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FORMATION AND SINTERING OF $\gamma$-$\text{Al}_2\text{O}_3$ WITH MgO ADDITIONS FROM COPRECIPITATED HYDRATES

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Résumé - Des poudres d'alumine-$\gamma$ avec un dopage homogène ont été obtenues par calcination des coprécipités AlOOH - Mg(OH)$_2$ formant des solutions solides. L'influence du dopage, pour des rapports Mg/Al de 0.02 à 0.06 sur le frittage a été analysée par mesure de la densité, de la porosité, des retraits linéaires ainsi que par détermination de la résistance à la traction.

Abstract - The gamma Al$_2$O$_3$ powders with homogeneous dopant distribution were obtained by calcination of coprecipitates consisted of AlOOH solid solutions with Mg(OH)$_2$. The effect of additive with Mg/Al ion ratio 0.02-0.06 on sintering was analysed by density, porosity, linear shrinkage and tensile strength determinations.

I - INTRODUCTION

In the previous papers /1,2/ it was shown that addition of MgO in the form of magnesium nitrate promoted compressibility and in some extent the sinterability of commercial grade gibbsite for production catalyst supports. It was demonstrated that brucite and gibbsite did not form solid solutions despite their similarity in structure, while boehmite formed metastable solid solutions with brucite /3/. These solid solutions can be formed as coprecipitates from mixtures of aluminum and magnesium salts with alkali /4,5/.

This paper deals with the effects of doping agent Mg(OH)$_2$, coprecipitated with pseudoboehmite on the formation and sintering of gamma Al$_2$O$_3$.

II - EXPERIMENTAL PROCEDURE

Material was prepared by precipitation method /4/ from 1.0 M solutions of aluminum and magnesium chlorides with 10% ammonium hydroxide at the constant temperature (65°C) and the pH value 9-10. After washing and drying precipitates were calcined at 500°C, 2h in order to obtain powders with high specific surface areas (Table 1). On the basis of the results obtained from thermal analyses (TGA and DTA) the temperature of calcination was chosen. The spectrochemical analysis was used for MgO content determination and nitrogen adsorption areameter for specific surface area measurements. The precipitates and calcined powders were wet ground in alumina ball mill in distilled water in order to deagglomerate particles. The prismatic samples (for dilatometric examinations) were made by cold pressing at 100 MPa and also cylindrical samples (for density and strength) at 100 and 150 MPa. The compacts were sintered at 700°C, 2h in air (heating rate 2°C/min). The sintering temperature was chosen on the basis of the X-ray results. Gamma Al$_2$O$_3$ without additive was transformed to theta phase on the
temperature higher than 700°C. The densities of pressed samples were determined by measuring dimensions and weights, the densities of sintered samples by immersion in xylene. The diametral compression test was used for measuring the tensile strength of pressed and sintered cylindrical samples /6/.

TABLE 1. THE CHARACTERISTICS OF CALCINED PONDERS AT 500°C

<table>
<thead>
<tr>
<th>NUMBER</th>
<th>Mg/Al ION RATIO</th>
<th>MgO % MASS</th>
<th>SPECIFIC SURFACE AREA ($m^2_g^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>0.00</td>
<td>0.00</td>
<td>260</td>
</tr>
<tr>
<td>2.</td>
<td>0.02</td>
<td>1.62</td>
<td>256</td>
</tr>
<tr>
<td>3.</td>
<td>0.03</td>
<td>2.14</td>
<td>247</td>
</tr>
<tr>
<td>4.</td>
<td>0.04</td>
<td>2.89</td>
<td>244</td>
</tr>
<tr>
<td>5.</td>
<td>0.05</td>
<td>4.64</td>
<td>190</td>
</tr>
<tr>
<td>6.</td>
<td>SPINEL</td>
<td>28.2</td>
<td>110</td>
</tr>
<tr>
<td>7.</td>
<td>MgO-PURE</td>
<td>100</td>
<td>28</td>
</tr>
</tbody>
</table>

III - RESULTS AND DISCUSSION

The precipitate products contained pseudoboehmite as poorly crystallized phase. The decreasing of IR absorption peaks in spectra presented in Fig.1, at frequency 1073 as well as at 3262 cm$^{-1}$ for boehmite was evidenced for coprecipitates. The sharp absorption peaks at 3780 and 900 cm$^{-1}$ for brucite were missed in coprecipitates IR spectra. These results and the broadening of X-ray peaks with increasing of Mg/Al ion ratio in precipitates (Fig.2a) pointed out that probably metastable solid solutions between pseudoboehmite and brucite were formed.

