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Fuel mixture approach for solution combustion synthesis of $Ca_3Al_2O_6$ powders

Robert Ianoş [a,*], Ioan Lazău [a], Cornelia Păcurariu [a], Paul Barvinschi [b]

[a] "Politehnica" University of Timişoara, Faculty of Industrial Chemistry and Environmental Engineering, P-ţa Victoriei No. 2, Timişoara 300006, Romania
[b] West University of Timişoara, Faculty of Physics, Bd. V. Pârvan No. 4, Timişoara 300223, Romania

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ABSTRACT

Single-phase $3CaO\cdot Al_2O_3$ powders were prepared via solution combustion synthesis using a fuel mixture of urea and β-alanine. The concept of using this fuel mixture comes from the individual reactivity of calcium nitrate and aluminum nitrate with respect to urea and β-alanine. It was proved that urea is the optimum fuel for $Al(NO_3)_3$ whereas β-alanine is the most suitable fuel for $Ca(NO_3)_2$. X-ray diffraction and thermal analysis investigations revealed that heating at 300 °C the precursor mixture containing the desired metal nitrates, urea and β-alanine triggers a vigorous combustion reaction, which yields single-phase nanocrystalline $3CaO\cdot Al_2O_3$ powder (33.3 nm). In this case additional annealing was no longer required. The use of a single fuel failed to ensure the formation of $3CaO\cdot Al_2O_3$ directly from the combustion reaction. After annealing at 900 °C for 1 h, the powders obtained by using a single fuel (urea or β-alanine) developed a phase composition comprising of $3CaO\cdot Al_2O_3$, $12CaO\cdot 7Al_2O_3$ and CaO.

1. Introduction

CaO–Al_2O_3 binary system is one of the most intensively studied oxide systems. Mainly, this is the consequence of the hydraulic properties developed by some of the oxide compounds present in this system—$CaO\cdot Al_2O_3$ (CA), $CaO\cdot 2Al_2O_3$ (CA_2), $12CaO\cdot 7Al_2O_3$ ($C_{12}A_7$)—exploited during aluminous cement production. The other two compounds—$CaO\cdot 6Al_2O_3$ (CA_6) and $3CaO\cdot Al_2O_3$ (C_3A)—do not find a place among high-alumina cements. If, in the case of CA_6, this is explained by the absence of its hydraulic properties, in the case of C_3A this is due to its exaggerated reactivity with respect to water. Yet, C_3A is one of the four important mineralogical compounds which occur in the Portland cement composition. Recently, note has been taken of the C_3A ability to generate solid solutions by various substitutions [1,2] as well as its influence as a doping phase on in vitro biocompatibility and bioactivity of CA [3].

One of the peculiarities of C_3A synthesis via ceramic method, based on solid state reactions of oxides and/or salt mixtures, is that its formation is always preceded by the formation of other calcium aluminates such as $C_{12}A_7$ [4,5]. Concerning the possible intermediate phases preceding the C_3A formation via ceramic method, the results obtained by various authors are often contradictory [6]. Even though there is a consensus in the case of $C_{12}A_7$ formation—a transitory phase in the C_3A synthesis—the same cannot be stated about the intermediate formation of other calcium aluminates such as CA.

Ghoroi and Suresh [4] have shown that the first and the only transitory phase that appears when heating a stoichiometric mixture of $CaCO_3$ and $Al(OH)_3$ for the synthesis of C_3A is $C_{12}A_7$. The same authors noticed that in the phase composition of the samples annealed at 1300 °C with a soaking time of 3 h, significant amounts of $C_{12}A_7$ were present alongside C_3A.

On the other hand, Mohamed and Sharp [5] have pointed out that in the $Ca_3Al_2O_6$ formation via ceramic method both, $C_{12}A_7$ and CA, were observed. With or without the intermediate formation of CA, one thing is for sure: in the classical method, $Ca_3Al_2O_6$ formation is always preceded by the formation of $C_{12}A_7$. In addition, the preparation of single-phase C_3A powders requires expensive thermal treatments even in the case of many chemical synthesis methods due to the formation of $C_{12}A_7$ as a transitory phase.

For instance, in order to obtain $Ca_3Al_2O_6$ using the organic steric entrapment method, Lee and Kriven [7] annealed the resulted precursor 1 h at 1000 °C; nevertheless they obtained a mixture of $Ca_3Al_2O_6$ and CaO. According to Yuan et al. [8], using the citrate route one can obtain single-phase $Ca_3Al_2O_6$ at temperatures as high as 1000 °C.

Considering the excellent results in the synthesis of other oxide compounds, the sol–gel route was one of the chemical methods by which one could expect C_3A synthesis to take place directly, without any intermediate phases. However, different authors [9] reached the same conclusion: after annealing the gel at 900 °C with a soaking time of 2 h, a mixture of C_3A, $C_{12}A_7$ and CaO was achieved. Geetha et al. [10] have shown that using gel to crystalline conversion route, the synthesis of pure $Ca_3Al_2O_6$ is achieved only after annealing at 1200 °C for 4 h.

So far, among all the soft chemical methods used for C_3A synthesis, thermal decomposition of complex combinations based on triethanolamine [11] led to the best results. Pati et al. [11] reported the formation of single-phase C_3A powder after annealing at 1000 °C an organic precursor based on triethanolamine.

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* Corresponding author. Tel.: +40 256 404167.
E-mail address: robert_ianos@yahoo.com (R. Ianoş).

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In the recent years, combustion synthesis has attracted significant attention as a new alternative for the preparation of various ceramic powders [12]. Briefly, this method consists of rapidly heating at 300 °C a saturated aqueous solution containing the desired metal nitrates and a suitable organic fuel (urea, glycine) until the mixture ignites and a self-sustaining combustion reaction takes place resulting in a dry, usually crystalline fine oxide powder. Among the most important advantages of this process are: low energy requirements, since no additional annealing is necessary, time saving (the entire process takes a few minutes only) and its environmentally friendly attribute—given the chemical nature of combustion by-products (N_2, CO_2 and H_2O).

