To control the SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} ratio in a starting clay material for the synthesis of β'-sialon by the carbothermal nitridation process, montmorillonite was pillared with Al\textsubscript{2}O\textsubscript{3}. Conversions to sialon of pillared clay (31% Al\textsubscript{2}O\textsubscript{3}) and reference unpillared montmorillonite (18% Al\textsubscript{2}O\textsubscript{3}) have been compared. Pillared montmorillonite yielded a mixture of β'-sialon and various oxynitrides and oxycarbides of alumina as intermediate products. Pillared clay transformed faster during annealing than structural components of smectite alone. For the proper thermal treatment and clay/carbon ratio, both pillared and unpillared clays resulted in β'-sialon solid solutions.

1. Introduction

Clays are potential aluminosilicate raw materials for β'-sialon powders which can be synthesized through simultaneous high-temperature carbothermal reduction and nitridation processes. Naturally occurring aluminosilicates are inexpensive and offer the possibility of an economically favourable alternative to silicon nitride and related products of sialon type. In natural aluminosilicates there are at least two chemical components (precursors) which are intimately mixed. Starting from Lee and Cutler [1], numerous studies of the carbothermal nitridation of clays have been published. Further studies describe sialons prepared from various species of clays, i.e. illite, kaolin, montmorillonites [2–5]. Parameters influencing the reaction rate and possible reaction mechanisms have been recognized in many studies [6–9]. Nitrides may be formed by heterogeneous gas–solid reactions and/or through the metal-silicide liquid phase by reaction between components of mixture and gaseous nitrogen.

The entire reaction can be expressed as

\[
(6 - z) \text{SiO}_2 + z/2 \text{Al}_2\text{O}_3 + y\text{Fe}_2\text{O}_3 + s\text{TiO}_2 + r\text{C} + 0.5(8 - z + 2y + 4/3s)\text{N}_2 \\
\text{Si}_{6-z}\text{Al}_z\text{O}_8\text{N}_{8-z} + 2/3 y\text{Fe}_3\text{C} + s\text{TiN} + (r - 2/3y)\text{CO} \tag{1a}
\]

where \(z, y, \) and \(s\) are deduced from the composition of starting raw material; \(r\) is defined by the stoichiometry of the reaction for carbothermal reduction of the above oxides and is equal to

\[
r = 1.5(8 - z + 2y + 4/3s) \tag{1b}
\]

The extent of reaction (conversion of components to products) to sialon is mainly controlled by temperature, nitrogen-flow, character and purity of raw materials including the carbon content of the clay/carbon mixture. Because there are gas–solid interactions in the system, size, distribution and interconnectivity of pores in pellets of the solid mixture are of great significance.

The SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} ratio of clay raw material depends on the clay deposit and on raw-material processing. For a specific commercial type of clay this ratio has a fixed value, and therefore, \(z\) in sialon cannot be changed as needed for a desired property, such as milling properties of pellets, sinterability of powder, mechanical properties of final product, etc.

To control the SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} ratio in starting material for the synthesis of β'-sialon by the carbothermal nitridation process, smectite was pillared with Al\textsubscript{2}O\textsubscript{3}. Conversions to sialon of the pillared clay material and the reference unpillared montmorillonite are compared in the present study.

2. Experimental procedure

2.1. Clay

A natural montmorillonite (STx-1) was used. This sample contains minor amounts of quartz and calcite. It was pretreated with sodium acetate solution buffered at pH = 5 to remove the CaCO\textsubscript{3} [10]. The sample, which is free of CaCO\textsubscript{3}, was dispersed in deionized water with the help of a dispersing agent, sodium hexametaphosphate, and < 2 µm fraction was separated by centrifugation. The fractionated sample was saturated with Ca\textsuperscript{2+} and CaCl\textsubscript{2} was removed by multiple washings with deionized water. The chemical analysis of < 2 µm calcium montmorillonite is given in Table I.

