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Influence of stabilizers on Na-β''-Al_2O_3 phase formation in Li_2O(MgO)-Na_2O-Al_2O_3 ternary systems

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The influences of stabilizers on β- and β''-Al_2O_3 phase formations in Li_2O(MgO)-Na_2O-Al_2O_3 systems were investigated. When stabilized with $4MgCO_3\cdot Mg(OH)_2\cdot 5H_2O$, most of the β''-Al_2O_3 phase formed below 1200 °C and further β- to β''-Al_2O_3 transformation with an increase of temperature was not observed. On the other hand, when stabilized with Li_2CO_3, β''-Al_2O_3 formation occurred by two steps. First, β''-Al_2O_3 was partly formed below 1200 °C, and, second, noticeable transformation from β-Al_2O_3 to β''-Al_2O_3 occurred at higher temperature ranges. It was shown that transient eutectic liquid in the Li_2O-Na_2O-Al_2O_3 system promoted the β- to β''-Al_2O_3 transformation at higher temperatures. Uniform distribution of both Mg^{2+} and Li^+ stabilizing ions enhanced β''-Al_2O_3 formation at low temperatures. In the Li-stabilized systems, however, homogeneous distribution of Li^+ ions hindered both the formation of transient eutectic liquid and the second β- to β''-Al_2O_3 phase transformation at high temperatures. © *1998 Kluwer Academic Publishers*

1. Introduction

β''-Al_2O_3 ceramics is a superionic conductor of Na^+ ions and has the highest level of ionic conductivity among ceramic materials. It has been used as a solid electrolyte in a Na/S secondary battery and as an electrode in an alkali metal thermoelectric converter (AMTEC). Applications of this material are being extended mainly to sensors and proton conductors by exchanging Na^+ ions with other conductive ions such as Ag^+, NH_4^+, H_3O^+, and so on.

β''-Al_2O_3 is not stable and decomposes over 1400 °C in a binary Na_2O-Al_2O_3 system [1], hence cations whose ionic radii are less than 0.097 nm are usually doped to stabilize β''-Al_2O_3, which has conductivity five times higher than β-Al_2O_3 has [2, 3]. Mg^{2+} or Li^+ ions have been most widely used as the stabilizing cations. Li^+ ions are known to be more effective for the β''-Al_2O_3 formation than Mg^{2+} ions are [4, 5]. The different behaviors of each stabilizing cation during the phase formation have not been provided yet, however; thus, it is difficult to clarify the different effect of each stabilizer on the phase formation and transformation.

The β- to β''-Al_2O_3 transformation mechanism as well as phase diagrams have still been confused in both Na_2O-Al_2O_3 binary and Li_2O(MgO)-Na_2O-Al_2O_3 ternary systems. According to the kinetic studies of Hodge [1] and Bera [4], in Na_2O-Al_2O_3 and Li_2O-Na_2O-Al_2O_3 systems, β''-Al_2O_3 formation and decomposition could be explained by the reaction of β-Al_2O_3 with γ-$NaAlO_2$ phase that might exist in the grain boundary. In addition, the rate of transformations between β- and β''-Al_2O_3 was slow and would be controlled by the diffusion of Al^{3+} ions. On the other hand, it was reported that transformations between β- and β''-Al_2O_3 were thought to be more polymorphic transformation than decomposition [6, 7], and stability of β- and β''-Al_2O_3 depended on the heat treatment history in the Na_2O-Al_2O_3 system [7]. Although those mechanisms were suggested, it has still been difficult to explain the β''-Al_2O_3 formation systematically during processing.

