

Preparation of $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ and $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$ by a precursor method

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Calcium aluminates $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ and $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$ were synthesized by thermal treatment of precursors prepared from aluminium nitrate, calcium nitrate, and tartaric acid. 1 M store aqueous solutions of $\text{Al}(\text{NO}_3)_3$ and $\text{Ca}(\text{NO}_3)_2$ were prepared by dissolution of metallic aluminium and CaCO_3 , respectively, in diluted nitric acid. After mixing these solutions at the stoichiometric ratio corresponding to the synthesized calcium aluminate tartaric acid (2 mol) for each mole of metal was added. On heating this solution at atmospheric pressure a solid precursor was obtained. It contained an organic component which was removed by calcinating the sample for 2 to 6 h in open atmosphere at the temperature of 950 °C. The synthesis of $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ and $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$ was finished after 4 h and 3 h heating of the intermediate products. The intermediate product contained no organic substances and the ratio of amounts of substances was $n(\text{CaO}) : n(\text{Al}_2\text{O}_3) = 3 : 1$ and $n(\text{CaO}) : n(\text{Al}_2\text{O}_3) = 12 : 7$, respectively, at the temperature of 1300 °C. In both cases firstly CaO and Al_2O_3 react in a reduction atmosphere caused by combustion of the organic component of precursor under formation of an orthorhombic phase $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$. In the case of the sample with the ratio $n(\text{CaO}) : n(\text{Al}_2\text{O}_3) = 3 : 1$ $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ reacts with CaO directly under formation of $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ without forming $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$ as an intermediate product. In the case of the sample with the ratio $n(\text{CaO}) : n(\text{Al}_2\text{O}_3) = 12 : 7$ $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ reacts under the influence of oxygen and/or water vapour and $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$ is formed.

Алюминаты кальция $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ и $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$ были синтезированы посредством термической обработки предшествующих продуктов, полученных из нитрата алюминия, нитрата кальция и винной кислоты. Запасные 1 М водные растворы $\text{Al}(\text{NO}_3)_3$ и $\text{Ca}(\text{NO}_3)_2$ были получены путем растворения металлического алюминия или CaCO_3 соответственно в разбавленной азотной кислоте. После смешивания этих растворов в стехиометрическом отношении, соответствующем синтезируемому алюминату кальция, было добавлено 2 моля винной кислоты на каждый моль металла. В результате нагревания этого раствора при атмосферном давлении был получен твердый предшествующий продукт. Он содержал органический компонент, который

был удален путем прокаливания образца в течение 2—6 часов на воздухе при температуре 950 °С. Синтезы $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ и $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$ были завершены после соответственно 4 и 3 часов нагревания промежуточных продуктов. Эти промежуточные продукты не содержали органических веществ, и отношение количеств окислов при температуре 1300 °С было соответственно $n(\text{CaO}):n(\text{Al}_2\text{O}_3) = 3:1$ и $n(\text{CaO}):n(\text{Al}_2\text{O}_3) = 12:7$. В обоих случаях CaO и Al_2O_3 первоначально взаимодействуют в восстановительной атмосфере, образующейся вследствие сгорания органического компонента предшествующего продукта, с образованием ромбической фазы $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$. В случае образца с отношением $n(\text{CaO}):n(\text{Al}_2\text{O}_3) = 3:1$ $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ взаимодействует с CaO с образованием непосредственно $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ без образования $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$ в качестве промежуточного продукта. В случае образца с отношением $n(\text{CaO}):n(\text{Al}_2\text{O}_3) = 12:7$ $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ реагирует под влиянием кислорода или паров воды с образованием $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$.

In preparative chemistry of solid substances the classical ceramic way of their preparation based on making mechanical mixtures from fine powdered solid particles of components which are subsequently thermally treated is less and less frequent. This procedure must be often several times repeated in order to achieve the desired degree of conversion.

In more recent procedure the mechanical homogenization of starting solid substances is replaced by more perfect homogenization in liquid or gaseous phase. This makes the conditions for synthesis of multicomponent phases with desired composition of solid phase more favourable.

For synthesizing the calcium aluminate phases $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ and $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$ the procedure developed by *Marcilly, Courty, and Delmon* [1] was used. According to this method the amorphous precursor containing elements in the desired ratio and an organic polyfunctional acid, e.g. citric, malic, tartaric, glycolic or lactic acid, is prepared. The precursor is obtained by evaporation of aqueous solution of the organic acid containing required elements.