2.2. Pillaring

About one-half of the above sample (in the wet state) was treated with an excess alumina-pillaring solution (50 ml/g clay) for 4 h at room temperature under constant stirring. After completion of the reaction, excess salt was removed by washing repeatedly with deionized water. The alumina-pillaring solution was
prepared by diluting 50% aluminium chlorohydrol solution 20 times with deionized water. The aluminium chlorohydrol in aqueous medium yields large hydroxy-Al-polyacations of the type \([\text{Al}_{13}\text{O}_{4}\text{(OH)}_{24}, (\text{H}_2\text{O})_{12}]^7^+\) [11], which replace \(\text{Ca}^{2+}\) from the interlayer exchange sites of the montmorillonite. The exchanged hydroxy-Al polymeric cations, after calcination, were converted to immobile (or fixed) oxide pillars in the interlayers that prop the layers apart with subsequent loss of swelling and generation of permanent microporosity. These pillars were found to be stable at least up to \(700\,\text{°C}\). The pillaring process will introduce a large amount of aluminium into the interlays of montmorillonite which will be in intimate contact with aluminosilicate structure. Further details of the preparation and properties of pillared clay can be found in Malla and Komarneni [12]. In Table I, the chemical analysis of alumina-pillared montmorillonite is compared with that of non-pillared calcium montmorillonite. The carbon mixtures with calcium montmorillonite will be designated MM and pillared samples PMM, hereafter. Both MM and PMM samples were suspended in water and mixed (in an ultrasurex mixer SD-45) with an appropriate amount of activated carbon (wet powder, 1.02 times the amount defined by Equations 1a and b; the excess 2% carbon is to compensate for the presumable reduction of \(\text{MgO}\) which is also present in the raw material). Here, it is noted, that the rheological properties (at the same concentration of solids) of suspensions used were quite different. While MM suspension provides characteristic plastic behaviour of montmorillonite-water systems, the PMM appears like a suspension of non-plastic fine solid particles only. After centrifugation and extrusion of pellets (3 mm diameter x 3 mm) both mixtures were dried at about \(150\,\text{°C}\) under a stream of flowing hot air. Dry pellets of MM mixture provide higher tap and volume densities compared with PMM mixture as shown in Table I. This is due to their different rheological behaviour.

### Table I Composition of raw material (wt%)

<table>
<thead>
<tr>
<th>Oxides</th>
<th>Unpillared montmorillonite</th>
<th>Pillared montmorillonite</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{SiO}_2)</td>
<td>72.97</td>
<td>64.25</td>
</tr>
<tr>
<td>(\text{Al}_2\text{O}_3)</td>
<td>18.00</td>
<td>31.31</td>
</tr>
<tr>
<td>(\text{Fe}_2\text{O}_3)</td>
<td>0.93</td>
<td>0.87</td>
</tr>
<tr>
<td>(\text{TiO}_2)</td>
<td>0.10</td>
<td>0.11</td>
</tr>
<tr>
<td>(\text{K}_2\text{O})</td>
<td>0.11</td>
<td>0.10</td>
</tr>
<tr>
<td>(\text{Na}_2\text{O})</td>
<td>0.06</td>
<td>0.04</td>
</tr>
<tr>
<td>(\text{CaO})</td>
<td>4.53</td>
<td>0.52</td>
</tr>
<tr>
<td>(\text{MgO})</td>
<td>3.23</td>
<td>2.85</td>
</tr>
<tr>
<td>(\text{Si}/\text{Al}) mol</td>
<td>3.5</td>
<td>1.8</td>
</tr>
<tr>
<td>(z)</td>
<td>1.35</td>
<td>2.19</td>
</tr>
</tbody>
</table>

### 2.4. Evaluation

The reacted material was weighed and analysed to determine the transformation, temperature, and time (TTT) dependence of the systems under study. The nitrogen content and unreacted (free) carbon content were determined by means of standard chemical procedures. Phase identification was performed with a Scintag (USA) powder diffractometer using nickel-filtered \(\text{CuK}_{\alpha}\) radiation. A data base of XRD patterns [13] was used for identification.

From the analytical results for raw materials and stoichiometric Equation 1 for synthesis, the final sialon should have a \(z\)-value of 1.35 for unpillared and 2.19 for the pillared samples, respectively.

In the present study the extent of the reaction, \(\alpha_i\), is expressed as

\[ \alpha_i = \frac{v_i}{v_{i0}} \]  

where \(i\) designates nitrogen and carbon, \(v_i\) is the mole of reacted carbon or bound nitrogen based on \(100\,\text{g}\) raw mixture, and \(v_{i0}\) is the total number of moles of carbon in \(100\,\text{g}\) raw mixture or moles of nitrogen theoretically bound in sialon formed by complete reaction from \(100\,\text{g}\) raw mixture (Equation 1).

Then

\[ \alpha_N = (1 - w_{\text{L,S}}) \frac{w_{\text{N,I}}}{(1 - w_{\text{L,S}}) w_{\text{N,S}}} \]  

where \(w\) is the weight fraction of nitrogen, \(N\), and weight loss, \(L\), after \(t\) h thermal treatment, \(w_{\text{N,S}}\) and \(w_{\text{L,S}}\) are the weight fractions of nitrogen and weight loss according to the stoichiometry of Equation 1, and

\[ \alpha_c = \frac{w_{c,\phi} - (1 - w_{\text{L,S}}) w_{c,I}}{w_{c,\phi}} \]  

where \(w_{c,\phi}\) and \(w_{c,I}\) are the weight fractions of carbon before and after thermal treatment.

### 3. Results and discussion

#### 3.1. Transformation–time dependence at \(1450\,\text{°C}\)

Mixture MM resulted in a nearly amorphous product after 1 h annealing (Fig. 1a). There is only one peak of low intensity (within the 20 interval indicated in Fig. 1) at the position of the main peak of silicon carbide and