allibert *et al.* /4/, then by Kumar and Kay /5/. Allibert *et al.* determined the standard free enthalpy of formation for $C_{12}A_7$, CA, CA_2 and CA_6 compounds in the temperature range 923K - 1223K (C and A denote here CaO and Al_2O_3, respectively. This notation will be used throughout this paper, exclusively for calcium aluminates). Kumar and Kay, however, determined it for C_3A, CA, CA_2 and CA_6 compounds in the temperature range 1000 K - 1500 K. In the above cited papers there is a detailed review of investigations concerning the thermodynamics of the $CaO-Al_2O_3$ system. Allibert *et al.* as well as Kumar and Kay used a solid-state galvanic cell method; calcium fluoride and calcium-β″-alumina were applied as solid electrolytes in galvanic cells studied in these works.

The crystal structures and transport properties of calcium aluminates are well known. Calcium monoaluminate (CA) has a crystal structure related to β-tridimite /6/. The calcium ions in it are accommodated in cavities formed by $\{AlO_4\}$ tetrahedrons. Along the b-axis the tetrahedrons form hexagons, in the (0 1 0) - plane the hexagons form two-dimensional layers. Transport of calcium ions is possible in these layers. CA appeared to be mixed electronic-ionic conductor. There was some discussion about the stability of dodecacalcium heptaaluminate $(C_{12}A_7)$. Nurse /2/ assumed that this compound was stable only in the presence of moisture in the gas phase. Other authors proved, however, that water was not necessary for the synthesis of $Ca_{12}A_7$ /7,8/. The structure /8/ of $C_{12}A_7$ is cubic and it may be described as a three-dimensional framework formed by the linking of eight-membered rings of $\{AlO_4\}$ tetrahedra which link up by sharing either three or four of their corners with other tetrahedra. Only 32 of the 33 oxygen ions in the formula unit belong to the aluminate framework. The additional oxygen ion and calcium ions occupy sites within the aluminate framework. Therefore, this compound is a high oxygen ion conductor /3,8/. The structure of calcium dialuminate (CA_2) consists of a skeleton of $\{AlO_4\}$ tetrahedra /9/. Between these tetrahedra there are narrow channels, in which calcium ions are placed. Transport of calcium ions could occur via the channels in the structure. Calcium hexaaluminate (CA_6) crystallizes in the magnetoplumbite-type structure /10/. The structure consists of cubic spinel-type blocks, containing aluminium and oxygen ions, separated by hexagonal close-packed blocks containing calcium and oxygen ions. Such a structure suggests that the compound is a rather poor ionic conductor. Tricalcium aluminate C_3A is the compound with the highest calcia content. Its crystal structure has a cubic symmetry /11/. Little is known about its thermal stability and its transport properties. Calcium decaaluminate CA_{10} is the compound with the highest alumina content. It has the β-alumina type structure /3/ in which spinel-type blocks of aluminium and oxygen ions are separated by loosely-packed planes containing sodium and oxygen ions. Because of the loose packing, space is available for movement of the mobile calcium ions in this plane, leading to the two-dimensional high ionic conductivity.

All the calcium aluminates (except CA_{10}) can be prepared by a normal sintering route from calcia and alumina. The only way to prepare calcium decaaluminate is an exchange of sodium ions in sodium-β″-alumina, performed in a molten calcium salt /3,12/; CA_{10} was proved to be thermally unstable when heated at higher temperatures.

In our previous work /13/, the standard free enthalpy of C_3A, CA, CA_2 and CA_6 formation (from oxides) at 1100 K was determined. The above cited work was aimed at illustrating the application of polycrystalline calcium-β″-alumina electrolyte. Calcium-β″-alumina is a quasi-ternary non-stoichiometric compound formed in the $CaO-MgO-Al_2O_3$ system. It has a Na-β″-alumina structure /5/. We concluded that this material appeared to be a promising electrolyte for various types of reversible solid-state galvanic cells and other electrochemical devices /14/.

In our last work /15/ we demonstrated that by dispersion of ultrafine α-Al_2O_3 particles into the calcium-β″-alumina phase a significant enhancement in ionic conductivity was observed. In the present paper such a type of solid electrolyte was used. This work was initiated to investigate thermodynamic properties of all the compounds existing in the solid state in the system $CaO-Al_2O_3$.

