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Solution combustion synthesis and sintering behavior of $CaAl_2O_4$

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Abstract

The influence of the quantity of urea on the synthesis of calcium aluminate by solution combustion method was studied. It was shown that the amount of urea has a big influence on morphological characteristic and phase composition of the combustion products.

The sintering behavior of the combustion products, before and after milling, was studied by rate controlled sintering method, based on which a thermal schedule was designed improving the sintering of $CaAl_2O_4$.

Keywords: A. Sintering; Synthesis; Combustion; Processing

1. Introduction

Calcium aluminates (CA) are widely used in the steel and cement industry due to their relatively low density, hardness, straightness, etc. [1,2]. They are important constituents for refractory castables and govern their applicability to the service temperature. Calcium aluminate ($CaAl_2O_4$) has received considerable attention as a material for (implants) bone graft application due to its unique combination of physical and mechanical, bioactive and biocompatible properties [2,3]. Also, CA-based glasses have technological importance in application of optical devices [4–8].

Various synthesis methods have been developed to obtain CA with controlled particle size.

Traditionally calcium aluminate is produced by solid state reactions. The main drawback of this method is the required high temperature and the presence of multiple and not desired phases with the end product [8–12]. Other methods are developed also using high temperatures [13]. In order to synthesize mono-phase calcium aluminate, a long treatment period is required which leads to decreasing of surface area of product. For example, Mercury et al. [10] carried out high energetic attrition milling prior to solid state reaction in order to decrease the formation temperature of $CaAl_2O_4$.

Park and Kim [8] suggested to use boric acid as a flux to accelerate the formation of the product by solid state reactions of CaO and Al_2O_3 powders. The molten flux leads to uniform distribution of compounds and enhances diffusion of the precursors. This method enables to decrease the synthesis temperature.

Many approaches are suggested to increase homogeneity of the precursors. Among them is sol–gel method [14,15]. In this case precursors containing gel are prepared firstly. Later on, the gel is crystallized by subsequent heating at relatively low temperature. The most obvious advantage of the sol–gel method is that reagents are mostly mixed in atomic level, which may increase the reaction rate and decrease the synthesis temperature.

Douy and Gervais [16] reported a synthesis method of amorphous $CaAlO_4$ powders by spray-drying aqueous solutions of calcium and aluminum nitrates, followed by calcinations of product in order to completely decompose the salts.

One of well known approaches of ceramic powder synthesis is Pechini method [6,17–20]. The process is based on the ability of certain organic acids to chelate the metal ion. Heating the chelates, polyesterification undergoes with the help of polyhydroxy alcohols and polymerized the resin forms. Then, the polymerized resin is calcined to obtain calcium aluminate. Also using chemical fixation of the cations by organic molecules Pati et al. [21] and Gaki et al. [22] have obtained nanoparticles of $CaAl_2O_4$ by versatile solution based precursor solution method.

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The combustion method is a convenient method for the synthesis of oxide materials [4,23–27]. It is a versatile, simple and rapid process, which allows to synthesize variety of materials without intermediate decomposition and/or calcining steps. This is a self-sustaining process and it is ignited in a temperature which is much lower than the actual phase transformation temperature.

The calcium monoaluminate ($CaAl_2O_4$) has been synthesized with high purity via solution combustion methods [26,27], using aqueous solution of calcium and aluminum nitrates as both oxidizer and source of the corresponding cations and urea as a fuel. However, obtained products are mainly agglomerated, nevertheless this method do not need high temperatures as other methods.

The objective of this work is to study the influence of the quantity of urea on the possibility of synthesizing of calcium aluminate by the solution combustion synthesis method, using calcium and aluminum nitrites as precursors. The mechanism of the sintering and sinterability of combustion products, as obtained and after milling process, was studied.