![Fig.1. Infrared absorption spectra of pseudoboehmite, brucite and coprecipitates.](image1)

![Fig.2. X-ray diffractograms of pseudoboehmite and coprecipitates (a) and powders calcined at 500°C (b).](image2)
Very intensive weight loss in the temperature range 200-400°C (completed about 500°C) and the endothermic peaks for dehydration and phase transformation to gamma Al₂O₃ in the temperature range 450-490°C were observed. From IR and X-ray data (Fig.2b) it was concluded that the calcined powders consisted from poorly crystallized gamma or eta Al₂O₃ and solid solutions with magnesia. It could be assumed that Mg²⁺ ions occupied the cation vacancies in tetrahedral positions in gamma alumina structure and formed the solid solutions. The observed broadening of X-ray peaks (Fig.2b) for the composition with 0.06 Mg/Al ratio would be attributed to the appearance of low crystallized MgAl₂O₄ (spinel) as well as some inhomogeneity in lattice constant within the crystallites.

![Graph](image1)

**Fig.3.** The relation between specific surface area and the temperature of calcination for pseudoboehmite and coprecipitate powders.

Very similar relation between specific surface area and calcination temperature for the samples with different Mg/Al ion ratio could be seen in the Fig.3. It was noticed that addition of Mg²⁺ ions had relatively small influence on the specific surface area up to 0.04 Mg/Al ratio. Some greater decrease was registered for 0.06 Mg/Al ratio. This could be caused by the presence of mixed magnesia alumina spinel, which had considerably smaller specific surface area (Table 1).

![Graph](image2)

**Fig.4.** Dilatometric curves of the samples obtained from oxides and hydroxides.
The sample obtained from oxide (calcined powder) without additive didn't shrink during sintering up to 800°C (the dilatometric curves in the Fig.4). The relative linear shrinkage of samples obtained from oxides with MgO additions depended from Mg/Al ratio. These shrinkages were up to 0.5% in the temperature range to 800°C. The shrinkage of samples obtained from hydroxides is very intensive up to 600°C and it was caused by dehydration and phase transformation, and also was influenced by MgO addition. The linear shrinkage for these samples in the range 600-800°C was about 1%.

### TABLE 2. THE CHARACTERISTICS OF PRESSED AND SINTERED SAMPLES OBTAINED FROM HYDROXIDE

<table>
<thead>
<tr>
<th>Ion Ratio</th>
<th>Pressing Pressure (MPa)</th>
<th>Density (g/cm³)</th>
<th>Mean Value of Tensile Strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Pressed</td>
<td>Sintered</td>
</tr>
<tr>
<td>0.00</td>
<td>100</td>
<td>1.25</td>
<td>1.16</td>
</tr>
<tr>
<td></td>
<td>150</td>
<td>1.42</td>
<td>1.23</td>
</tr>
<tr>
<td>0.02</td>
<td>100</td>
<td>1.30</td>
<td>1.16</td>
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<td></td>
<td>150</td>
<td>1.35</td>
<td>1.26</td>
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<tr>
<td>0.04</td>
<td>100</td>
<td>1.25</td>
<td>1.12</td>
</tr>
<tr>
<td></td>
<td>150</td>
<td>1.44</td>
<td>1.24</td>
</tr>
<tr>
<td>0.06</td>
<td>100</td>
<td>1.31</td>
<td>1.10</td>
</tr>
<tr>
<td></td>
<td>150</td>
<td>1.50</td>
<td>1.25</td>
</tr>
</tbody>
</table>

The densities and tensile strength of pressed and sintered samples (shown in the Tables 2 and 3) depended on pressing pressure but they were practically independent from MgO addition. Previously observed effect of MgO addition was not pronounced in the coprecipitated samples. The densities and mean tensile strengths of the sintered samples obtained from hydroxides were some higher than those from oxides. However, the high value of standard deviations from mean values of tensile strength measurements raised difficulties for interpretation of results.

### IV. CONCLUSIONS

- Chemical precipitation method was used to prepare homogeneous doped pseudoboehmite with brucite. Coprecipitated products were consisted of metastable solid solutions
as poorly crystallized gels.
- The calcined powders were poorly crystallized gamma or eta $\text{Al}_2\text{O}_3$ as well as solid solutions with magnesia. The $\text{Mg}^{2+}$ ion addition caused the specific surface area decrease and in the same time the gamma $\text{Al}_2\text{O}_3$ phase stability improvement.
- The densities and mean tensile strengths of the sintered samples obtained from hydroxides were higher than those from oxides.
- The addition of $\text{Mg}^{2+}$ ions up to 0.06 $\text{Mg}/\text{Al}$ ratio had relatively small effect on linear shrinkage during sintering, on densities and tensile strengths in comparison with pure gamma $\text{Al}_2\text{O}_3$.

REFERENCES