Segadaes et al. [13] already reported the synthesis of CA, $C_{12}A_7$ and CA_2 powders by the combustion reaction of metal nitrates with urea. Kingsley et al. [14] and Taş [15] are among the few authors which aimed to prepare C_3A powders by combustion synthesis. The experimental research done by Taş [15] pointed out that after annealing the powders prepared by using urea, glycine or carbohydrazide up to 950 °C with a soaking time of 48 h a mixture of C_3A, $C_{12}A_7$ and CA was obtained. According to the same author, the C_3A formation as a single phase required temperatures of at least 1050 °C, with a soaking time of 48–72 h. During the preparation of C_3A–TiB_2 matrix composites by Self-propagating High-temperature Synthesis (SHS) Yi et al. [16] also noticed the formation of undesired $C_{12}A_7$ and CaO.

Considering the difficulty of synthesizing single-phase tricalcium aluminate, the work that fallows describes an innovative version of the combustion synthesis based on the redox reaction of the corresponding metal nitrates with fuel mixtures [17,18]. This new version enables the formation of single-phase tricalcium aluminate, $Ca_3Al_2O_6$, directly from the combustion reaction without any additional annealing.

2. Experimental

The starting raw materials were of pro analysis purity degree (Merck, Germany); $Ca(NO_3)_2 \cdot 4H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ were used as oxidizing agents whereas CH_4N_2O (urea, U) and $C_3H_7NO_2$ (β-alanine, β-Ala) were used as fuels. In addition, a mixture of urea and β-alanine (U:β-Ala = 5:2) was tested. Stoichiometric metal nitrates/fuel molar ratios were used in all samples. The stoichiometry of each combustion reaction was calculated according to Jain et al.'s [19] indications. Batches were calculated to obtain 0.04 moles of $Ca_3Al_2O_6$. The necessary raw material amounts were dissolved in 30.0 mL of distilled water. Subsequently, the capsule with the sample was rapidly heated to 300 °C in a heating mantle to promote water evaporation and the initiation of the combustion reaction. The time interval between the initiation of combustion reaction and its ending was established based on digital video recordings of combustion experiments.

Thermogravimetric analysis (TG) and differential thermal analysis (DTA) studies were conducted (Netzsch STA 449 C) on the precursor mixtures at a constant heating rate of 10 °C/min up to 900 °C, in air static atmosphere, using alumina crucibles. BET specific surface area (S_{BET}) of the powders was measured using a Micromeritics ASAP 2020 instrument and nitrogen as the adsorption gas.

Losses on ignition were determined after annealing the as-resulted powders at 900 °C for 1 h. The evolution of the crystalline phases was monitored by XRD, using a Bruker D8 Advance System, $Cu_{K\alpha}$ monochromated radiation. The crystallite size was determined based on the XRD patterns (800 and 844 *hkl* planes) using the Sherrer's Eq. (1):

$$D = \frac{0.9 \cdot \lambda}{\beta \cdot \cos\theta} \tag{1}$$

where: D is the crystallite size in nm, λ is the radiation wavelength ($Cu_{K\alpha}$, 0.15406 nm), β is the full width at half of the maximum in radians, and θ is the Bragg-angle.

Table 1
Combustion reaction occurrence in stoichiometric metal nitrate/fuel binary systems.

Fuel	$Ca(NO_3)_2$			$Al(NO_3)_3$		
	T_{ad} (K)	Reaction time (s)	$Ca(NO_3)_2$:Fuel (molar ratio)	T_{ad} (K)	Reaction time (s)	$Al(NO_3)_3$:Fuel (molar ratio)
U	1284	No combustion reaction, white product	3:5	1456	10, flame combustion, white powder	2:5
β-Ala	2213	<1, violent explosion, white powder	3:2	2073	240, smoldering combustion, black powder	2:2

Taking into account the cubic symmetry of C_3A, the lattice parameter, a, was calculated using Eq. (2):

$$a = d_{hkl}\left(h^2 + k^2 + l^2\right)^{1/2} \tag{2}$$

where: d_{hkl} is the spacing between adjacent members of the *hkl* planes, *hkl* are the Miller indices for the same crystal-lattice planes as those used for D calculus (800 and 844).

Assuming that combustion reactions are complete, the adiabatic temperature of each reaction was calculated, Eq. (3), by using the FactSage 5.5 thermochemical software and its associated database:

$$T_{ad} = T_0 + \frac{\Delta H_r - \Delta H_p}{c_p} \tag{3}$$

where: T_{ad} is the adiabatic temperature in K; T_0 is 298 K; ΔH_r and ΔH_p are the standard enthalpies of formation of reactants and reaction products in kJ/mol, respectively; c_p is the heat capacity of reaction products at constant pressure in kJ/molK.

The adiabatic temperature is the maximum temperature reached within the reactant system assuming the combustion reaction is performed under adiabatic conditions. Obviously, in reality the combustion temperature is considerably lower than the adiabatic temperature due to various factors such as heat loss, incomplete combustion etc.

3. Results and discussion

3.1. The combustion behavior of stoichiometric metal nitrate/fuel binary mixtures

The individual reactivity of calcium nitrate and aluminum nitrate with respect to urea and β-alanine has been tested initially in order to establish the most suitable fuel for each metal nitrate [17,18]. Table 1 summarizes the behavior of each combustion process as well the adiabatic temperature corresponding to each reaction.

