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Low temperature synthesis of $MgO \cdot Al_2O_3$ spinel powders using a mechanochemical process

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Mixtures of $Mg(OH)_2$ and gibbsite, mechanically activated by grinding in a planetary ball mill, were heat treated to obtain $MgAl_2O_4$ spinel. $Mg(OH)_2$ is hardly amorphized and dehydrated by a separate grind. However, when $Mg(OH)_2$ and gibbsite powders are ground together, rapid amorphization of $Mg(OH)_2$ takes place. The formation of $MgAl_2O_4$ spinel was significantly enhanced by the mechanical treatment of mixtures. When the mixtures were ground over 30 minutes, single phase $MgAl_2O_4$ can be obtained by heat treatment at 800°C for 1h.

Key words: Mechanical activation, ball-milling, $MgAl_2O_4$ spinel.

Introduction

Magnesium aluminate spinel ($MgAl_2O_4$) is used as a refractory material because of its high melting temperature, good chemical inertness, and mechanical properties [1, 2]. Generally, $MgAl_2O_4$ spinel has been synthesized by a solid-state reaction of mixed powders. This method is the classical and cheapest route, but high temperature heat treatments, often above 1200°C, must be carried out to achieve a complete reaction [3, 4].

Reactivity of a solid changes significantly due to preliminary grinding. Grinding a multi-component solid mixture is becoming a useful technique of solid state synthesis to decrease the synthesis temperature [5, 6]. It would therefore be beneficial to be able to obtain the magnesium aluminate precursor by mechanochemical processing, presumably because this could then be converted at relatively low temperatures to a spinel with a high surface area and low particle size to achieve good sintering behavior.

In the present work we have synthesized magnesium aluminate precursors from a mechanically treated mixture of aluminum hydroxide and magnesium hydroxide and investigated the conversion of the precursor materials into the spinel phase by heating.

Experimental

Magnesium hydroxide ($Mg(OH)_2$, Aldrich) and Gibbsite ($Al(OH)_3$, Korea General Chemical) were used in this work. These two materials were separately ground to examine their mechanochemical properties. For the mechanochemical reaction, a mixture of $Mg(OH)_2$ and $Al(OH)_3$ in the molar ratio 1 : 2 were ground using a planetary ball mill (Fritsch Pulverisette-7) in air with various grinding times. The balls to powder weight ratio was 15 : 1. The milling was suspended for 10 minutes after every 10 minute milling to avoid an excess temperature increase inside the mill pots during prolonged milling. Ground mixtures were calcined at 700~1000°C in an atmospheric condition.

X-ray diffraction (XRD) analysis was carried out with Cu-Kradiation to investigate the phase contents and crystallinity of the ground and calcined powders. The ground samples were characterized simultaneously by differential thermal analysis (DTA) and thermogravimetry (TG) in air at a heating rate of 20°C/minute.

Results and Discussion

Figure 1 shows the XRD patterns of ground gibbsite powders. The intensity of the diffraction $Al(OH)_3$ peaks decreased with increasing grinding time. This indicates that gibbsite is amorphized by grinding. In the DTA curves for ground gibbsite(Fig. 2(a)) a large and broad endothermic peak is observed. This peak shifts towards lower temperatures with increasing grinding time. After grinding for 120 minutes, an additional endothermic peak appeared at about 150°C. Figure 2(b) shows the deriva-tive thermogravimetric (DTG) curves obtained simulta-neously with the DTA curve. The course of the DTG is in complete accord with that of the DTA. This means that the endothermic peak results from weight loss by dehydration, and that the grinding enhances dehydration.

On the other hand, $Mg(OH)_2$ was hardly amorphized by mechanical treatment, as shown in Fig. 3. The diffraction peaks become a little broadened but the structure of $Mg(OH)_2$ was still evident after grinding up to 120

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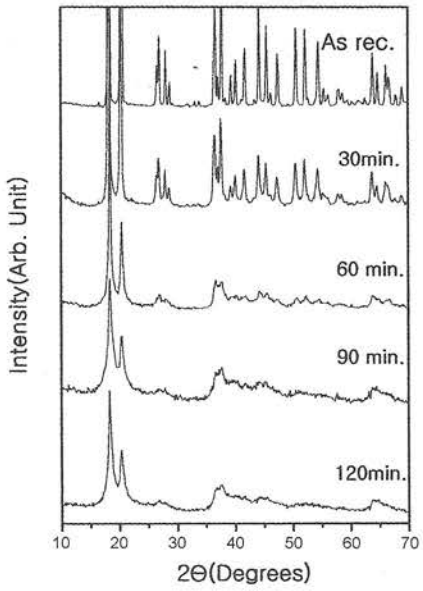

Fig. 1. X-ray diffraction of aluminum hydroxides with milling time.

