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Original Article

Thermodynamic modeling of the K_2O-Al_2O_3 and K_2O-MgO-Al_2O_3 systems with emphasis on β- and β″-aluminas

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ABSTRACT

A critical evaluation and thermodynamic modeling study including key phase diagram experiments was performed to investigate the K_2O-Al_2O_3 and K_2O-MgO-Al_2O_3 systems. For the first time, potassium β- and β″-alumina solid solutions were described using the Compound Energy Formalism with accurate cation distributions in their sublattices. From the new experimental results, the stability of potassium β″-alumina was assured up to 1600 °C. A large discrepancy reported in the literature, the eutectic temperature between $KAlO_2$ and β-alumina in the K_2O-Al_2O_3 system, was resolved. A set of self-consistent Gibbs energy functions for all stable phases in the K_2O-MgO-Al_2O_3 system was obtained. As a result, any phase diagram sections and thermodynamic properties of the K_2O-MgO-Al_2O_3 system can be calculated from the optimized Gibbs energy functions. In particular, the cation distribution in the β- and β″-alumina solid solutions is calculated depending on the non-stoichiometry of solution and temperature.

1. Introduction

β- and β″-aluminas are excellent solid ionic conductors, which make them attractive for energy storage applications. Alkali metal thermal electric converter (AMTEC) is being considered as a new energy conversion technology for spacecraft [1] because it can be five times more efficient than the traditional heat to electric conversion from radioisotope (plutonium-238) heat sources used in spacecrafts. Na β″-alumina has been used as a solid electrolyte in AMTEC. More recently, K β″-alumina was found to have advantages over Na β″-alumina [2]. The higher ionic conductivity and vapor pressure of K at low temperatures make K β″-alumina AMTEC 25% more efficient than Na β″-alumina ones [3]. At the same time, K β″-alumina cells have longer lifetime due to low operation temperature [2]. However, there is a very limited understanding on the thermodynamic properties and stabilities of K β- and β″-alumina. Studying the K_2O-MgO-Al_2O_3 system is essential for the K β- and β″-alumina in battery applications.

In the thermodynamic optimization, all the phase diagram and thermodynamic data are critically evaluated and optimized to obtain a set of self-consistent thermodynamic functions to reproduce all available and reliable experimental data. Thermodynamic models employed to describe the solid and liquid solutions are based on the structure of the respective solution to capture the nature of configurational entropy more accurately. Using the optimized thermodynamic functions, unexplored phase stability and thermodynamic properties can be accurately predicted in a thermodynamically correct manner.

There is no comprehensive thermodynamic description of the K_2O-MgO-Al_2O_3 system. Up to now, only the binary K_2O-Al_2O_3, K_2O-MgO, and MgO-Al_2O_3 systems have been studied [4–11]. There are large uncertainties in the phase diagram data in the literature due to the high hygroscopicity and volatility of K_2O and the high melting point of Al_2O_3. In the K_2O-Al_2O_3 system, there are large discrepancies in the eutectic temperature between $KAlO_2$ and β-alumina in the literature. Moya et al. [12] reported the eutectic temperature to be at 1450 °C. Roth [13] measured it at 1910 °C. Schaefer et al. [14] proposed it to be at 1780 °C. For the K_2O-MgO-Al_2O_3 system, the isothermal sections at 1100 and 1400 °C were reported by Van Hoek et al. [15]. However, only the one at 1400 °C was considered to be under equilibrium condition. Schaefer et al. [14] also proposed several isothermal sections based on different alumina starting materials. Overall, accurate phase diagrams of the K_2O-Al_2O_3 and K_2O-MgO-Al_2O_3 systems and thermodynamic properties of the β- and β″-alumina solutions are not available.

This study aims at thermodynamic optimization of the K_2O-MgO-Al_2O_3 system. In order to resolve inconsistencies in the available

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experimental data regarding the thermal stabilities of β- and β″-aluminas and the eutectic temperature in the K_2O-Al_2O_3 system, equilibration/quenching experiments and thermal analyses were also conducted in the present study. In the experiments, sealed Pt capsules were used to avoid hydration and evaporation of K_2O. Accurate thermodynamic models considering the structures of β- and β″-aluminas were developed for the first time and applied to the description of the thermodynamic and structural properties of the β- and β″-alumina solutions. The phase stability and structural changes of β- and β″-aluminas in the K_2O-Al_2O_3 and K_2O-MgO-Al_2O_3 systems were well predicted. All thermodynamic calculations were performed using the FactSage thermochemical software [16].

2. Experiments on the binary K_2O-Al_2O_3 system

In order to resolve the uncertainties in the eutectic reaction between $KAlO_2$ and β-alumina in the K_2O-Al_2O_3 system, key phase diagram experiments were performed.

2.1. Starting materials

Starting materials were prepared using reagent grade K_2CO_3 (99.997 wt.%, Alfa Aesar) and Al_2O_3 (99.99 wt.%, Alfa Aesar). Batches of 5 to 10 g of the materials were mixed for 1 h with isopropyl alcohol (H_2O < 0.02 vol.%) to prevent moisture pickup from air. To dry off the alcohol, the mixtures were kept in a drying oven at 120 °C for more than 12 h and then cooled down to room temperature in a desiccator. To obtain K_2O, which is extremely hygroscopic, the decarbonation of K_2CO_3 ($K_2CO_3 \rightarrow K_2O + CO_2$) was conducted just before each experiment. The decarbonation temperature with minimum volatile loss of K_2O was set to be 830 °C according to the preliminary Thermo-Gravimetric Analysis (TGA). The weight of each sample was measured before and after decarbonation to confirm the completion of the decarbonation reaction. After decarbonation, the mixtures of K_2O and Al_2O_3 were stored in a drying oven to cool them down to 120 °C and subsequently in a desiccator to reach room temperature. The mixtures were then crushed and packed into one-side-sealed platinum (Pt) tubes with dimensions of about 17 mm in length, 3.2 mm in outer diameter, and 0.2 mm in wall thickness. The open end of the Pt tubes were gently crimped to remove the air and sealed off using an electric arc welder to ensure gas-tight condition. The integrity of the welding was checked with an optical microscope before experiments. Samples with the starting composition of 35 mol% K_2O and 65 mol% Al_2O_3 were prepared for Differential Thermal Analysis (DTA) and equilibration/quenching experiments.