As can be seen in Table 1, there is no combustion reaction in the case of $Ca(NO_3)_2$:urea mixture, whereas $Al(NO_3)_3$ reacts very fast with urea, with the appearance of a glowing incandescent area. The reaction product between $Ca(NO_3)_2$ and urea is a white compact solid material, consisting of a mixture of calcium nitates (Fig. 1), which is in agreement with our previous findings [17,18] concerning the absence of the combustion reaction in the $Ca(NO_3)_2$/urea system due to urea hydrolysis [20] which takes place at temperatures above 80 °C, according to Eq. (4):

$$CO(NH_2)_2 + H_2O \rightarrow CO_2 + 2NH_3 \tag{4}$$

On the other hand, the mixture containing $Al(NO_3)_3$ and urea leads to the formation of single-phase crystalline α-Al_2O_3 (Fig. 2), in agreement with the highly exothermic nature of the combustion reaction. Stoichiometric $Al(NO_3)_3$/β-alanine mixture leads to the formation of a black amorphous powder (Fig. 2), which indicates an incomplete combustion reaction. Unlike $Al(NO_3)_3$ which gives a slow

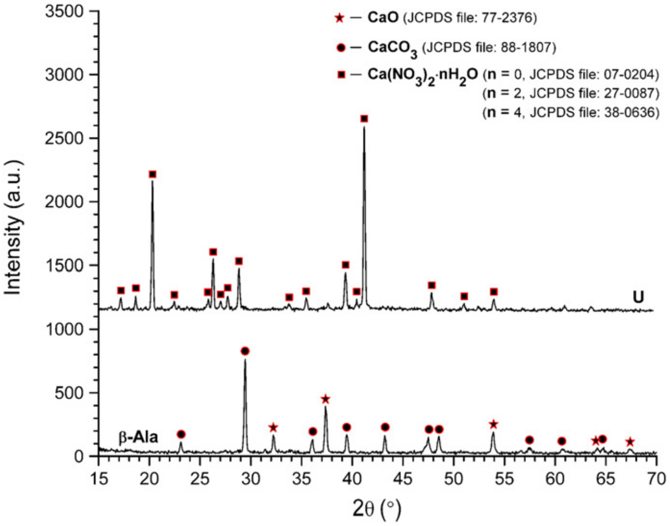

Fig. 1. XRD patterns of the powders prepared by the combustion reaction of calcium nitrate with urea or β-alanine.

smoldering combustion reaction with β-alanine, $Ca(NO_3)_2$ reacts extremely violently with β-alanine (Table 1). In this last case the combustion reaction is an explosion. The XRD pattern of the resulted powder indicates the presence of $CaCO_3$ and CaO (Fig. 1).

These results suggest that there is a predilection of $Ca(NO_3)_2$ and $Al(NO_3)_3$ with respect to urea and β-alanine [17,18]. Taking into account the adiabatic temperature on one hand and the practical evolution of combustion reactions on the other hand, one can notice that there is no obvious correlation between these parameters (Table 1). In other words, an elevated adiabatic temperature does not necessarily imply a vigorous combustion reaction and vice versa.

A more reasonable explanation for the predilection of metal nitrates with respect to urea and β-alanine comes from the initiation mechanism of combustion reactions. According to different authors [21–23] the initiation of the combustion process usually takes place between the gaseous decomposition products of metal nitrate and fuel. Therefore it can be inferred that a prerequisite for the occurrence of combustion reaction in metal nitrate/fuel systems is the existence of an overlapping temperature interval in which thermal decomposition of metal nitrate and fuel occurs simultaneously.

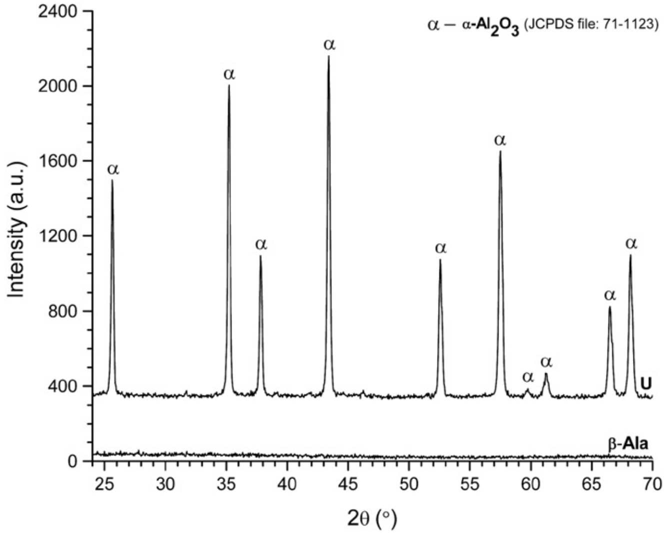

Fig. 2. XRD patterns of the powders prepared by the combustion reaction of aluminum nitrate with urea or β-alanine.

Table 2
Solution combustion synthesis of $Ca_3Al_2O_6$ powders.

Sample	Fuel	$Ca(NO_3)_2$:$Al(NO_3)_3$:Fuel (molar ratio)	Reaction time (s)	T_{ad} (K)	Color of the powder	Loss on ignition (%)
5	U	3:2:10	No combustion reaction	1447	Yellowish	49.6
6	B-Ala	3:2:4	15, red incandescence	2143	Light gray	9.1
7	U + β-Ala	3:2:5:2	60, glowing incandescence	1767	White	0.1

Since $Ca(NO_3)_2$ starts decomposing into CaO and nitrogen oxides above 400 °C [24] one can note that at this temperature the entire amount of urea has already been consumed in the hydrolyses reaction (3) and thermal decomposition process, which takes place at 133 °C [20]. As a result of urea depletion, no combustion reaction occurs in the calcium nitrate/urea system. At the same time, β-alanine, which has the ability of generating complex combinations, decomposes above 200 °C and reacts with $Ca(NO_3)_2$ triggering a vigorous explosion.