The degree of homogeneity of additives can have a substantial effect on β''-Al_2O_3 phase formation. In order to enhance the homogeneity during mixing, the chemical routes such as coprecipitation or sol-gel method have been attempted. But, in comparison with solid state reaction, these sophisticated processes had drawbacks forming metastable structures such as γ-Al_2O_3 and m-Al_2O_3 that were not desirable to form β- and β''-Al_2O_3 phases [8]. When prepared by solid state reaction, the homogenization of powder mixtures can be improved by altering the source of stabilizers. In the so-called zeta process, $Li_2O\cdot 5Al_2O_3$ (zeta lithium aluminate) was used instead of Li salts like Li_2CO_3 or $LiNO_3$. The zeta-processed powder was proved to attain five times more uniform distribution of Li^+ ions than conventionally prepared powders did [9, 10].

The objective of the present study is to examine the different effects of Li and Mg stabilizing agents on the β''-Al_2O_3 phase formation process. The influence

TABLE I Composition of samples

Designation	Composition
M1	$0.33MgO{\cdot}0.87Na_2O{\cdot}5.2Al_2O_3$
M2	$0.33MgO{\cdot}1.17Na_2O{\cdot}5.2Al_2O_3$
M3	$0.66MgO{\cdot}0.87Na_2O{\cdot}5.2Al_2O_3$
L1	$0.147Li_2O{\cdot}0.87Na_2O{\cdot}5.2Al_2O_3$
L2	$0.147Li_2O{\cdot}1.17Na_2O{\cdot}5.2Al_2O_3$
L3	$0.294Li_2O{\cdot}0.87Na_2O{\cdot}5.2Al_2O_3$

of transient eutectic liquid and the distribution effect of stabilizing ions on the phase transformation were studied by varying the chemical compositions and the sources of stabilizing ions.

2. Experimental

The compositions for this study are summarized in Table I. M1 and L1 are widely accepted compositions to fabricate β''-Al_2O_3 ceramics. M2 and L2 are Na_2O-rich compositions that were prepared by adding 0.3 mol of Na_2O to the compositions of M1 and L1. M3 and L3 are stabilizer-rich compositions and are prepared by adding twice as many moles of MgO and Li_2O compared with the compositions of M1 and L1, respectively. In compositions of M1–M3 and L1–L3, $4MgCO_3{\cdot}Mg(OH)_2{\cdot}5H_2O$ and Li_2CO_3 were used as Mg and Li sources, respectively. To compare the distribution effect, MgO and $Li_2O{\cdot}5Al_2O_3$ were used as stabilizing sources for the same compositions of M1 and L1. High purity α-Al_2O_3 and reagent-grade salts of Na_2CO_3, MgO, $4MgCO_3{\cdot}Mg(OH)_2{\cdot}5H_2O$, and Li_2CO_3 were used as starting materials. In order to prepare $Li_2O{\cdot}5Al_2O_3$, appropriate amounts of Li_2CO_3 and α-Al_2O_3 were mixed and then calcined at 1250 °C for 3 h. XRD patterns proved the complete formation of the $Li_2O{\cdot}5Al_2O_3$ phase. Appropriate amounts of powders were weighed and then mixed by ball milling for 8 h using acetone as a liquid medium. After drying and sieving, the precursor powders were packed in MgO crucibles with MgO covers and calcined at temperatures ranging from 1000 °C to 1600 °C for 240 min.

The phase compositions of calcined samples were measured by x-ray diffractometry. The relative amounts of phases were determined by calculating the line intensities of well-separated peaks of each phase using the following equations [11, 12].

$$\%\text{ of }\alpha = \left[\left[\left\{I(\alpha 012)\frac{10}{7.4}+I(\alpha 113)\right\}\times\frac{1}{2}\right]\Big/ X\times 100(\%)\right. \quad (1)$$

$$\%\text{ of }\beta'' = \frac{I(\beta''0111)}{X}\times\frac{10}{4}\times 100(\%) \quad (2)$$

$$\%\text{ of }\beta = \frac{I(\beta 017)}{X}\times\frac{10}{4}\times 100(\%) \quad (3)$$

$$\%\text{ of }\gamma = \frac{I(\gamma 120)}{X}\times 100(\%), \quad (4)$$

where $X=\{I(\alpha 012)\frac{10}{7.4}+I(\alpha 113)\}\frac{1}{2}+I(\beta 017)\frac{10}{4}+I(\beta''0111)\frac{10}{4}+I(\gamma 120)$