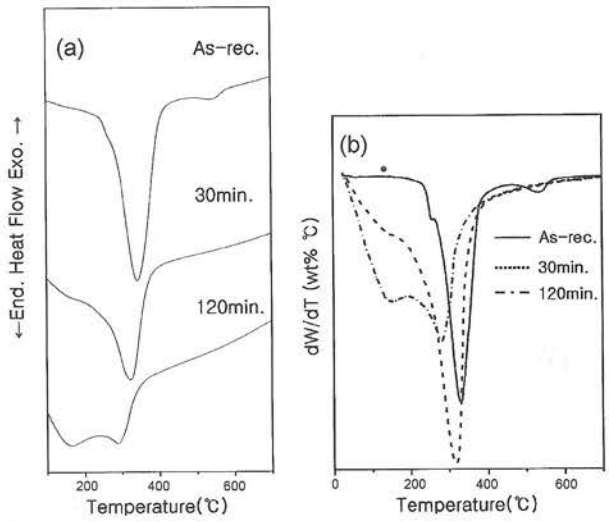

Fig. 2. DTA(a) and DTG(b) profiles of aluminum hydroxides with milling time.

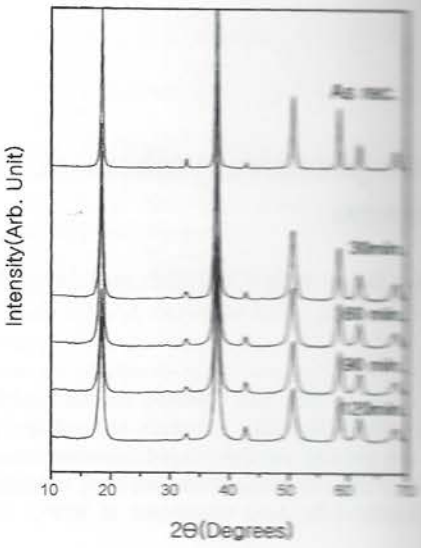

Fig. 3. X-ray diffraction of magnesium hydroxides with milling time

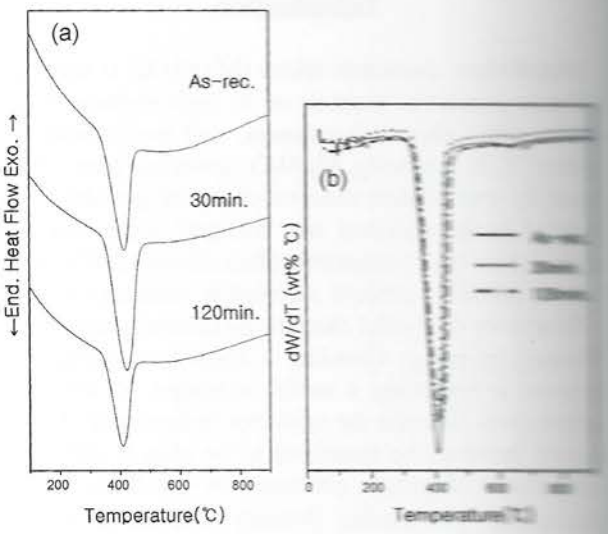

Fig. 4. DTA(a) and DTG(b) profiles of magnesium hydroxides with milling time.

minutes. No significant change in the DTA/DTG profiles was observed for $Mg(OH)_2$ by grinding; show-ing a different behavior from those of gibbsite (Fig. 4) This suggests that $Mg(OH)_2$ is difficult to dehydrate during mechanochemical treatment.

Figure 5 shows the XRD patterns of the gibbsite and $Mg(OH)_2$ mixtures ground for different times. The peak intensity of the starting materials decreased markedly after 30 minutes grinding. The mixture was rapidly amorphized by mixed grinding. In the case of further grinding, peaks of boehmite (AlO(OH)) were observed, implying that the dehydration of gibbsite occurred during grinding.