When the precursor is heated the organic substances decompose and a homogeneous mixture of initial oxides is formed. Final product of the synthesis is obtained by suitable thermal treatment of this oxide mixture. Macrostructure and composition of amorphous precursors, a detailed description of their pyrolysis and the influence of conditions of preparation on their macrostructure and other properties are described in paper [2]. Suitability of application of this method for the preparation of calcium aluminates was verified by *Figusch and Kanclíř* [3]. *Proks and Adamkovičová* [4] modified this method also for the synthesis of silicate phases.

Experimental

Preparation of store solutions of aluminium nitrate and calcium nitrate

The calculated amount of metallic aluminium in the form of cuttings was dissolved in diluted nitric acid. (Aluminium was supplied by the Research Institute of Metals, Panenské Břežany and its purity was in the range 99.9 to 99.999 % Al.) Diluted nitric acid was prepared by mixing 200 cm³ of concentrated (65 mass %) HNO₃, anal. grade (Lachema, Brno) and 150 cm³ of distilled water. Reaction was carried out in a beaker made of SiO₂ glass immersed in water bath. Dissolution of aluminium lasts 3—7 days depending on the purity of aluminium. In order to prevent passivation of aluminium by concentrated nitric acid evaporated distilled water is added. After complete dissolution of metal the total volume of solution was filled up to 500 cm³ by distilled water. Thus 1 M solution of Al(NO₃)₃ was obtained.

50.0445 g of CaCO₃ (Specpure, JMC) was carefully dissolved in diluted (volume ratio = 1 : 1) and later in concentrated nitric acid under mild heating. (Small excess of HNO₃ does not interfere.) The obtained solution was filled in by distilled water up to the total volume 500 cm³, which results in preparation of 1 M solution of Ca(NO₃)₂.

From both store solutions doses were pipetted in the ratios corresponding to the stoichiometry of the synthesized aluminates 3CaO · Al₂O₃ and 12CaO · 7Al₂O₃, respectively. By mixing these two solutions 100—150 cm³ of clear solution was obtained. Then tartaric acid C₄H₅O₆ (2 mol) for each mole of metal was added. Tartaric acid was anal. grade (Lachema, Brno) and it was added in the form of saturated aqueous solution. At the presence of tartaric acid nitrates of metals do not crystallize at thickening of their aqueous solutions. This allows to obtain homogeneous and X-ray amorphous dry matter. The optimum amount of tartaric acid was found empirically. The obtained precursor had a suitable macrostructure and the organic substances could be easily removed by heating.

Drying of solutions and thermal treatment of precursors

Pure colourless solutions were thickened in vessels made of SiO₂ glass by heating at atmospheric pressure. Solutions changed to viscous liquid foamed with evolved gases. Suddenly the system increased several times its volume and solidified under formation of soft white foam consisting of brittle opaque material. In the last stage it is advantageous to heat the voluminous solid foam of precursor by an infrared lamp. At the places having the highest temperature, *viz.* those lying on the bottom of beaker placed on the heating element of heater, the colour of precursor turned brown as a result of partial pyrolysis. The prepared dry matter was X-ray amorphous.

Thermal decomposition of dry residue was done by its heating for 2—6 h in a laboratory furnace in open atmosphere at the temperature of 950 °C. The rate of heating was about 300 °C h⁻¹. The organic substances were burnt and the volume of solid foam decreased by 1/3—1/2. This intermediate product was white and very porous.

Synthesis of $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ was finished after 4 h heating of the intermediate product having the ratio of amounts of substances $n(\text{CaO}) : n(\text{Al}_2\text{O}_3) = 3 : 1$ at the temperature of 1300°C . Synthesis of $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$ was finished by heating the intermediate product with the ratio $n(\text{CaO}) : n(\text{Al}_2\text{O}_3) = 12 : 7$ for 3 h at the temperature of 1300°C .