$I(\alpha 012)$: X-ray intensity of (012) plane of α-Al_2O_3 phase

$I(\alpha 113)$: X-ray intensity of (113) plane of α-Al_2O_3 phase

$I(\beta 017)$: X-ray intensity of (017) plane of β-Al_2O_3 phase

$I(\beta''0111)$: X-ray intensity of (0111) plane of β''-Al_2O_3 phase

$I(\gamma 120)$: X-ray intensity of (120) plane of γ-$NaAlO_2$ phase

3. Results and discussion

Phase transformation largely depended on the calcination temperature and showed much difference between Mg- and Li-stabilized systems. Fig. 1 shows the phase formations of M1, M2, and M3 compositions that were stabilized with $4MgCO_3{\cdot}Mg(OH)_2{\cdot}5H_2O$ and calcined at 1000–1600 °C for 240 min. In Fig. 1, it is noticeable that the phase formation was almost completed below 1200 °C. In all compositions of M1–M3 α-Al_2O_3 disappeared at 1200 °C, and γ-$NaAlO_2$ also disappeared at 1200 °C in M1 and M3, but not in M2 composition that was a Na_2O-rich composition. Most of the β- and β''-Al_2O_3 phases were formed at 1200 °C, especially β''-Al_2O_3 as a main phase, and the formed phases were maintained up to 1600 °C. Further, β- to β''-Al_2O_3 phase transformation above 1200 °C was not observed.

Fig. 2 presents the phase formation curves of L1–L3 compositions stabilized with Li_2CO_3. In all compositions, α-Al_2O_3 phase disappeared below 1200 °C. In L1, γ-$NaAlO_2$ phase also disappeared below 1200 °C, but it existed up to higher temperatures in L2 and L3. Although the β- and β''-Al_2O_3 phases were formed at 1200 °C as main phases, the amounts of β''-Al_2O_3 phase (53%, 45%, and 36% for L1, L2, and L3, respectively) were much less compared with the $4MgCO_3\cdot Mg(OH)_2{\cdot}5H_2O$-stabilized systems (79%, 71%, and 84% for M1, M2, and M3, respectively). Around 1500 °C, rapid increases of β''-Al_2O_3 fraction occurred by β-Al_2O_3 to β''-Al_2O_3 transformation and the β''-Al_2O_3 formation was completed. Such two-step formation of β''-Al_2O_3 was characteristic in Li_2CO_3- stabilized systems and was not observed in $4MgCO_3\cdot Mg(OH)_2{\cdot}5H_2O$-stabilized systems. The temperature ranges for second β''-Al_2O_3 formation were 1400–1500 °C for L3 and 1500–1600 °C for L1 and L2. This indicates that the different amount of Li caused the different temperature ranges for the second transformation because L3 was a Li-rich composition that contained twice as many moles of Li compared with L1 and L2.

It has been reported that β''-Al_2O_3 densified in a few minutes, and such rapid densification was attributed to the ternary transient eutectic liquids that formed at 1460–1470 °C in the $LiAlO_2$-$NaAlO_2$-Al_2O_3 system [10, 13]. Even though L1, L2, and L3 compositions are not exactly in accord with the eutectic composition in the $LiAlO_2$-$NaAlO_2$-Al_2O_3 system, it is well-known that the eutectics do not form exactly at the eutectic