2.2. Thermal analysis

DTA/TGA measurements were conducted using a Jupiter STA 449 F3 thermal analyzer under an argon (Ar) flowing atmosphere at a rate of 20 mL min^{-1}. The sealed Pt capsules were placed inside an Al_2O_3 crucible with an outer diameter of 8 mm and a height of 23 mm for the DTA/TGA measurements. The heating and cooling cycles were performed at a rate of 10 K min^{-1}. TGA was simultaneously run to confirm that there was no leakage of the sealed capsules during the experiments. Three heating and cooling cycles were run for each sample to obtain reliable and reproducible results. Temperature and sensitivity calibrations were conducted by measuring the melting temperatures and enthalpies of the eight reference materials: indium (In), tin (Sn), bismuth (Bi), zinc (Zn), aluminum (Al), silver (Ag), gold (Au), and nickel (Ni). The reliability of using sealed Pt capsules by thermal analysis was determined in the previous study [17].

2.3. Equilibration/quenching method

For the equilibration/quenching experiments, a muffle box furnace (ST-1700C, SentroTech, $MoSi_2$ heating elements) was used. The temperature of the furnace was controlled using a PID controller within ± 1 °C. For each experiment, several Pt capsules containing the K_2O-Al_2O_3 mixtures were placed in a porous Al_2O_3 holder, which was then placed in the box furnace. Equilibration was conducted at 1500 and 1600 °C for 1 and 2 h, respectively. After the equilibration, the samples contained in Pt capsules were immediately quenched in cold water, then mounted in epoxy resin. Grinding and polishing were performed using lapping oil (AUTOMET® Buehler) as the water-free lubricating fluid. Polishing was performed just before phase characterization to avoid the hydration of K_2O. For the transportation to characterization, the polished samples were put in a glass vial filled with desiccants in a vacuumed desiccator.

Phase characterization was conducted using X-Ray Diffractometer (Bruker D8 Discover, Madison, WI, Cu *K*α-radiation) equipped with a VANTEC detector. All XRD profiles were identified using the Powder Diffraction Files (PDF) of the International Centre for Diffraction Data (ICDD) with the DIFFRAC.EVA software package (Bruker AXS, Karlsruhe, Germany, 2000). As K_2O is extremely volatile, it was very difficult to perform quantitative analysis using electron probe micro-analyzer (EPMA) (see Section 2.4). Therefore, only micrographs were taken to investigate the sample morphology. The EPMA analysis with an accelerating voltage of 8 kV, a beam current of 4 nA, a beam size of 20 μm, and correction with ZAF method (this was deemed reasonable for Na oxide samples) was performed on the samples.

2.4. Experimental results

The discrepancy in the eutectic reaction between $KAlO_2$ and β-alumina, which was reported at 1450 and 1910 °C by Moya et al. [12] and Roth [13], respectively, was successfully resolved in this study. In three different DTA measurements, no heat incident was recorded in the temperature range from 1250 to 1550 °C. The XRD results of the samples equilibrated at 1500 and 1600 °C are shown in Fig. 1(a). For both samples, hydrated $KAlO_2$ phase ($KAlO_2{\cdot}1.5H_2O$) and β″-alumina phase ($K_{1.59}Al_{10.8}O_{17}$) were identified. Thus, the stability of the β″-alumina phase was confirmed up to 1600 °C using the equilibration/quenching experiments followed by XRD for phase analysis. The $KAlO_2$ phase easily gets hydrated into $KAlO_2{\cdot}1.5H_2O$ during transportation of the samples. Unfortunately, quantitative analysis of these two phases was impossible using EPMA due to the volatile loss of K_2O and the hydration of the sample surface. Fig. 1(b) shows the images of hydrated surface of the sample inside the microscope, all quantitative analysis results showed about 65 wt.% total counts. In Fig. 1(b), two phases with different morphologies can be seen: needle-shape and more round shape. The round shape phase is considered to be $KAlO_2{\cdot}1.5H_2O$, which readily absorbs moisture as shown in the X700 image. Therefore, the needle-like phase should be β″-alumina. Based on these experimental results, β″-alumina is confirmed to be stable up to 1600 °C and the eutectic temperature between $KAlO_2$ and β-alumina should be above 1600 °C.

3. Thermodynamic models

3.1. Stoichiometric compounds

The Gibbs energy of a stoichiometric compound is described as:

$$G_T^o = \Delta H_{298.15K}^o + \int_{298.15K}^{T} C_P dT - T\left(S_{298.15K}^o + \int_{298.15K}^{T} C_P/T dT\right) \quad (1)$$

where $\Delta H_{298.15K}^o$ and $S_{298.15K}^o$ are the standard enthalpy of formation and standard entropy at 298.15 K, respectively; C_P is the heat capacity as a function of temperature; T is the absolute temperature.