Unlike $Ca(NO_3)_2$, $Al(NO_3)_3$ starts decomposing above 150 °C [25]. Obviously the urea hydrolysis process reaches some extent in this case too. However, there is still enough fuel in the raw material mixture to trigger the initiation of the combustion reaction. On the other hand, β-alanine gives a smoldering combustion reaction with aluminum nitrate, as aluminum nitrate begins its decomposition earlier. In this case, the slower evolution of the combustion reaction could be assigned to the partial depletion of aluminum nitrate.

3.2. Fuel mixture approach for $Ca_3A_2O_6$ combustion synthesis

Considering the experimental results presented above, it can be inferred that urea is a more appropriate fuel for $Al(NO_3)_3$ whilst β-alanine is more adequate for $Ca(NO_3)_2$ [17,18]. On these bases, an attempt has been made to obtain pure, well-crystallized C_3A powders by combustion synthesis. While recipes 5 and 6 are the reference samples (Eqs. (5) and (6)), meaning classical combustion recipes involving the use of a single fuel, recipe 7 represents the innovative element, which consists in using a fuel mixture containing the most suitable fuel for each metal nitrate: urea for aluminum nitrate and β-alanine for calcium nitrate (Eq. (7)). Assuming that $Al(NO_3)_3$ will react with urea whereas $Ca(NO_3)_2$ will react with β-alanine and using

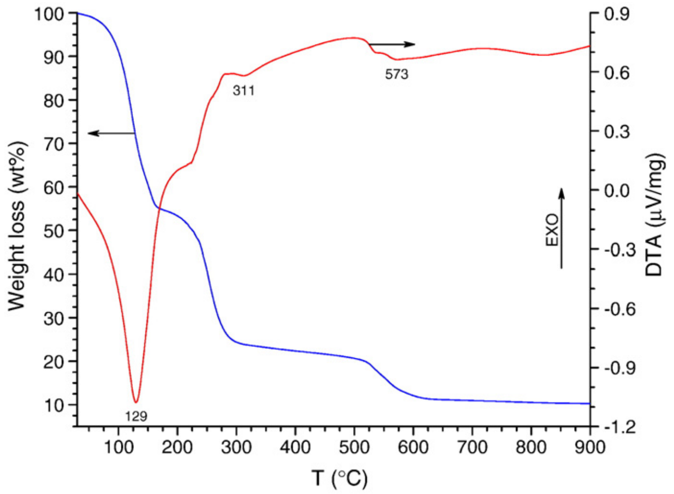

Fig. 3. TG and DTA curves of the $Ca_3Al_2O_6$ precursor mixture consisting of calcium nitrate, aluminum nitrate and urea (sample 5).

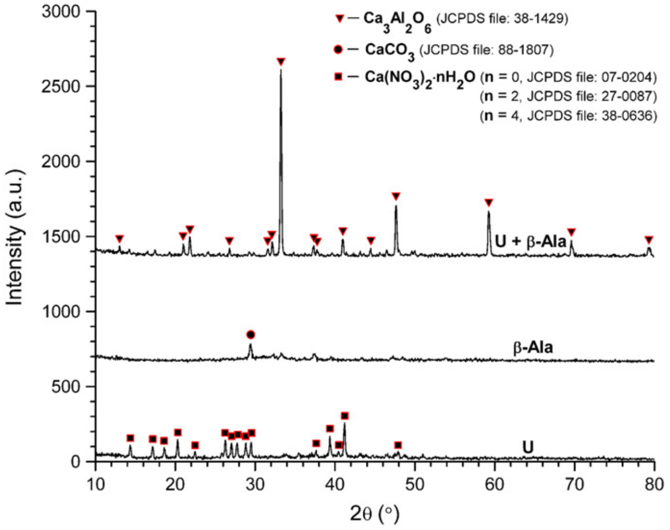

Fig. 4. XRD patterns of the powders prepared by the combustion reaction of calcium nitrate, aluminum nitrate with different fuels.

stoichiometric metal nitrate/fuel proportions one reaches a molar ratio of urea:β-alanine = 5:2 (Eq. (7)).

$$3Ca(NO_3)_2 + 2Al(NO_3)_3 + 10CH_4N_2O \rightarrow Ca_3Al_2O_6 + 10CO_2 + 20H_2O + 16N_2 \quad (5)$$

$$3Ca(NO_3)_2 + 2Al(NO_3)_3 + 4C_3H_7NO_2 \rightarrow Ca_3Al_2O_6 + 12CO_2 + 14H_2O + 8N_2 \quad (6)$$

$$3Ca(NO_3)_2 + 2Al(NO_3)_3 + 2C_3H_7NO_2 + 5CH_4N_2O \rightarrow Ca_3Al_2O_6 + 11CO_2 + 17H_2O + 12N_2 \quad (7)$$

As can be seen in Table 2, the combustion behavior of recipes consisting of $Ca(NO_3)_2$, $Al(NO_3)_3$ and a single fuel or mixture of fuels is essentially different. Adiabatic temperature calculations (Table 2) indicate that urea gives the lowest adiabatic temperature, whilst β-alanine leads to the highest adiabatic temperature. In terms of $Ca_3Al_2O_6$ formation, these values indicate that the reaction of β-alanine with calcium nitrate and aluminum nitrate (Eq. (6)) would generate the highest temperature and thus the formation of tricalcium aluminate would be significantly enhanced. Nevertheless, the experimental results proved that the formation of $Ca_3Al_2O_6$ cannot be discussed only in terms of adiabatic temperature.