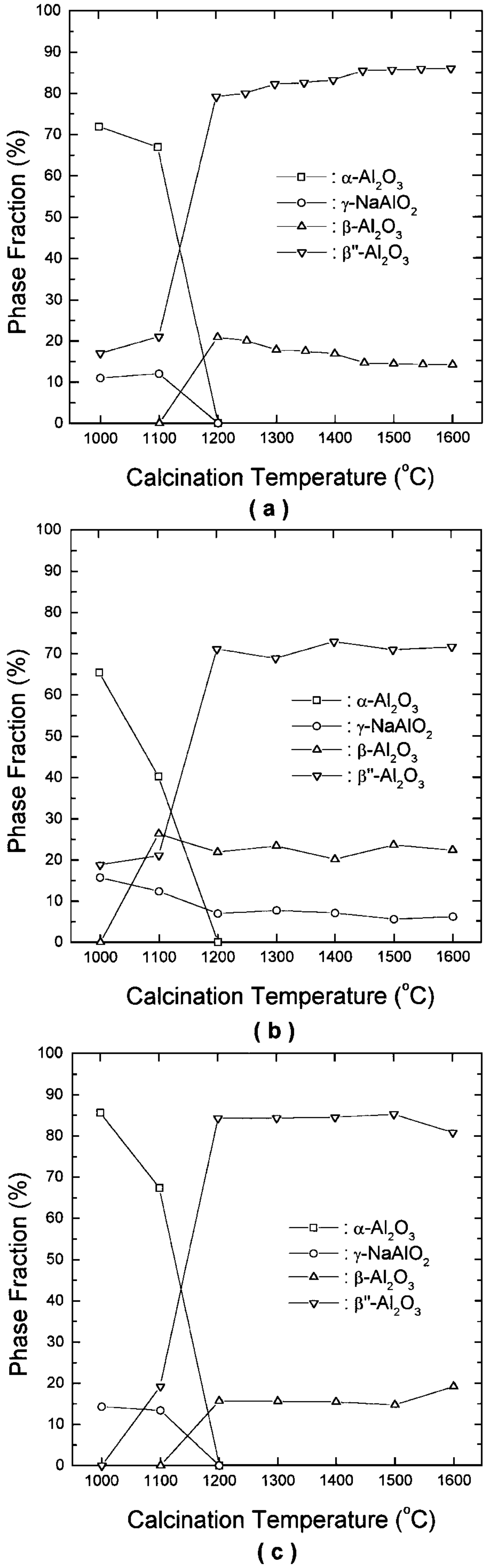

Figure 1 Phase fraction of samples stabilized with $4MgCO_3 \cdot Mg(OH)_2 \cdot 5H_2O$ as a function of calcination temperature (a) M1, (b) M2, (c) M3.