2. Experimental

To synthesize monocalcium aluminate via solution combustion method, $Al(NO_3)_3·9H_2O$ (95%, Merck) and $Ca(NO_3)_2·4H_2O$ (99.5%, Merck), as cation precursors and oxidizers, and urea (99%, Merck) as a fuel were used. The appropriate amount of $Al(NO_3)_3·9H_2O$ and $Ca(NO_3)_2·4H_2O$ according to the stoichiometry of Eq. (1) were solved in the deionized water (1 g $Ca(NO_3)_2·4H_2O$ with 10 ml water) and urea with different proportion was added.

$$3Ca(NO_3)_2·4H_2O + 6Al(NO_3)_3·9H_2O + 20nCO(NH_2)_2 = 3CaAl_2O_4 + 20nCO_2 + 35nN_2 + 53H_2O + (24 - 24n)NO_2 + (6 - 6n)O_2 \quad (1)$$

where n is the ratio of quantity of used urea to the quantity of needed urea providing stochiometric ratio of fuel to oxidizer ($n = 1$).

The solution was heated up to 400 °C in a furnace (with 25 °C/min heating rate), where ignition took place. After 30 min the sample was taken out from the furnace. A dry, white and very fragile foam was produced, that easily crumbled into powder.

The phase identification of the combustion reaction powder was carried out by X-ray diffraction using a Bruker diffractometer (D8) with CuKα radiation. Specific surface area of the powder was determined by BET model with data provided by a chromatographic adsorption equipment from Quantachrome (Monosorb). Field emission scanning electron microscopy (FESEM S-4700, Hitachi, Japan) was used to characterize the microstructure of the combustion product, which beforehand was coated with gold.

The synthesized powder was attrition milled in a 250 ml jar coated with PTFE and using 100 ml of YTZ grinding media (Tosoh Corp., Japan) 1 mm in size. Particle size was measured using laser scattering method (Mastersizer, Malvern Instruments, UK).

The sintering behaviors of the combustion products were studied by dilatometry (Setaram Setsys TMA-18, France). The samples were pressed, using as synthetised and milled powders, uniaxially at 200 MPa into cylindrical pellets with 8 mm in diameter. Later on they were placed in a platinum dish and were heated in a controlled sintering speed (RCS). According to this method, the sinter process is performed in a given densification profile. If the real sintering rate is lower than the predefined sintering rate, the temperature is raised to achieve a higher sintering rate and the heating will be lowered when the predefined sintering rate exceeds the given value. The RCS measurements were carried out between room temperature and 1400 °C at an initial heating rate of 5°/min and a maximum sintering rate of 0.05%/min.

Based on RCS experiments, a heating schedule was designed to obtain monocalcium aluminate with high density. Selected combustion products were pressed uniaxially at 150 MPa into cylindrical pellets with 8 mm in diameter and were heated from room temperature to 1100 °C at a rate of 5°/min, then they were heated up to 1370 °C and 1390 °C at a heating rate of 1°/min, where it was held constant for 1/2 h and then cooled to room temperature at 10°/min. The density of the sintered material was determined by Archimedes method in Hg.

3. Results and discussion

The X-ray diffraction patterns of the combustion products obtained at various quantities of urea ($n = 0.12$–1) are shown in Fig. 1. At low content of urea ($n = 0.12$), the combustion product mainly consists of $Ca(NO_3)_2$, γ-Al_2O_3 and $Ca_{12}Al_{14}O_{33}$ ($C_{12}A_7$). The increase of the ratio of fuel ($n = 0.5$) leads to formation of an amorphous product. The peaks related to $Ca(NO_3)_2$ disappear partially and metastable γ-Al_2O_3 transforms to α-Al_2O_3. At higher content of urea ($n = 0.75$) crystallization of transitory phases (those are $Ca_{12}Al_{14}O_{33}$, $CaAl_4O_7$, $CaAl_2O_4$ and $Ca_4(Al_2O_4)_3O$) occurs from the amorphous phase. The crystallinity of the combustion product increases with increasing the ratio of the fuel ($n = 0.85$). Finally, complete formation of single-phase $CaAl_2O_4$ takes place at $n = 1$.