2. EXPERIMENTAL PROCEDURES

2.1. Preparation and characterization of the solid electrolyte

Sodium-β″-alumina containing α-Al_2O_3 as a disperse phase was a precursor for the preparation of calcium ion electrolyte. The starting materials were α-Al_2O_3, Na_2CO_3 and $MgCO_3$. The sintering procedure was similar to that described in paper /14/. The obtained samples consisted of 83 m/o Na-β″-Al_2O_3 and of 17 m/o α-Al_2O_3. They were pellets 2-3 mm thick and 10 mm in diameter. Calcium-β″-alumina was prepared by an ion exchange of the pellets in molten calcium salt. The exchange experiments were performed in an α-alumina crucible filled by an eutectic salt mixture {42.5 m/o $CaCl_2$ + 57.5 m/o $Ca(NO_3)_3$}. The sodium-β″-alumina pellets were dipped in the fused salt bath, covered with an active carbon layer and held there over 24 h. In such a way a salt was separated from moisture in the ambient atmosphere. The temperature of the bath was 850 K, exceeding the eutectic temperature. After exchange the pellets were treated with dilute nitric acid and then with anhydrous ethyl alcohol to remove excess respective salt. The phase composition of the electrolyte was determined by X-ray diffraction analysis. The samples contained two main phases: β″-Al_2O_3, α-Al_2O_3 and a minute amount of a magnetoplumbite-type phase. The microstructure of the samples revealed nearly random distribution of α-alumina particles in a calcium-β″-alumina matrix. The size of the α-Al_2O_3 particles did not exceed 3 μm. The electrical conductivity of the samples appeared to be purely ionic and it amounted to 0.01 $(ohm{\cdot}cm)^{-1}$ at 900 K.

2.2. Preparation and characterization of the half-cells

Calcium aluminates CA_6, CA_2, CA, $C_{12}A_7$ and

C_3A were prepared from reagent-grade anhydrous α-alumina and calcium carbonate powders. After drying they were mixed in a stoichiometric ratio, pressed into pellets and heat-treated in dry inert gas. The mixtures were initially heated at 1270 K, then quenched, ground, repelletized and finally sintered for 48 h at a temperature in the range 1500 K - 1850 K, depending on the composition. To prepare $C_{12}A_7$ the final sintering occurred at 1620 K for 72 h. X-ray diffraction analysis of the preparations showed the presence of the required aluminates.

The right half-cell pellets were obtained in the following way: The pellets of all calcium aluminates were crushed and milled. The seven different two-phase mixtures were prepared by mixing of two-component powders according to cell schemes (see 2.3). To make the two-phase mixture more conductible, a small quantity of Pt powder was admixed to it. The left half-cell pellet was prepared by mixing of calcium-β″-alumina powder with a pure calcia. A minute amount of Pt powder was also added to this mixture. The mixture was then pressed into pellets. Thus, each pellet contained pure calcia as a separate phase, and the electrode could serve as a calcia reference electrode.

All the pellets were 2-3 mm thick and 10 mm in diameter.

2.3. Galvanic cells

The half-cells and electrolyte pellets were assembled in a simple spring-loaded alumina holder according to one of the following schemes:

$Pt/O_2/CaO//Ca\text{-}\beta''\text{-}Al_2O_3 //CA_6,Al_2O_3 /O_2/Pt$ (1)
$Pt/O_2/CaO//Ca\text{-}\beta''\text{-}Al_2O_3 //CA_2,CA_6/O_2/Pt$ (2)
$Pt/O_2/CaO//Ca\text{-}\beta''\text{-}Al_2O_3 //CA,CA_2/O_2Pt$ (3)
$Pt/O_2/CaO//Ca\text{-}\beta''\text{-}Al_2O_3 //C_{12}A_7,CA/O_2/Pt$ (4)
$Pt/O_2/CaO//Ca\text{-}\beta''\text{-}Al_2O_3 //C_3A,C_{12}A_7/O_2/Pt$ (5)
$Pt/O_2/CaO//Ca\text{-}\beta''\text{-}Al_2O_3 //CA_{10},Al_2O_3/O_2/Pt$ (6)
$Pt/O_2/CaO//Ca\text{-}\beta''\text{-}Al_2O_3 //CA_6,CA_{10}/O_2/Pt$ (7)