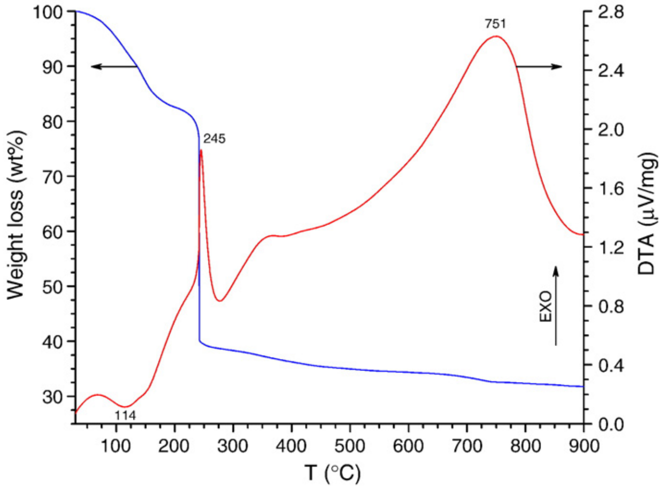

Fig. 6. TG and DTA curves of the $Ca_3Al_2O_6$ precursor mixture consisting of calcium nitrate, aluminum nitrate and β-alanine (sample 6).

In the case of sample containing urea as fuel (sample 5) no combustion reaction occurred. Thermal analysis investigations conducted on the precursor mixture containing calcium nitrate, aluminum nitrate and urea (Fig. 3) confirm the absence of the combustion reaction, the significant loss on ignition (Table 2) and the presence of residual calcium nitrate on the XRD pattern of the resulted powder (Fig. 4). No intense exothermic peak, which is typical for combustion reactions, could be seen on the DTA curve, whereas the TG curve suggests a three-step decomposition process of the precursor mixture.

Moisture elimination, urea decomposition [20] and aluminum nitrate partial decomposition [25] are responsible for the first and the most important weight loss (44.1%), which occurs up to 162 °C and is accompanied by an endothermic effect on the DTA curve. The finalization of aluminum nitrate decomposition process is responsible for the weight loss over the temperature range 229–280 °C [25]. Considering that the powder prepared by heating the precursor mixture at 300 °C still contains unreacted calcium nitrate (Fig. 4), one can conclude that the weight loss which occurs between 511 and 594 °C is due to the decomposition of calcium nitrate [24].

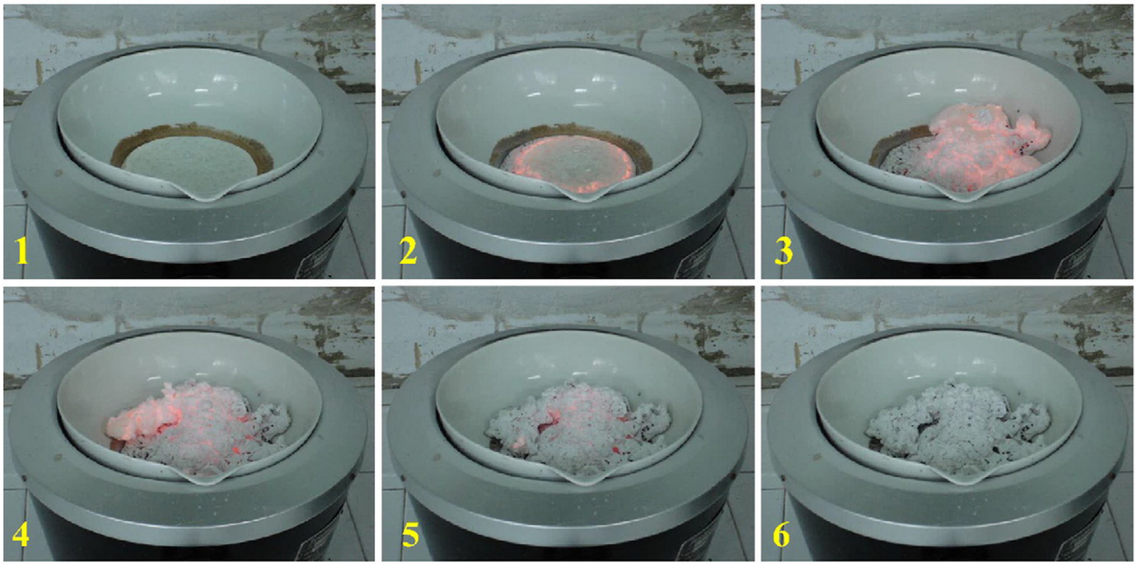

Fig. 5. The evolution of combustion reaction (6); $Ca(NO_3)_2$:$Al(NO_3)_3$:β-alanine = 3:2:4.

