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Analysis of the phase formation of $Na-\beta/\beta''$ -aluminas using MgO and Li₂O as phase stabilizers

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Na- β "-aluminas in the ternary system Na₂O-Al₂O₃-MgO(Li₂O) were synthesized via a liquid state reaction using MgO and Li₂O as stabilizers, and the influence of calcination temperature, precursor pH value, and composition on the phase formation of Na- β "-aluminas were investigated. For the analysis of the phase fraction of Na- β - and β "-alumina, the sodium oxide concentration was varied to give molar ratios of [Na₂O] : [Al₂O₃] = 1 : 4, 1 : 5, 1 : 6 and 1 : 8, and the precursor pH was varied from 1.0 to 9.0 by increments of 1.0. The samples were calcined at 1100-1500 °C for 2 hours and characterized by X-ray diffraction, a particle size analyzer, and an SEM. We then compared the phase formation of the Na- β "-aluminas when the stabilizer MgO was used versus when Li₂O was used. The average particle sizes of the synthesized powders were about 300-500 nm.

Key words: Na⁺-B''-alumina, liquid state reaction, transient eutectic liquid.

Introduction

In recent years, a growing interest in new approaches to energy storage technology has provided a strong stimulus for the investigation and development of high-temperature batteries. Rechargeable high-temperature battery technologies that use a metallic sodium anode are being explored for a number of large-scale energy storage applications, such as electric power generation and distribution (e.g., load leveling and peak shaving), motive power (e.g., for electric cars and buses), and power for use in space [1]. The first high-temperature battery to be commercialized was the sodium sulfur battery, which uses liquid sulfur for the positive electrode, liquid sodium as the negative electrode, and a sodium β'' -alumina solid electrolyte. Later developments include the ZEBRA battery [2], which uses nickel chloride as the cathode. Both systems have an operating temperature of about 300 °C.

Na-β-alumina is prepared by various methods. Rankin and Merwin (1916) observed small hexagonal platelets of Na-β-alumina upon cooling of molten aluminum oxide. Na-β-alumina crystallizes from melts containing aluminum oxide plus sodium oxide or other sodium compounds, such as sodium fluoride, sodium hexafluoroaluminate (cryolite), or sodium nitrate. During the preparation of Na-β-alumina, the metastable form Na-β"-alumina is often encountered. Na-β"-alumina is considered a nonstoichiometric form with the sodium oxide content ranging from Na₂O·5Al₂O₃ to Na₂O·8.5Al₂O₃ [3]. The crystalline structure of Na-β"alumina is rhombohedral with an R3m space group, and the lattice constants are a = 5.614 and c = 33.85 Å. Generally, its a axis is similar to the a axis in the Na- β -alumina structure, but the length of the c axis is 1.5 times longer than in Na- β -alumina, and the concentration of alkaline ions on the conduction plane is higher. Thus the Na- β ''alumina has a much higher ionic conductivity [4].

Na- β "-alumina is not stable and decomposes at temperatures above 1400 °C in the binary system Na₂O-Al₂O₃ [5], so cations whose ionic radii are less than 0.097 nm are usually doped to stabilize Na- β "-alumina, which has a conductivity five times higher than β -alumina [6]. Mg²⁺ and Li⁺ ions have been the most widely used stabilizing cations. Li⁺ ions are known to be more effective for Na- β "-alumina formation than Mg²⁺ ions [7, 8]. However, the behavior of the different stabilizing cations during phase formation have not yet been elucidated, so it is difficult to determine the precise effects that each stabilizer has on the phase formation and transformation.

There is still confusion concerning the Na-B-alumina to Na- β'' -alumina transformation mechanism and the phase diagrams in both the Na₂O-Al₂O₃ binary and the Na₂O-Al₂O₃-MgO (Li₂O) ternary systems. According to the kinetic studies of Hodge [5] and Bera [7], in both the Na₂O-Al₂O₃ and the Na₂O-Al₂O₃-MgO (Li₂O) systems, Na-β"-alumina formation and decomposition can be explained by the reaction of Na- β -alumina with the γ -NaAlO₂ phase that might exist in the grain boundaries. Furthermore, the rate of transformation between Na-B-alumina and Na-B"-alumina is slow and would be controlled by the diffusion of Al^{3+} ions. On the other hand, it has been reported that the transformation between Na-β-alumina and Na-β"-alumina appear to be more a polymorphic transformation than a decomposition [9, 10], and the stability of Na- β -alumina and Na- β'' -alumina depend on the heat treatment in the Na₂O-Al₂O₃ system [10]. Although these mechanisms have

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been suggested, it has been difficult to systematically explain how Na- β'' -Al₂O₃ forms during processing.