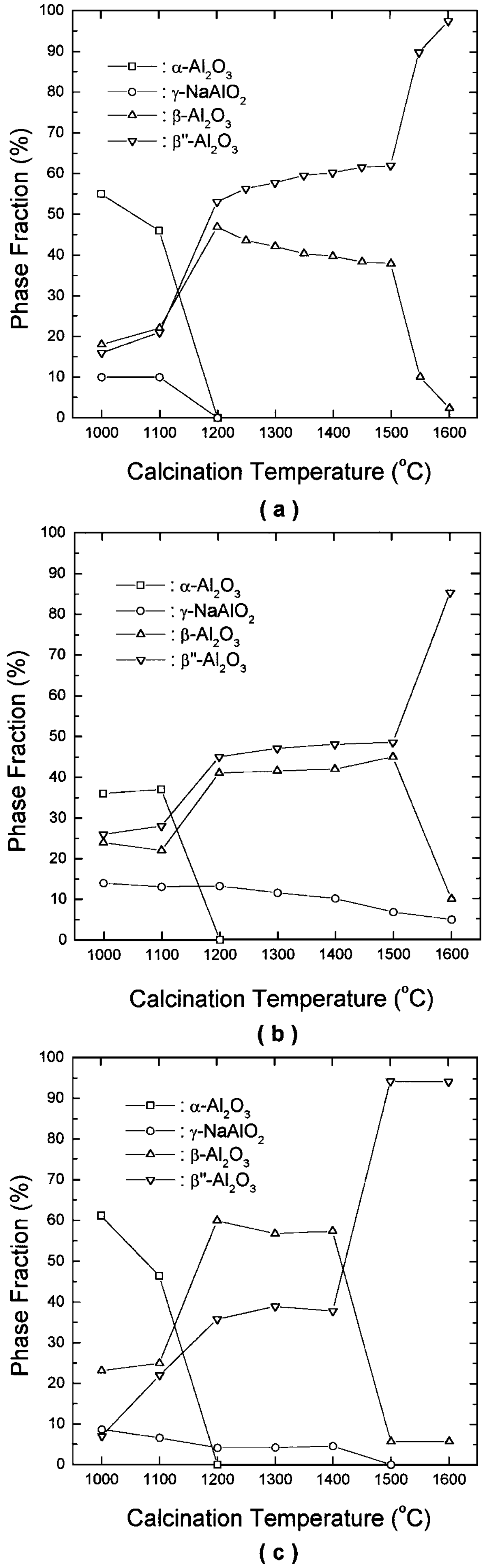

Figure 2 Phase fraction of samples stabilized with Li_2CO_3 as a function of calcination temperature (a) L1, (b) L2, (c) L3.

composition. Eutectics can be formed in local inhomogeneity regions and have hardly been observed in micrographs because the transient eutectic liquid has high solid solubility, and they disappear after complete homogenization caused by diffusional process [14].

Stabilization of β''-Al_2O_3 is basically the substitution of the Al^{3+} ions by the stabilizing cations, and the compensating Mg^{2+} ions generally substitute the tetrahedral Al^{3+} ions, and Li^+ ions substitute octahedral Al^{3+} ions in the spinel block [15, 16]. Thus it can be thought that β''-Al_2O_3 phase formation is mainly controlled by diffusion of stabilizing ions. The ternary eutectic liquid is expected to be the fast path for the diffusion and enhance the β- to β''-Al_2O_3 transformation.

The decrease of transition temperature range with increasing Li amount implies that the transient eutectic liquids provide the fast diffusion path and are responsible for the second β''-Al_2O_3 formation from β-Al_2O_3 in the systems stabilized with Li_2CO_3. That is, the higher Li content led to the more eutectic liquids and lowered the temperature range at which the second transformation occurred. Thus the temperature range could differ a little according to the composition that determined the amount of liquid phase.

In comparison with Li_2CO_3-stabilized compositions, the $4MgCO_3{\cdot}Mg(OH)_2{\cdot}5H_2O$-stabilized system had no rapid transformation from β- to β''-Al_2O_3 above 1200 °C. Since ternary eutectic liquid does not exist in the MgO-Na_2O-Al_2O_3 system, diffusion is likely to occur through solid state or binary eutectic liquid in the Na_2O-Al_2O_3 system. Binary phase diagrams are still in controversy. According to DeVries and Roth [17], eutectic liquid formed at 1410 °C, whereas Weber and Venero [18] reported it at 1585 °C. Because the sintering of binary and Mg-stabilized ternary systems is also completed in several minutes, the binary eutectic liquid is expected to exist and also acts as a fast path for diffusion.

Mg-stabilizing ions do not seem to be soluble in binary eutectic liquid, however, so binary eutectics do not affect the movement of Mg^{2+} ions. In fact, the influence of binary eutectic liquid on the phase transformation was not found in the $4MgCO_3{\cdot}Mg(OH)_2{\cdot}5H_2O$-stabilized system as well as in the Li_2CO_3-stabilized system. Therefore, it can be concluded that binary eutectics do not contribute to phase transformation in both Mg and Li ternary systems, whereas the eutectics of Li ternary system enhance the phase transformation at high temperatures.

At the low temperature range of 1000–1200 °C, direct transformation from α-Al_2O_3 and γ-$NaAlO_2$ phases to β- and β''-Al_2O_3 occurred in both systems, which was in agreement with previous research [17–20]. However, the difference in the amount of β''-Al_2O_3 at 1200 °C between $4MgCO_3{\cdot}Mg(OH)_2{\cdot}5H_2O$-stabilized and Li_2CO_3-stabilized systems demands a more detailed explanation.