Results

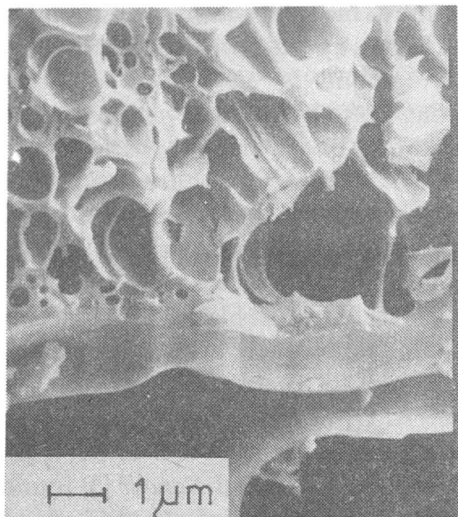
When the samples with the ratio $n(\text{CaO}) : n(\text{Al}_2\text{O}_3) = 3 : 1$ were heated at 950°C the first crystalline phases determined by X-ray analysis were CaO and $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$. Diffraction pattern of $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ was identified according to [5]. With increasing time of thermal treatment the diffraction lines corresponding to CaO diminished, while the diffraction lines of $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ were stronger. Also the first diffraction lines of $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ appeared. The samples with the ratio $n(\text{CaO}) : n(\text{Al}_2\text{O}_3) = 12 : 7$, when heated at 950°C , contained mainly $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ and small amounts of $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$ and CaO . After 3 h heating at 1200°C these samples contained mainly $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$ and only a small amount of $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$. Results of qualitative X-ray diffraction analysis of phase composition of samples in different stages of preparation of $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ and $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$ are summarized in Table 1. Estimation of the relative composition of different phases is indicated by nonequilibrium signs between mass fractions of the phases.

SEM pictures taken in different stages of preparation of $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ at the temperatures of 250°C , 950°C , and 1300°C are presented in Fig. 1.

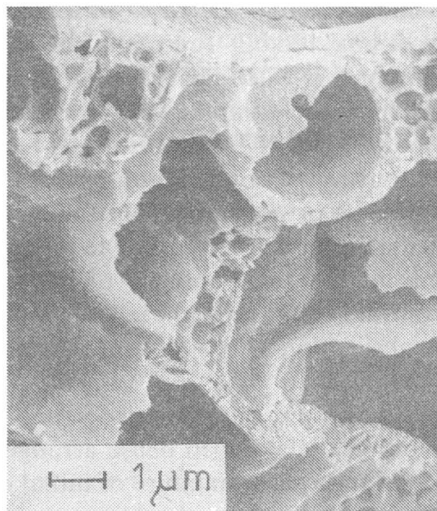
Table 1

Phase composition of samples at different stages of preparation of $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ and $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$

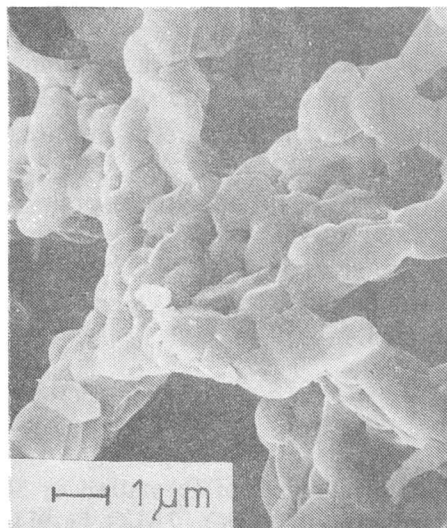
Composition $\frac{n(\text{CaO})}{n(\text{Al}_2\text{O}_3)}$	Temperature $\frac{\theta}{^\circ\text{C}}$	Time $\frac{t}{\text{h}}$	Estimation of the relative content of phases
3 : 1	950	2	$w(\text{CaO}) > w(5\text{CaO} \cdot 3\text{Al}_2\text{O}_3)$
3 : 1	950	6	$w(\text{CaO}) > w(3\text{CaO} \cdot \text{Al}_2\text{O}_3)$ $w(5\text{CaO} \cdot 3\text{Al}_2\text{O}_3) > w(3\text{CaO} \cdot \text{Al}_2\text{O}_3)$
3 : 1	1300	4	$w(3\text{CaO} \cdot \text{Al}_2\text{O}_3) = 1$
12 : 7	950	2—6	$w(5\text{CaO} \cdot 3\text{Al}_2\text{O}_3) \gg w(12\text{CaO} \cdot 7\text{Al}_2\text{O}_3)$ $w(5\text{CaO} \cdot 3\text{Al}_2\text{O}_3) \gg w(\text{CaO})$
12 : 7	1200	3	$w(12\text{CaO} \cdot 7\text{Al}_2\text{O}_3) \gg w(5\text{CaO} \cdot 3\text{Al}_2\text{O}_3)$
12 : 7	1300	3	$w(12\text{CaO} \cdot 7\text{Al}_2\text{O}_3) = 1$