In order to understand the phase formation of Na- β'' -Al₂O₃, in this study we analyzed the phase fraction of Na- β'' -Al₂O₃ in the presence of the stabilizers MgO and Li₂O. We synthesized Na- β'' -aluminas with a liquid state reaction, varying the reaction factors, including the composition, the precursor pH, and the calcination temperature.

Experimental

The synthesis of Na- β'' -aluminas was carried out in the same way as in our previous study [11]. Appropriate amounts of aluminum nitrate nonahydrate (Al(NO₃)₃·9H₂O), sodium hydroxide (NaOH), and ethyl alcohol (C₂H₅OH) were dissolved in deionized water. Magnesium carbonate hydroxide (4MgCO₃Mg(OH)₂5H₂O) and lithium carbonate (Li₂CO₃) were used as starting materials for the two stabilizers, magnesium oxide (MgO) and lithium oxide (Li₂O), respectively, and their content was fixed at 0.4 wt.%. The stabilizers were also dissolved in deionized water. Each aqueous solution was mixed by stirring for 1 h at 80 °C, after which a clear solution was obtained. The pH of the solution was adjusted by ammonia water (NH₄OH) within a range of 1 to 9 at 80 °C, and the pH-adjusted mixture was then aged for one day at room temperature. After that the mixture was oven-dried for one day at 90 °C and calcined at 1100-1500 °C for 2 h.

The microstructure and particle size were determined with a scanning electron microscope (SEM; Model JSM-6380, JEOL, JAPAN) and a particle size analyzer (PSA; Brookhaven Instruments Co.). The phase compositions of the calcined samples were measured by an X-ray diffractometer (D/max 2200, Rigaku, Japan). The relative amounts of the phases were determined by calculating the line intensities of the well-separated peaks for the different phases using the following equations [12, 13]:

% of
$$\alpha = \frac{f(\alpha)}{f(\alpha) + f(\beta) + f(\beta'')} \times 100$$
 (1)

% of
$$\beta = \frac{f(\beta)}{f(\alpha) + f(\beta) + f(\beta'')} \times 100$$
 (2)

% of
$$\beta'' = \frac{f(\beta'')}{f(\alpha) + f(\beta) + f(\beta'')} \times 100$$
 (3)

$$f(\alpha) = \frac{1}{2} \left\{ I_{\alpha(104)} \times \frac{10}{9} + I_{\alpha(113)} \right\}$$
(4)

$$f(\beta) = \frac{1}{3} \left\{ I_{\beta(012)} \times \frac{10}{3} + I_{\beta(026)} \times \frac{10}{3.5} + I_{\beta(017)} \times \frac{10}{5.5} \right\}$$
(5)

$$f(\beta'') = \frac{1}{2} \left\{ I_{\beta''(10\underline{11})} \times \frac{10}{4} + I_{\beta''(20\underline{10})} \times \frac{10}{8} \right\}$$
(6)

where $I_{\alpha(104), \alpha(113)} = X$ -ray intensities of (104), (113) planes of the α -alumina phase,

 $I_{\beta(012), \beta(026), \beta(017)} =$ X-ray intensities of (012), (026), (017) planes of the β -alumina phase, and

 $I_{\beta''(01\underline{11}), \beta''(20\underline{10})} = X$ -ray intensities of (01<u>11</u>), (20<u>10</u>) planes of the β'' -alumina phase

Results and Discussion

Fig. 1 shows the phase fractions of MgO-stabilized Na- β'' -aluminas for varying compositions at the calcination temperature 1200 °C; Fig. 2 shows the corresponding phase fractions of Li2O-stabilized Na-B"-aluminas under the same conditions. When MgO was used as a stabilizer, the phase fraction of Na- β'' -alumina was generally around 30% at the molar ratios $[Na_2O]$: $[Al_2O_3] = 1:6$ and 1:8, and the Na- β "-alumina phase reached its highest level — about 50% at the molar ratio $[Na_2O]$: $[Al_2O_3] = 1 : 5$. At this temperature, the α -alumina was observed in all compositions. When Li₂O was used as a stabilizer, the phase fraction of Na- β'' -alumina reached its highest level — about 50 to 60% when the pH was 1 and 9. Thus, when the calcination temperature was fixed at 1200 °C and only the composition was varied, using Li₂O as a stabilizer was more favorable for the formation of Na- β "-alumina than using MgO.