Introduction of urea is a way to introduce energy in the system. Introducing low amount of urea ($n = 0.12$) aluminum nitrate decomposes into γ-Al_2O_3, while $Ca(NO_3)_2$ decomposes partly forming CaO. CaO reacts immediately with Al_2O_3 obtaining $C_{12}A_7$. It is worth to note that the formation of $C_{12}A_7$ via CaO–Al_2O_3 reaction is exothermic and has a high negative value of ΔG [10]. Introducing more energy in the system via increasing the amount of the fuel ($n = 0.5$) more quantity of $Ca(NO_3)_2$ decomposes and melts, forming glasslike or amorphous powder. Transitory phases begin to crystallize increasing the amount of fuel. Although the system reaches to the equilibrium state only after increasing the ratio of urea in the initial mixture to the stochiometric quantity ($n = 1$).

The microstructures of the combustion product at $n = 0.12$, 0.75, 1 studied by FESEM are presented in Fig. 2. At $n = 0.12$ agglomerates are formed (Fig. 2a), which are constituted by

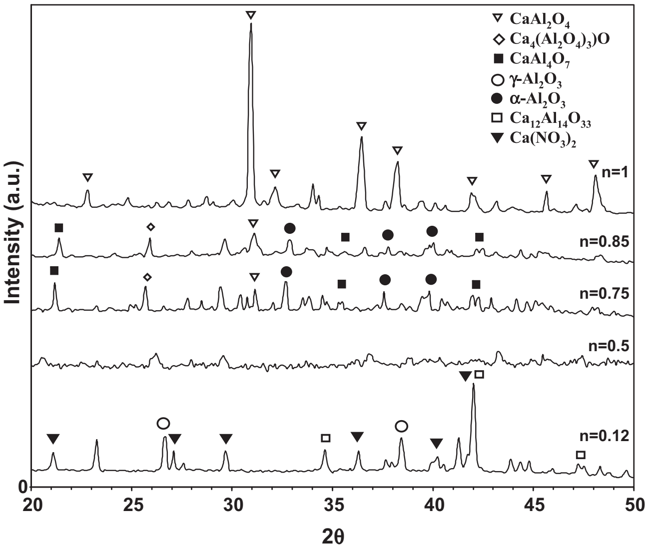

Fig. 1. XRD patterns of combustion products obtained at various quantities of urea ($n = 0.12$–1).

un-reacted compounds and $C_{12}A_7$ (Fig. 1). The specific surface area (SSA) of this product is 20 m^2/g (Fig. 3). With increasing the amount of the fuel ($n = 0.75$), the compounds with low melting point melt, leading to the formation of agglomerations and consequently decreasing the SSA of the product until 9 m^2/g. It can be seen in Fig. 2b and c that the agglomerates have two different microstructures; continuous (Fig. 2b) and grainy (Fig. 2c). It can be distinguished that the phases are distributed unhomogenously in the agglomerates with continuous structure. While the agglomerates with grainy structure look like homogenous, which are consisted of nanocrystals smaller than 70 nm in size (Fig. 2c). It should be noted that the both types of agglomerates are compact. With increasing the ratio of urea from 0.75 to 1, the grainy compact agglomerates are not changed morphologically, but they are changed in chemical content (Fig. 1). Whereas the compact agglomerates with continuous structure transform to porous ones, keeping continuous feature of the morphology. Those distinctive morphologies of combustion product indicate the different condition of their formation caused by non homogenous distribution of energy over the sample during the combustion process. Increasing the quantity of energy in the system, the SSA of the combustion product increases caused by formation of pores in continuous agglomerates and disjoining of grainy agglomerates, followed by growth of crystals in them (Fig. 3).

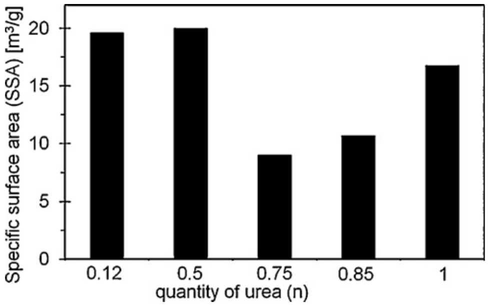

Fig. 3. Specific surface area of combustion products as a function of quantity of urea.

