Thermodynamic studies on and with Na-beta-Al_2O_3

H. Näfe
Max-Planck-Institut für Metallforschung
Pulvermetallurgisches Laboratorium
Heisenbergstraße 3, D-70569 Stuttgart, Germany

The solid state electrochemical characterization of the thermodynamic stability of ceramic systems comprising sodium compounds is complicated due to the extremely low sodium activity prevailing in most of these systems. Therefore, the results obtained so far must be expected to be falsified by a substantial impact of electronic conductivity in Na-beta-Al_2O_3 (NBA) [1, 2] which is usually employed in such measurements as solid electrolyte.

In order to overcome this problem, a new experimental approach has been put forward that is based on a potentiometric solid electrolyte galvanic cell with yttria stabilized zirconia (YSZ) as solid electrolyte and with sintered ceramic pellets of Na-beta-Al_2O_3 as components of the electrodes. The cell has the following structure (ES: electrode system to be characterized):

$$\mathrm{Pt}\,|\,\mathrm{Au},\ O_2,\ CO_2\,|\,Na_2CO_3\ (\mathrm{Au})\,|\,\mathrm{NBA}\ (\mathrm{Au})\,|\,\mathrm{YSZ}\,|\ \mathrm{NBA}\ (\mathrm{Au})\,|\,\mathrm{ES}\,|\,\mathrm{Pt} \qquad (1)$$

with the pellets of both NBA and Na_2CO_3 being electronically short-circuited by randomly distributed gold wires inside the bodies.

Cell (1) enables the sodium and oxygen potentials to be appropriately transformed into each other with the voltage equation reading as follows:

U = **Error!** (2)

where a'_{Na}, a''_{Na}, a'_{Na_2O} and a''_{Na_2O} are the sodium and sodium oxide activities at the interfaces NBA/ES, Na_2CO_3/ gas, NBA/YSZ(right) and NBA/YSZ(left), respectively.

For determining a_{Na_2O}, another electrochemical approach has been realized which, for the first time, enables the phase equilibrium in Na-beta-Al_2O_3 to be characterized as a function of the phase composition [3]. This is also based on a potentiometric solid state oxygen concentration cell.

By means of two examples for a heterogeneous, sodium containing system, the use of the measuring techniques described above is substantiated and the complexity of the procedure of data analysis is demonstrated. The results obtained from these measurements are consistent with other kind of information about the systems under consideration.

[1] H. Näfe, Solid State Ionics 113-115 (1998) 205.
[2] H. Näfe et al., J. Electrochem. Soc. 149 (2002) E311.
[3] H. Näfe et al., Electrochim. Acta 45 (2000) 1631.