To explain the different β''-Al_2O_3 fractions at 1200 °C and examine the distribution effect of stabilizing ions, stabilizing sources were changed to vary the distribution of stabilizing ions by controlling the volume of stabilizer. Instead of Li_2CO_3 and $4MgCO_3{\cdot}Mg(OH)_2{\cdot}5H_2O$, $Li_2O{\cdot}5Al_2O_3$ and MgO were used as stabilizing sources, respectively. When the same amount of Li^+ and Mg^{2+} were contained, $4MgCO_3{\cdot}Mg(OH)_2{\cdot}5H_2O$ and $Li_2O{\cdot}5Al_2O_3$ had more volume than MgO and Li_2CO_3 had, respectively, and induced the more uniform distribution of stabilizing ions during mechanical mixing.

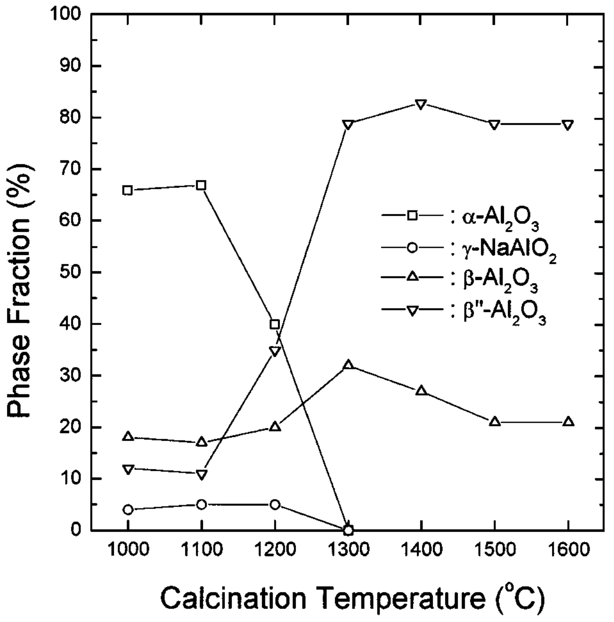

Figure 3 Phase fraction of L1 composition stabilized with $Li_2O{\cdot}5Al_2O_3$ as a function of calcination temperature.

Fig. 3 shows the phase fractions of L1 composition stabilized with $Li_2O{\cdot}5Al_2O_3$, the so-called zeta process. It has been known that $Li_2O{\cdot}5Al_2O_3$ enhances the homogeneity of Li^+ ions and increases the fraction of β''-Al_2O_3 after sintering [9]. As shown in Fig. 3, most of the β''-Al_2O_3 was formed at the temperature range of 1100–1300 °C and maintained above 1300 °C, and the second increase of β''-Al_2O_3 by β- to β''-Al_2O_3 transformation did not occur. Such a transformation process differed from the L1 composition stabilized with Li_2CO_3 but was very similar to the phase formation phenomena in the $4MgCO_3{\cdot}Mg(OH)_2{\cdot}5H_2O$-stabilized systems.

As mentioned earlier, transient eutectics readily form in the compositionally inhomogeneous regions and disappear by diffusional homogenization. The uniform dispersion of Li^+ ions by $Li_2O{\cdot}5Al_2O_3$ prevented the formation of transient eutectic liquid at the high temperatures; therefore, the second conversion from β- to β''-phase could not occur. It can be concluded from Fig. 3 that the second conversion in the Li_2CO_3-stabilized systems was attributed to the ternary transient eutectic liquid that existed locally due to the inhomogeneous dispersion of Li^+ ions.