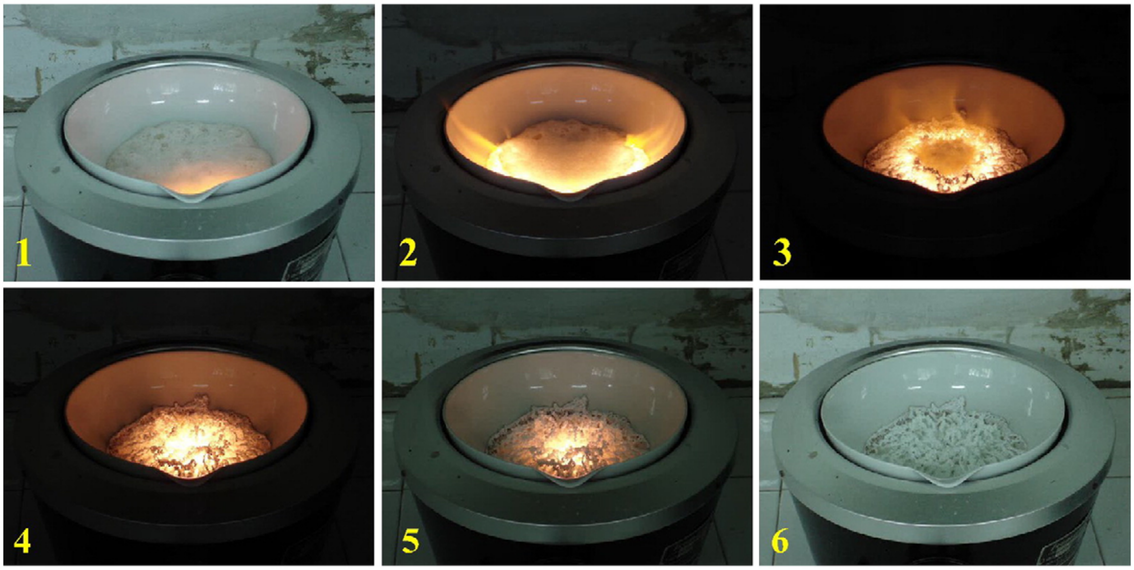

Fig. 7. The evolution of combustion reaction (7); $Ca(NO_3)_2$:$Al(NO_3)_3$:β-alanine:urea = 3:2:2:5.

Taking into account the different reactivity of $Ca(NO_3)_2$ and $Al(NO_3)_3$ with respect to urea (Table 1) as well the thermal analysis results of sample 5 (Fig. 3), one can conclude that in the raw material mixture designed for the C_3A synthesis, $Ca(NO_3)_2$ acts as an inhibitor preventing the occurrence of the combustion reaction.

On the other hand, β-alanine (sample 6)—which reacts very fast with $Ca(NO_3)_2$ and considerably slower with $Al(NO_3)_3$—triggers an exothermic combustion reaction characterized by the appearance of a red incandescent area (Fig. 5).

Despite the rapid evolution of this reaction and the high adiabatic temperature (Table 2), XRD analysis proved that the resulted powder was poorly crystalline, since there is only one peak on the XRD pattern, which could be assigned to $CaCO_3$, calcite (Fig. 4). The absence of the desired crystalline phase, C_3A, the color and the loss on ignition of this powder suggest that the temperature within the reactant system was far below the adiabatic one.

Thermal analysis investigations conducted on precursor mixture consisting of calcium nitrate, aluminum nitrate and β-alanine (sample 6) indicate that combustion reaction occurs at 245 °C, when a significant weight loss appears on the TG curve, associated with an exothermic peak on the DTA curve (Fig. 6). The endothermic effect from 114 °C could be assigned to water elimination as well as to the beginning of aluminum nitrate decomposition process [25].

The gradual weight loss, which can be seen on the TG curve at temperatures higher than 245 °C could be assigned to the removal of carbon impurities, originating from the incomplete evolution of the combustion reaction. This is consistent with the loss on ignition (Table 2) and the gray color of the combustion synthesized powder (Fig. 5). Moreover, the wide and intense exothermic peak situated at 751 °C suggests the superposition of several exothermic processes, such as residual carbon oxidation and crystallization of $C_{12}Al_7$ and C_3A.

Table 3

BET surface area, crystallite size and lattice parameter of $Ca_3Al_2O_6$ before and after annealing.

Sample	Fuel	Before annealing			After annealing at 900 °C/1 h		
		S_{BET} (m^2/g)	D_{XRD} (nm)	*a* (Å)	S_{BET} (m^2/g)	D_{XRD} (nm)	*a* (Å)
5	U	–	–	–	2.8	23.1	15.240
6	β-Ala	–	–	–	1.9	21.3	15.243
7	U + β-Ala	1.6	33.3	15.247	1.5	36.3	15.252

The occurrence of the combustion reaction in the system containing β-alanine as fuel cannot be explained only by the higher value of the adiabatic temperature, but rather by considering that β-alanine, unlike urea, is able to generate combustion reactions with each metal nitrate separately (Table 1). Considering the individual reactivity the two metal nitrates manifest with respect to β-alanine (Table 1) it can be inferred that in the case of samples 6, $Al(NO_3)_3$ moderates the violent reaction of $Ca(NO_3)_2$ with β-alanine. In other words, $Ca(NO_3)_2$ accelerates the development of the combustion reaction between $Al(NO_3)_3$ and β-alanine.

Taking into account the adiabatic temperature criterion, one could expect that the use of urea and β-alanine fuel mixture (sample 7) would have a less favorable combustion behavior by comparison to sample 6. However, the combustion reaction between calcium nitrate, aluminum nitrate and the fuel mixture consisting of urea and β-alanine was actually the most exothermic one, as the reaction was accompanied by the appearance of a bright glowing incandescent area. After combustion reaction ended (60 s) a white powder (Fig. 7) with a specific surface area of 1.6 m^2/g was obtained.

The most eloquent piece of evidence which stands for the higher exotermicity of reaction (7) is represented by the formation of single-phase C_3A directly from the combustion reaction (Fig. 4). The resulted

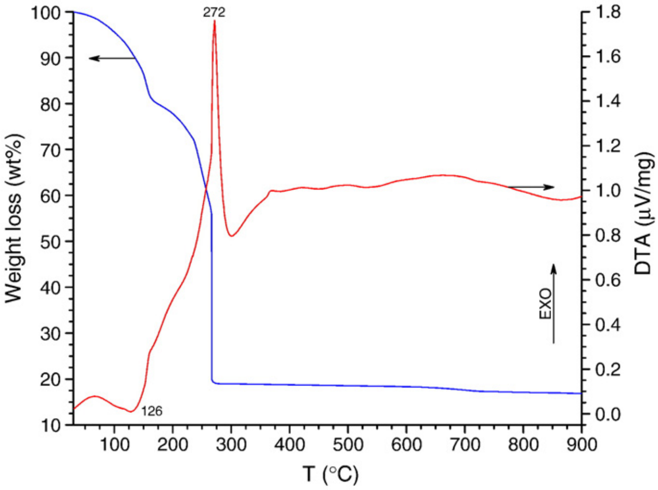

Fig. 8. TG and DTA curves of the $Ca_3Al_2O_6$ precursor mixture consisting of calcium nitrate, aluminum nitrate, urea and β-alanine (sample 7).