To investigate how the phase fraction varied with the calcination temperature, we varied the molar ratio of $[Na_2O]$: $[Al_2O_3]$ between 1 : 4 and 1 : 6, and varied the calcination temperature between 1100 and 1500 °C. The results are shown in Fig. 3 and Fig. 4. When MgO was used as a stabilizer, the phase fraction of Na- β ''-alumina changed only slightly with changes in the molar ratio and calcination temperature at an arbitrary pH. By contrast, when Li₂O was used, the Na- β ''-alumina fraction was significantly higher at 1500 °C across the pH range and for all composition ratios.

Figs. 5 and 6 show how the β'' -alumina fraction depended on the calcination temperature at a pH of 1, 5, and 9. As above in Fig. 3 and 4, when MgO was used as a stabilizer, the phase fraction of Na- β'' -alumina remained almost constant as the calcination temperature was increased. For Li₂O, however, the Na- β'' -alumina fraction was sharply higher at 1500 °C.

Figs. 7 and 8 show the XRD patterns of the synthesized powders. When Li₂O was used as a stabilizer, the growth of the (01<u>11</u>), (20<u>10</u>) plane corresponding to the Na- β "-alumina phase could be observed with rising temperature. When MgO was the stabilizer, however, this tendency was not observed.

It has been reported that Na- β'' -alumina densifies in a few minutes, and such rapid densification is attributed to the ternary transient eutectic liquids that form at 1460-1470 °C in the LiAlO₂-NaAlO₂-Al₂O₃ system [14]. Even though the compositions used in this study are not exactly the same as the eutectic composition in the LiAlO₂-NaAlO₂-Al₂O₃ system, it is well-known that eutectics do not form exactly at the eutectic composition. Eutectics can be formed



Fig. 1. Phase fraction of MgO-stabilized Na- β'' -aluminas at the molar ratios $[Na_2O] : [Al_2O_3] = (a) \ 1 : 4$, (b) 1 : 5, (c) 1 : 6, (d) 1 : 8, calcined at 1200 °C.



Fig. 2. Phase fraction of Li₂O-stabilized Na- β'' -aluminas at the molar ratio [Na₂O] : [Al₂O₃] = (a) 1 : 4, (b) 1 : 5, (c) 1 : 6, (d) 1 : 8, calcined at 1200 °C.

Phase Fraction (%)

Phase Fraction (%)

Phase Fraction (%)



Fig. 3. Phase fraction of MgO-stabilized Na- β'' -alumina as a function of calcination temperature at the molar ratios [Na₂O] : [Al₂O₃] = (a) 1 : 4, (b) 1 : 5, (c) 1 : 6.

in regions of local inhomogeneity, and they are difficult to observe in micrographs because the transient eutectic liquid has a high solid solubility and it disappears after

Fig. 4. Phase fraction of Li₂O-stabilized Na- β "-alumina as a function of calcination temperature at the molar ratios [Na₂O] : [Al₂O₃] = (a) 1 : 4, (b) 1 : 5, (c) 1 : 6.

complete homogenization caused by a diffusional process [15]. The stabilization of Na- β ''-alumina basically comes about when stabilizing cations are substituted for the Al³⁺



Fig. 5. Phase fraction of MgO-stabilized Na- β "-alumina as a function of calcination temperature at (a) pH 1, (b) pH 5, (c) pH 9.

Fig. 6. Phase fraction of Li_2O -stabilized Na- β'' -alumina as a function of calcination temperature at (a) pH 1, (b) pH 5, (c) pH 9.

ions; the compensating Mg^{2^+} ions generally substitute for the tetrahedral Al^{3^+} ions, and Li^+ ions substitute for octahedral Al^{3^+} ions in the spinel block [16, 17]. Thus we can think of Na- β "-alumina phase formation as being mainly

controlled by the diffusion of stabilizing ions. The ternary eutectic liquid is expected to be the fast path for the diffusion and for enhancing the transformation of Na- β -alumina to Na- β ''-alumina.