Each cell was placed in an electrical resistance furnace and heated to the measurement temperature. The electromotive force (EMF) was monitored with a high-ohmic digital voltmeter Unitra 1321. EMF was measured in the temperature range 1050 K - 1450 K. A dried air flow was passed through the furnace during the measurements. The reversible behaviour of the galvanic cells under investigation was tested by passing a small current (not exceeding 20 μA) through the cell and noting whether the observed voltages returned to their original values.

3. RESULTS AND DISCUSSION

The overall cell reactions can be written in the following way:

cell (1) $CaO + 6Al_2O_3 = CA_6;\ \Delta G_1^\circ = -2FE_1$ (8)
cell (2) $2CaO + CA_6 = 3CA_2;\ \Delta G_2^\circ = -4FE_2$ (9)
cell (3) $CaO + CA_2 = 2CA;\ \Delta G_3^\circ;\ = -2FE_3$ (10)
cell (4) $5CaO + 7CA = C_{12}A_7;\ \Delta G_4^\circ = -10FE_4$ (11)
cell (5) $9CaO + C_{12}A_7 = 7C_3A;\ \Delta G_5^\circ = -18FE_5$ (12)
cell (6) $CaO + 10Al_2O_3 = CA_{10};\ \Delta G_6^\circ = -2FE_6$ (13)
cell (7) $2CaO + 3CA_{10} = 5CA_6;\ \Delta G_7^\circ = -4FE_7$ (14)

Here E_i denotes the EMF of the cells (1) - (7) and ΔG_i° the standard free enthalpy of the corresponding cell reaction.

It was found that EMF of the investigated cells varied linearly with temperature. The temperature dependence : $E_i = a_i + b_iT$ is presented in Table 1. The data were derived on the basis of five independent series of measurements carried out for each cell. The EMF values of the cells (5) and (7) were of several millivolts, too low to be measured accurately. However, the EMF of the cell (6) ceased to be stable over the temperature of 1200K. In Table 2. The temperature dependence: $\Delta G_i^\circ = A_i + B_iT$, calculated from the equations (8) - (14), is shown. On the basis of the data given in Table 2, the standard free enthalpies of formation of calcium aluminates (from CaO and Al_2O_3), $\Delta G_i^\circ(i)$, were calculated by the equations:

$\Delta G_f^\circ\ (CA_6) = \Delta G_1^\circ$ (15)
$\Delta G_f^\circ\ (CA_2) = (1/3)\Delta G_1^\circ + (1/3)\Delta G_2^\circ$ (16)
$\Delta G_f^\circ\ (CA) = (1/6)\Delta G_1^\circ + (1/6)\Delta G_2^\circ + (1/2)\Delta G_3^\circ$ (17)
$\Delta G_f^\circ\ (C_{12}A_7) = (7/6)\Delta G_1^\circ + (7/6)\Delta G_2^\circ + (7/2)\Delta G_3^\circ + \Delta G_4^\circ$ (18)
$\Delta G_f^\circ\ (C_3A) = (1/6)\Delta G_1^\circ + (1/6)\Delta G_2^\circ + (1/2)\Delta G_3^\circ + (1/7)\Delta G_4^\circ + (1/7)\Delta G_5^\circ$ (19)
$\Delta G_f^\circ\ (CA) = \Delta G_7^\circ$ (20)

In Table 3 the standard free enthalpy of formation is presented as a linear function of temperature, $\Delta G_f^\circ\ (i) =$

Table 1

Electromotive forces of the cells (1) - (7) as functions of temperature: $E_i = a_i + b_iT$

No. of the cell	Temperature range/K	a_i/ (mV)	b_i/ ($mV.K^{-1}$)
1	1050-1450	95.2(±2.4)	0.197(±0.006)
2	1050-1450	63.3(±0.6)	0.097(±0.002)
3	1050-1450	90.8(±0.2)	0.055(±0.001)
4	1050-1450	-15.6(±0.4)	0.085(±0.001)
5	920-1200	0(±3.8)	
6	920-1200	208.4(±0.7)	0.092(±0.003)
7	920-1450	0(±6.4)	