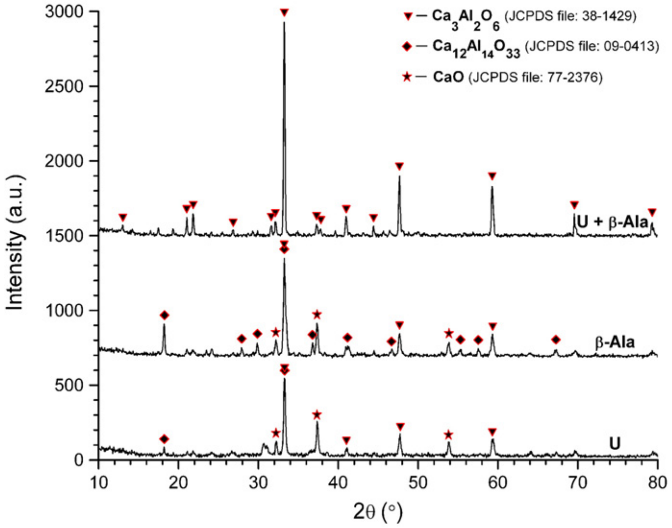

Fig. 9. XRD patterns of the powders obtained from $Ca(NO_3)_2$, $Al(NO_3)_3$ and various fuels after annealing at 900 °C for 1 h.

C_3A had an average crystallite size of 33.3 nm (Table 3) and the calculated lattice parameter (15.247 Å) proved to be very close to the value given in JCPDS file 38–1429 for pure $Ca_3Al_2O_6$ (15.26 Å). To the best of our knowledge this is the first time when pure $C_3A_2O_6$ is prepared directly from the combustion reaction, without any additional annealing. This result indicates that the use of urea and β-alanine fuel mixture, as we suggest, is definitely more efficient that the use of a single fuel, as other authors reported [14,15]. On the other hand, this behavior validates once again the experimental observation concerning the individual reactivity of $Ca(NO_3)_2$ and $Al(NO_3)_3$ with respect to urea and β-alanine (Table 1).

Thermal analysis investigations revealed that the precursor mixture containing calcium nitrate, aluminum nitrate, urea and β-alanine (sample 7) self-ignites at 272 °C (Fig. 8). Above this temperature the sample does not undergo any important transformations, which indicate that combustion reaction reached completion. The absence of any other phenomena involving weight loss after the combustion reaction ended is also supported by the insignificant loss on ignition of the as-resulted white powder (Table 2). Also in this case the initiation of the combustion reaction is preceded by an endothermic effect (126 °C), which can be attributed to water elimination and partial decomposition of urea and aluminum nitrate [20,25].

Considering the absence of crystalline C_3A as well as the important loss on ignition (Table 2) of the powders obtained by using a single fuel (samples 5 and 6), one can conclude that these recipes do not represent an efficient solution for C_3A combustion synthesis. Furthermore, the subsequent annealing of these powders at 900 °C leads to the formation of a phase mixture consisting of C_3A, $C_{12}A_7$ and CaO (Fig. 9), which is very much alike the results reported by Taş [15]. Similar to the ceramic method, in this initial version of the combustion synthesis—involving the use of a single fuel—additional thermal treatments are required to promote the formation of single-phase tricalcium aluminate.

On the other hand, the subsequent thermal treatment has practically no influence on the phase composition of sample 7, which resulted directly from the combustion reaction, since the only crystalline phase present on the XRD pattern is C_3A (Fig. 9). Another aspect that needs to be emphasized is that the crystallinity degree of the C_3A obtained by using the urea and β-alanine fuel mixture does not modify significantly after annealing as long as the crystallite size and the lattice parameter exhibit only a slight increase (Table 3). In addition, the specific surface area of the powder slightly decreases after annealing to 1.5 m^2/g. This means that during the combustion reaction, the existing thermal conditions within the reactant system were at least equivalent to a subsequent thermal treatment at 900 °C for 1 h.

Among all combustion-synthesized powders, the one obtained by using the urea and β-alanine fuel mixture consists of single-phase C_3A, exhibits the lowest loss on ignition (Table 2), the lowest surface area and the largest crystallite size (Table 3). In other words, the use of urea and β-alanine fuel mixture maximizes the exothermic effect of the combustion reaction, ensuring the prerequisites for the direct formation of pure nanocrystalline $Ca_3Al_2O_6$, without any additional annealing.

4. Conclusions

The obtained results suggest that there is a predilection of calcium nitrate and aluminum nitrate with respect to urea and β-alanine. Urea proved to be a more adequate fuel for aluminum nitrate while β-alanine proved to be more appropriate for calcium nitrate.

Adiabatic temperature calculations and the evolution of combustion reactions in metal nitrate/fuel systems suggested that kinetic factors overrule the thermodynamic factors.

Since calcium nitrate and aluminum nitrate exhibit a different reactivity with respect to urea and β-alanine, it was proved in the case of C_3A preparation the best results are obtained when a mixture of urea and β-alanine is used.

The use of a single fuel (urea or β-alanine)—as is usually done in the initial version of the combustion synthesis—does not allow the formation of single-phase $Ca_3Al_2O_6$ directly from the combustion reaction. Whereas urea failed to act as fuel, β-alanine yields a poorly crystalline powder consisting of $CaCO_3$. After annealing these powders at 900 °C with 1 h soaking time several crystalline phases occurred: $Ca_3Al_2O_6$, $Ca_{12}Al_{14}O_{33}$ and CaO.