Fig. 7. X-ray diffraction patterns of MgO-stabilized Na- β'' -alumina at different calcination temperatures, at (a) pH 1, (b) pH 5, (c) pH 9. The molar ratio is [Na₂O] : [Al₂O₃] = 1 : 5.

Fig. 8. X-ray diffraction patterns of Li₂O-stabilized Na- β'' alumina at different calcination temperatures, at (a) pH 1, (b) pH 5, (c) pH 9. The molar ratio [Na₂O] : [Al₂O₃] = 1 : 5.

In contrast with the Li₂O-stabilized system, the MgOstabilized system had no rapid transformation of Na-βalumina to Na- β'' -alumina above 1200 °C. Since ternary eutectic liquid does not exist in the Na₂O-Al₂O₃-MgO system, diffusion is likely to occur through the solid state or the binary eutectic liquid in the Na₂O-Al₂O₃ system. There is still debate about the binary phase diagrams. According to Devries and Roth [18], a binary eutectic liquid forms at 1410 °C, whereas Weber and Venero [19] report that it forms at 1585 °C. Because the sintering of the binary and Mg-stabilized ternary systems is completed in several minutes, it is likely that the binary eutectic liquid exists and acts as a fast path for diffusion. Mg-stabilizing ions do not seem to be soluble in the binary eutectic liquid, however, so the binary eutectics do not affect the movement of Mg^{2+} ions. Therefore, we can conclude that the binary eutectics do not contribute to phase transformation in the MgO-ternary system, while the eutectics of the Li₂Oternary system enhance the phase transformation at high temperatures.

Fig. 9 shows the particle sizes of the synthesized powders



Fig. 9. Particle size of powders calcined at 1200 $^{\circ}$ C with stabilizer (a) MgO and (b) Li₂O.



Fig. 10. SEM images of powders calcined at 1200 °C for the molar ratio $[Na_2O]$: $[Al_2O_3] = 1 : 5$ for (a) pH 1 and (b) pH 9, both MgO stabilized; and (c) pH 1 and (d) pH 9, both Li₂O stabilized.

calcined at 1200 °C in each composition. In the compositions stabilized with MgO, the largest particle sizes — about 570 nm — were observed at pH 1 and at a molar ratio of $[Na_2O] : [Al_2O_3] = 1 : 4$. The smallest particle sizes — about 220 nm — were observed at pH 4 and at a molar ratio of $[Na_2O] : [Al_2O_3] = 1 : 6$. Stabilizing with Li₂O produced particle sizes larger than in the other powders — up to 870 nm at pH 1 and a molar ratio of $[Na_2O] : [Al_2O_3] = 1 : 5$. The smallest particle sizes in the Li₂O-stabilized compositions — about 290 nm — were observed at pH 8 and a molar ratio of $[Na_2O] : [Al_2O_3] = 1 : 6$. Particle sizes were largest at pH 1 in both the MgO- and the Li₂O-stabilized systems.

Fig. 10 shows SEM images of the synthesized powders. The powder synthesized at pH 9 has a smaller crystalline size than the powder synthesized at pH 1 in both the MgO- and the Li₂O-stabilized systems.

Conclusions

In this study, we investigated the phase formation of Na- β'' -aluminas under the influence of the stabilizers MgO and Li₂O. Na- β'' -aluminas was synthesized by a liquid state reaction, which was carried out at varying calcination temperatures, precursor pH values, and compositions of the reaction variables. When MgO was used as a stabilizer, the Na- β'' -alumina fraction reached its highest levelabout 50% - at a molar ratio $[Na_2O]$: $[Al_2O_3] = 1 : 5$ and at 1200 °C. For the molar ratios $[Na_2O]$: $[Al_2O_3] = 1 : 6$ and 1 : 8, the Na- β'' -alumina fraction remained at around 30% across the entire pH range, and the phase fraction of Na- β'' -alumina changed only slightly with an increasing calcination temperature. When Li₂O was used as a stabilizer, the phase fraction of Na- β'' -alumina calcined at 1200 °C was at its highest level-between 50 and 60% - for pH 1 and pH 9. As the temperature was increased to 1500 °C,

the Na- β ''-alumina fraction increased rapidly because of the transient eutectic liquid which promotes the transformation of β -alumina to β ''-alumina.

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