Table 2

Standard free enthalpy changes for the reactions (8) - (14) as functions of temperature: $\Delta G_i^\circ = A_i + B_iT$

No. of the reaction	Temperature range/K	A_i/ (J)	B_i/ ($J.K^{-1}$)
8	1050-1450	-18364(±463)	-38.02(±1.16)
9	1050-1450	-24447(±232)	-37.48(±0.77)
10	1050-1450	-17530(±39)	-10.61(±0.10)
11	1050-1450	15081(±386)	-82.02(±0.96)
12	1050-1450	0(±6600)	
13	920-1200	-40218(±135)	-17.75(±0.58)
14	920-1450	0(±2470)	

Table 3

Standard free enthalpies of calcium aluminate formation (from oxides) as functions of temperature:

$\Delta G_{f,i}^\circ = \alpha_i + \beta_iT$

Calcium aluminate	Temperature range/K	$\alpha_i/(J.mol^{-1})$	$\beta_i/(J.mol^{-1}K^{-1})$
CA_{10}	920-1200	-40218(± 135)	-17.75(±0.58)
CA_6	1050-1450	-18364(± 463)	-38.02(±1.16)
CA_2	1050-1450	-14270(± 232)	-25.16(±0.64)
CA	1050-1450	-15900(± 135)	-17.88(±0.37)
$C_{12}A_7$	1050-1450	-96220(±1333)	-207.20(±3.60)
C_3A	1050-1450	-13745(±1132)	-29.61(±0.44)

Table 4

Standard free enthalpies of calcium aluminate formation (from oxides) at 1200K ($-\Delta G_{f,i}°$ in $kJ.mol^{-1}$)

Calcium aluminate	this work	Reference	
		4	5
CA_6	66.76	64.79	67.94
CA_2	46.30	48.79	46.95
CA	38.66	41.81	38.28
$C_{12}A_7$	359.99	361.02	-
C_3A	48.00	-	45.37

$\alpha_i + \beta_i T$, for each calcium aluminate formed in the system $CaO–Al_2O_3$. The mean values of the standard enthalpy $\Delta H_f°$ (i) and the standard entropy $\Delta S_f°$ (i) of formation in the temperature range under study can be obtained directly from the straight line coefficients : $\Delta H_f°$ (i) is equal to $-\alpha_i$ and $\Delta S_f°$ (i) is equal directly to β_i. The data for calcium decaaluminate CA_{10} are new in literature. In Table 4 the results for other calcium aluminates are compared with those obtained by Kumar and Kay /5/ and Allibert *et al.* /4/, calculated for the temperature of 1200K. The difference between them lies in the limit of a few kilojoules.

The standard free enthalpy of formation data made it possible to estimate two-phase coexistence regions in the $CaO-Al_2O_3$ system. The set of the relevant reactions is presented in Table 5. For all the reactions (except reaction 1 in this table) $\Delta G°$ is positive in the temperature range under study. It means that calcium aluminates, being reactants in reactions 2 - 6, can coexist as stable phases in the two-phase mixture. Only calcium hexaaluminate CA_6 and calcium decaaluminate CA_{10} cannot coexist in temperatures over 1078 ±120K, as calculated from the $\Delta G°$ equation for reaction 1. Thus, calcium decaaluminate becomes unstable over 1078K. This finding is in agreement with experimental results described in literature: heat treatments of CA_{10} aluminate at 1173K and 1373K showed that this compound decomposed to CA_6 and Al_2O_3 /3,12/. It is impossible, therefore, to prepare calcium decaaluminate directly by sintering calcia and alumina powders.