On the other hand, the version we suggest—that is, the use of a fuel mixture consisting of urea and β-alanine (molar ration 5:2)—allows the formation of pure, well-crystallized $Ca_3Al_2O_6$ powder directly from the combustion reaction, without any further annealing.

References

[1] K. Fukuda, S. Inoue, H. Yoshida, Cationic substitution in tricalcium aluminate, Cem. Concr. Res. 33 (2003) 1771–1775.
[2] X. Gao, L. Lei, C. Lv, Y. Sun, H. Zheng, Y. Cui, Preparation and photoluminescence property of a loose powder, $Ca_3Al_2O_6:Eu^{3+}$ by calcination of a layered double hydroxide precursor, J. Solid State Chem. 181 (2008) 1776–1781.
[3] S.H. Oh, R. Finones, S. Jin, S.Y. Choi, K.N. Kim, Influence of tricalcium aluminate phase on in vitro biocompatibility and bioactivity of calcium aluminate bone cement, J. Mater. Res. 19 (2004) 1062–1067.
[4] C. Ghoroi, A.K. Suresh, Solid–solid reaction kinetics: formation of tricalcium aluminate, AIChE J. 53 (2007) 502–513.
[5] B.M. Mohamed, J.H. Sharp, Kinetics and mechanism of formation of tricalcium aluminate, $Ca_3Al_2O_6$, Thermochim. Acta 388 (2002) 105–114.
[6] J.M.R. Mercury, A.H. De Aza, X. Turrillas, P. Pena, The synthesis mechanism of $Ca_3Al_2O_6$ from soft mechanochemically activated precursors studied by time-resolved neutron diffraction up to 1000 °C, J. Solid State Chem. 177 (2004) 866–874.
[7] S.J. Lee, W.M. Kriven, Synthesis and hydration study of Portland cement components prepared by the organic steric entrapment method, Mater. Struct. 38 (2005) 87–92.
[8] X. Yuan, Y.B. Xu, Y.Y. He, Synthesis of $Ca_3Al_2O_6$ via citric acid precursor, Mater. Sci. Eng. A 447 (2007) 142–145.
[9] D. Stephan, P. Wilhalm, Synthesis of pure cementitous phases by sol–gel process as precursor, Z. Anorg. Allg. Chem. 630 (2004) 1477–1483.
[10] K. Geetha, A.M. Umarji, T.R.N. Kutty, Ceramic joining through reactive wetting of alumina with calcium aluminate refractory cements, Bull. Mater. Sci. 23 (2000) 243–248.
[11] R.K. Pati, A.B. Panda, P. Pramanik, Preparation of nanocrystalline calcium aluminate powders, J. Mater. Synth. Process. 10 (2002) 157–161.
[12] S.T. Aruna, A.S. Mukasyan, Combustion synthesis and nanomaterials, Curr. Opin. Solid State Mater. Sci. 12 (2008) 44–50. DOI: 10.1016/j.cossms.2008.12.002.
[13] A.M. Segadeas, D.A. Fumo, M.R. Morelli, Combustion synthesis of calcium aluminates, Mater. Res. Bull. 31 (1996) 1243–1255.
[14] J.J. Kingsley, K. Suresh, K.C. Patil, Combustion synthesis of fine-particle metal aluminates, J. Mater. Sci. 25 (1990) 1305–1312.

[15] A.C. Taş, Chemical preparation of the binary compounds in the calcia-alumina system by self-propagating combustion synthesis, J. Am. Ceram. Soc. 81 (1998) 2853–2863.

[16] H.C. Yi, J.I. Guigné, J.J. Moore, F.D. Schwowengerdt, L.A. Robinson, A.R. Manerbino, Preparation of calcium aluminate matrix composites by combustion synthesis, J. Mater. Sci. 37 (2002) 4537–4543.

[17] R. Ianoş, I. Lazău, C. Păcurariu, P. Barvinschi, Peculiarities of $CaO \cdot 6Al_2O_3$ formation by using low-temperature combustion synthesis, Eur. J. Inorg. Chem. (2008) 925–930.

[18] R. Ianoş, An efficient solution for the single-step synthesis of $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ powders, J. Mater. Res. 24 (2009) 245–252.

[19] S.R. Jain, K.C. Adiga, V.R. Pai Verneker, A new approach to thermochemical calculations of condensed fuel-oxidizer mixtures, Combust. Flame 40 (1981) 71–79.

[20] I.V. Tokmakov, S. Alavi, D.L. Thompson, Urea and urea nitrate decomposition pathways: a quantum chemistry study, J. Phys. Chem. A. 110 (2006) 2759–2770.

[21] J.J. Kingsley, K.C. Patil, A novel combustion process for the synthesis of fine particle α-alumina and related oxide materials, Mater. Lett. 6 (1988) 427–432.

[22] C. Hwang, J. Tsai, T. Huang, Combustion synthesis of Ni–Zn ferrite by using glycine and metal nitrates-investigations of precursor homogeneity, product reproducibility, and reaction mechanism, Mater. Chem. Phys. 93 (2005) 330–336.

[23] P. Erri, P. Pranda, A. Varma, Oxidizer–fuel interactions in aqueous combustion synthesis. 1. Iron(III) nitrate-model fuels, Ind. Eng. Chem. Res. 43 (2004) 3092–3096.

[24] P. Badica, G. Aldica, A. Crisan, Decomposition of Ca:Cu = 1:1 nitrate powder: thermal analysis and structural studies, J. Mater. Sci. 37 (2002) 585–594.

[25] B. Pacewska, M. Keshr, Thermal transformations of aluminium nitrate hydrate, Thermochim. Acta 385 (1–2) (2002) 73–80.