Figure 6 shows DTA-DTG curves of the mixtures ground for various times. The behavior of the DTG is virtually the same as the DTA curve for the endothermic reaction. This indicates again that the endothermic peak results from weight loss by dehydration. The DTA curve of the unground mixture shows three main endothermic peaks at around 300°C, 450°C and 530°C. These peaks corresponded to the dehydration of Mg $(OH)_2$ (400°C) and gibbsite (300°C and 530°C), respectively, by comparing with Figs. 2 and 4. After 30 minutes grinding, the peak at 300°C and 400°C decreased and the peak at 530°C disappeared. Besides, an additional broad endothermic peak at around 150°C and exothermic peak at 800°C appeared. The weight loss began at a much lower temperature in a wider temperature range with grinding. The exothermic peak at 800°C is related with the crystallization of $Mg_2Al_4O_5$. Fig. 7 shows the XRD profiles of the samples ground

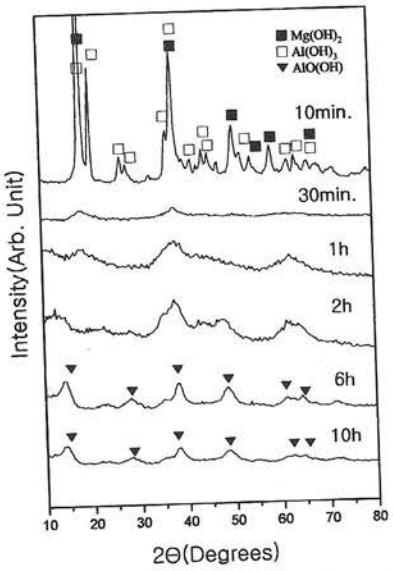

Fig. 5. XRD patterns of the mixtures ground for various duration of time.

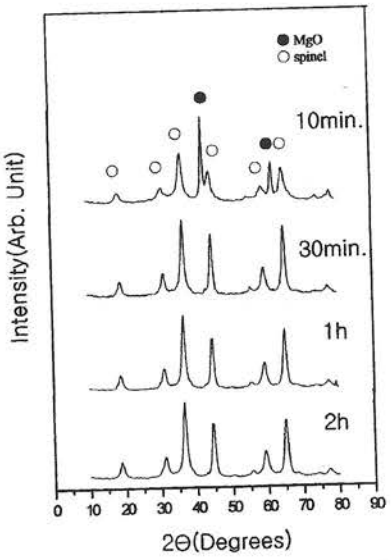

Fig. 8. XRD patterns of the ground mixtures thermally treated at 900°C for 1h.

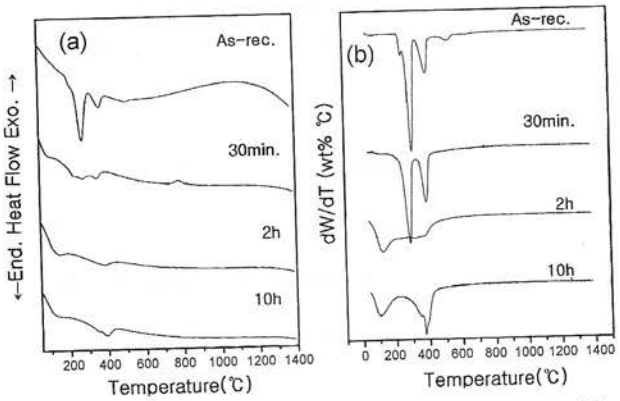

Fig. 6. DTA(a) and DTG(b) profiles of the mixtures ground for various duration of time.

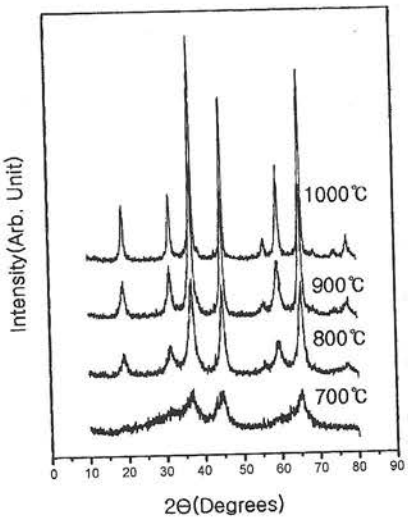

Fig. 9. XRD patterns of the 30 minutes ground mixtures thermally treated at various temperatures for 1h.