4. SUMMARY AND CONCLUSIONS

1. The standard free enthalpies of solid calcium aluminates from their component oxides were measured with solid-state galvanic cells.
2. The polycrystalline composite solid electrolyte,

Table 5

Standard free enthalpy changes for the reactions of calcium aluminate decomposition, as functions of temperature: $\Delta G_i° = A_i + B_i T$

[reaction (1) - temperature range 1050K-1200K, reactions (2)-(6) - temperature range 1050K-1450K]

No. of the reaction	The reaction	$\mathcal{A}_i$ / (J)	$\mathcal{B}_i$ ($J.K^{-1}$)
1	$CA_{10} = CA_6 + 4\ Al_2O_3$	21854(±598)	-20.27(±1.74)
2	$CA_6 = CA_2 + 4\ Al_3O_3$	4094(±695)	12.86(±1.80)
3	$CA_2 = CA + Al_2O_3$	-1630(±367)	7.28(±1.01)
4	$12\ CA = C_{12}A_7 + 5\ Al_2O_3$	94580(±2953)	7.36(±0.80)
5	$C_{12}A_7 = 4\ C_3A + 3\ Al_2O_3$	41240(±5865)	88.76(±5.32)
6	$C_3A = 3\ CaO + Al_2O_3$	13745(±1132)	29.61(±0.44)

consisting of Ca-β''-Al_2O_3 and α-Al_2O_3 phases, was used in the galvanic cells under study.

3. The results obtained for CA_6, CA_6, CA, $C_{12}A_7$ and C_3A compounds were compared with literature data. They did not differ significantly from each other.
4. The ΔG_f^o values determined for the CA_{10} compound are the first reported in literature.
5. Calcium decaaluminate CA_{10} was determined to be thermodynamically unstable at temperatures exceeding 1078 ±120K.
6. A solid-state galvanic cell method appeared to be promising in determining thermodynamic values for composite oxide systems. The choice of Ca-β''-alumina composite electrolyte as a galvanic cell was adequate for the study of $CaO-Al_2O_3$ systems.

ACKNOWLEDGEMENTS

This work was carried out under contract with the Polish Scientific Research Committee.

REFERENCES

1. E.M. Levin, C.R. Robbins and H.F. McMurdie, *Phase Diagrams for Ceramists,* 1964 (Suppl. 1969, 1975), M.K. Reser (ed.), The American Ceramic Society, Inc., Columbus, OH; Figs. 231-233, 2295, 2296 and 4308.
2. R.W. Nurse, J.H. Welch and A.J. Majumdar, *Trans. Brit. Ceram. Soc.*, **64**, 409 (1965).
3. J.A.M. van Hoek, F.J.J. van Loo, R. Metselaar, J.W. de Haan and A.J. van den Berg, *Solid State Ionics,* **45**, 93 (1991).
4. M. Allibert, C. Chatillon, K.T. Jacob and R. Lourtau, *J. Amer. Ceram. Soc.*, **64**, 307 (1981).
5. R.V. Kumar and A.D.R. Kay, *Metall. Trans.*, **16B**, 107 (1985).
6. W. Hoerkner and H.K. Mueller-Buschbaum, *J. Inorg. Nucl. Chem.*, **38**, 983 (1976).
7. J. Jeevaratman, F.P. Glasser and L.S. Dent, *J. Amer. Ceram. Soc.*, **47**, 105 (1964).
8. M. Lacerda, J.T.S. Irvine, F.P. Glasser and A.R. West, *Nature,* **332**, 525 (1988).
9. V.I. Ponomarev, D.M. Kheiker and N.V. Belov, *Sov. Phys. Crystall.*, **15**, 995 (1971).
10. R.W.G. Wyckoff, *Crystal Structures,* 2nd Ed., Vol. 3, p. 497, Wiley-Interscience, New York (1965).
11. A.E. Moore, *Magaz. Concrete Res.*, **18**, 59 (1966).
12. J. Kirchnerova, A. Petric, C.W. Bale and A.D. Pelton, *Mat. Res. Bull.*, **26**, 527 (1991).
13. G. Rόg, K. Zakula, W. Pycior and A. Rόg-Kozlowska, *High Temperature Materials and Processes,* **10**, 239 (1992).
14. G. Rόg, W. Pycior, K. Zakula, A. Rόg-Kozlowska and M. Bućko, *Electrochim. Acta,* **38**, 365 (1993).
15. M. M. Bućko, G. Rόg and K. Zakula-Sokόl, *Bol. Soc. Esp. Ceram. Vid.*, (1993), in press.