a



b



c

Fig. 1. SEM pictures of samples at different stages of preparation of $3\text{CaO} \cdot \text{Al}_2\text{O}_3$.
a) $\theta = 250^\circ\text{C}$; *b)* $\theta = 950^\circ\text{C}$; *c)* $\theta = 1300^\circ\text{C}$.

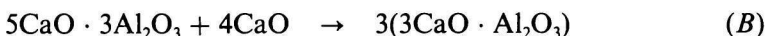
Discussion

In this work it was proved that beside the procedure described in paper [1], a homogeneous and perfectly amorphous precursor with properties suitable for synthesis of $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ and $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$, which contains substantial amount of tartaric acid, can be also prepared by thickening aqueous solutions

of chosen composition at atmospheric pressure at the temperatures substantially exceeding 100 °C. Precursor prepared in this way readily loses its organic components when heated to the temperature about 950 °C.

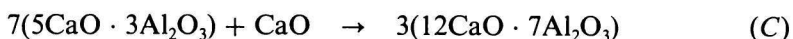
When the samples with the ratio $n(\text{CaO}):n(\text{Al}_2\text{O}_3) = 3:1$ and $n(\text{CaO}):n(\text{Al}_2\text{O}_3) = 12:7$ were heated in reduction atmosphere (this originates by the combustion of organic components of precursor) at the temperatures lower than 950 °C an orthorhombic crystalline phase $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ was formed as intermediate product. According to [6] this phase is stable in the system $\text{CaO}-\text{Al}_2\text{O}_3$ only at the total absence of oxygen (partial pressure of oxygen 10^{-25} Pa). Contrary to that the phase $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$ is stabilized at higher temperatures by absorption of oxygen from the surrounding atmosphere even at the partial pressure of 10^{-3} Pa [7]. A possible explanation of the preferential formation of $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ in comparison to $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$ at these conditions can be found in the assumed dense arrangement of ions in the structure of homogeneous amorphous mixture of initial oxides. Also *Figusch* and *Kanclíř* [3] found $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ to be the primary crystalline phase in intermediate products of synthesis of $3\text{CaO} \cdot \text{Al}_2\text{O}_3$, $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$, and $4\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ when the method based on decomposition of tartrates was used. *Figusch* [8] has found that $5\text{CaO} \cdot \text{Al}_2\text{O}_3$ is formed in vacuum also in the initial stage of crystallization of precursors obtained by thermal decomposition of calcium nitrate and aluminium nitrate in mixtures with the ratio $n(\text{CaO}):n(\text{Al}_2\text{O}_3) = 3:1$ and $n(\text{CaO}):n(\text{Al}_2\text{O}_3) = 12:7$.

From X-ray analysis of our samples it follows that when the ratio $n(\text{CaO}):n(\text{Al}_2\text{O}_3) = 3:1$ the reaction of CaO with Al_2O_3 in non-oxygen atmosphere gives $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ which at these conditions reacts with CaO under formation of $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ and the intermediate product $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$ is not formed.



This mechanism of formation of $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ is advantageous because the formation of $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$ [3, 9] (especially in the form of $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$) negatively influences the rate of formation of $3\text{CaO} \cdot \text{Al}_2\text{O}_3$.

At heating samples with the ratio $n(\text{CaO}):n(\text{Al}_2\text{O}_3) = 12:7$ firstly the intermediate product $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ is formed in reduction atmosphere (eqn (A)) and this, in the presence of oxygen or water vapour (which acts as a catalyst [6] or a source of oxygen) further reacts with CaO under formation of $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$.



The rate of this reaction is low. Even after 3 h heating at 1200 °C at the sufficient transport of air the reaction mixture was cleared of organic components but it still contained an amount of $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ which could be detected by X-ray analysis. This experience might be probably used for preparation of the pure phase $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ by heating precursor on the base of tartaric acid at the temperature about 950 °C at controlled supply of oxygen.

No analysis on the presence of OH groups in the structure of the synthesized $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$ was carried out.

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