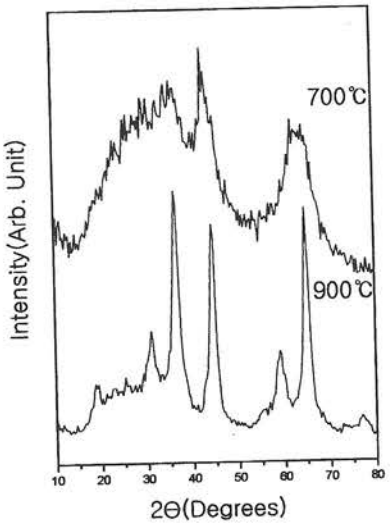

Fig. 7. XRD patterns for the 30 minutes ground mixture which had been heated from room temperature up to 700°C and 900°C at a rate of 20°C/minute and cooled rapidly to room temperature

for 30 minutes, which were heated to 700°C and 900 °C, *i.e.* before and after the exothermic peak, respectively, and then quickly cooled to room temperature. It was found that the $MgAl_2O_4$ spinel phase was well deve-loped after the exothermic reaction. However, for the samples with longer mixed grinding, the exothermic peak at 800°C disappeared. This might be attributed to the easier nucleation of the $MgAl_2O_4$ crystals. Figure 8 shows the XRD patterns of the ground mixtures calcined at 900°C for 1 h. When calcined the mixture ground for 10 minutes, the $MgAl_2O_4$ phase was formed significantly, though diffraction peaks of MgO were observed. In the case of mixtures ground for more than 30 minutes, a single crystalline phase of $MgAl_2O_4$ was obtained.

Figure 9 shows the XRD patterns of the 30 minutes

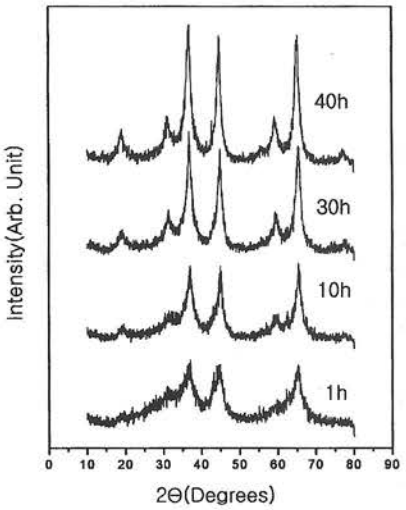

Fig. 10. XRD patterns of the 30 minutes ground mixtures thermally treated at 700°C for various times.

ground mixtures thermally treated at various temperatures for 1 h. With the heat treatment at temperatures above 800°C, a single $MgAl_2O_4$ phase was obtained. It should also be noted that the diffraction peaks of $MgAl_2O_4$ were detected in the mixture thermally treated at 700°C while the width of each peak is large. In the case of heat treatment at 700°C, the crystallinity of the $MgAl_2O_4$ phase was greatly improved by increasing the heating time, as shown in Fig. 10. This result reveals that the synthesis temperature is much lower than those reported in previous studies. It appears that the mechanical treatment through ball-milling activates the mixed particles, which is favorable for the solid-state reaction of the reactant particles forming the $MgAl_2O_4$ phase during subsequent heat treatment. Additionally, we assume that traces of the reaction product are formed in the contact area between the reactant particles during grinding, favoring the formation of the spinel during thermal treatment. Experimental proof for the mechanochemical reaction between $Mg(OH)_2$ and gibbsite, however, cannot be found on the basis of the present data. Further intensive work is necessary to clarify the mechanism of the spinel formation enhanced by mechanical activation.

Conclusion

$Mg(OH)_2$ is hardly amorphized and dehydrated by separate grinding. However, when $Mg(OH)_2$ and gibbsite powders are ground together, rapid amorphization of $Mg(OH)_2$ takes place. As a result of mixed- grinding, the formation of the $MgAl_2O_4$ spinel phase was significantly enhanced when the mixtures were ground for more than 30 minutes.

Acknowledgement

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