Fig. 4 shows the phase composition of M1 composition when MgO was used as a stabilizing source instead of $4MgCO_3{\cdot}Mg(OH)_2{\cdot}5H_2O$. The β''-Al_2O_3 fraction was lower and the β-Al_2O_3 fraction was higher in all temperature ranges than the fractions of the same composition (M1) stabilized with $4MgCO_3{\cdot}Mg(OH)_2{\cdot}5H_2O$ were. Reactions from

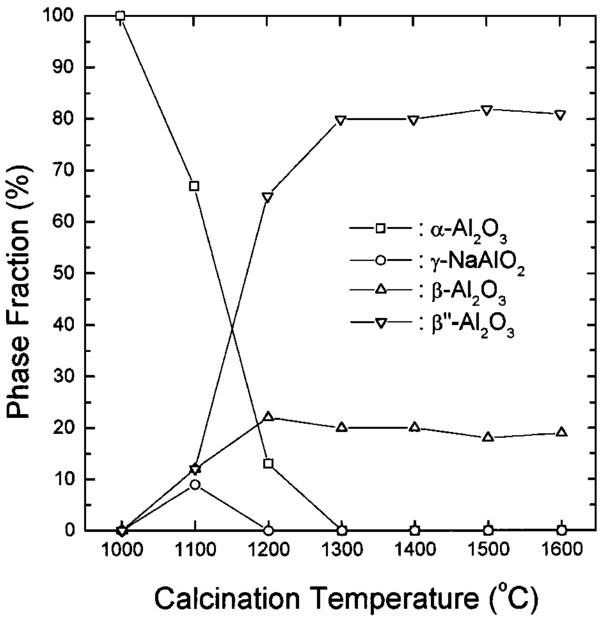

Figure 4 Phase fraction of M1 composition stabilized with MgO as a function of calcination temperature.

α-Al_2O_3 to β- and β''-Al_2O_3 were completed at a little higher temperature of 1300 °C compared with the $4MgCO_3{\cdot}Mg(OH)_2{\cdot}5H_2O$-stabilized system (1200 °C). It can be known from Fig. 4 that the uniform distribution of stabilizers allowed the β''-Al_2O_3 phase formation at the lower temperature range and gave a higher β''-Al_2O_3 fraction.

Homogeneous dispersion of the stabilizing ions played a very important role in the β''-Al_2O_3 formation at the low temperature range as shown in the systems stabilized with $Li_2O{\cdot}5Al_2O_3$, MgO, and $4MgCO_3{\cdot}Mg(OH)_2{\cdot}5H_2O$. By contrast, the β- to β''-phase transformation mainly occurred by ternary transient eutectics in the systems stabilized with Li_2CO_3.

4. Conclusions

Phase transformation process in the β- and β''-Al_2O_3 systems with different stabilizers was analysed during calcination at 1000–1600 °C for 240 min. In $4MgCO_3{\cdot}Mg(OH)_2{\cdot}5H_2O$-stabilized compositions, β''-Al_2O_3 formation almost completed at 1200 °C, and the formed β''-Al_2O_3 was maintained at higher temperatures. In Li_2CO_3-stabilized compositions, β''-Al_2O_3 formation occurred in two steps. One was β''-Al_2O_3 formation from α-Al_2O_3 and γ-$NaAlO_2$ at lower temperatures and the second was β- to β''-Al_2O_3 transformation at higher temperatures. The transformation temperature ranges decreased with the increase of Li amount, and ternary eutectic liquid was responsible for the second β- to β''-Al_2O_3 transformation. Through the distribution study, it was shown that the better distribution of stabilizing ions led to more β''-Al_2O_3 formation at lower temperatures. When $Li_2O{\cdot}5Al_2O_3$ was used as a stabilizer, a second β- to β''-Al_2O_3 transformation at high temperatures did not occur because uniform dispersion of Li^+ ions suppressed the transient eutectic liquid formation. The implication of the present study is that ternary transient eutectics can accelerate the β- to β''-Al_2O_3 phase transformation in Li-stabilized system and β''-Al_2O_3 formation is controlled by the distribution of stabilizers.

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