The combustion product obtained using stoichiometric amount of urea ($n = 1$) was crushed in an Agatha mortar and

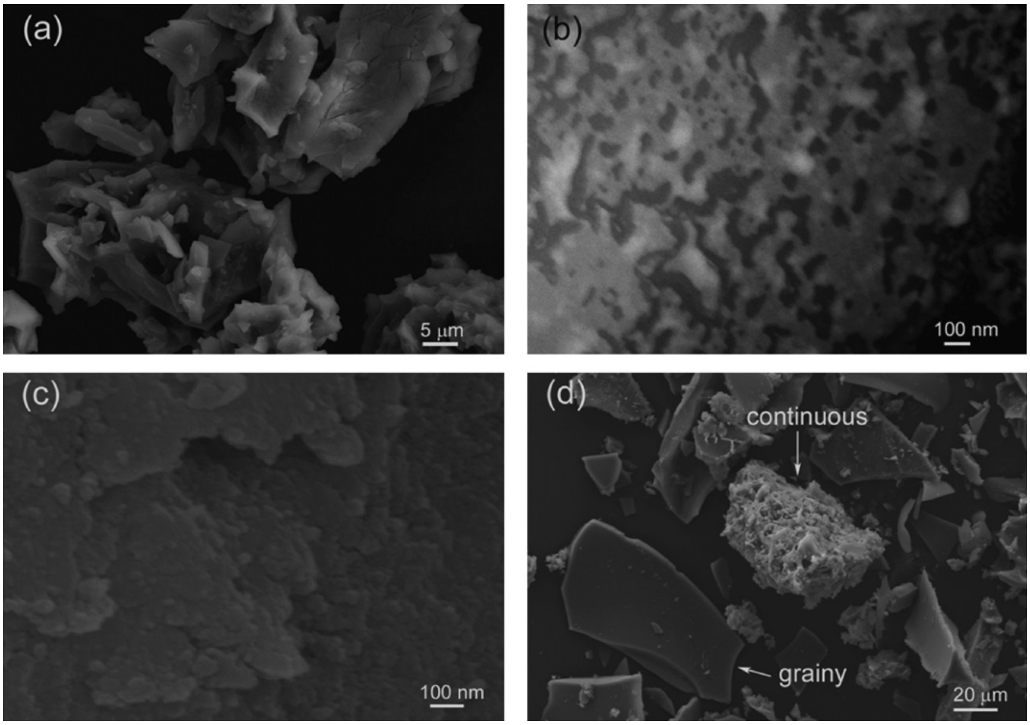

Fig. 2. Microstructures of combustion products obtained at various quantities of urea: (a) $n = 0.12$, (b) $n = 0.75$, (c) $n = 0.75$, (d) $n = 1$.

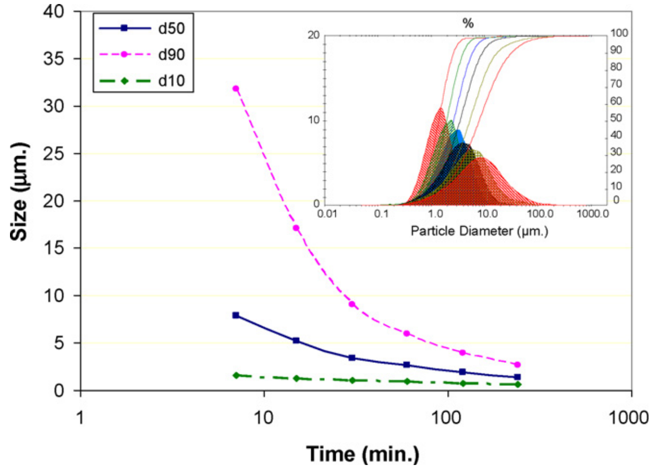

Fig. 4. Milling curve of the CA synthesized with $n = 1$.

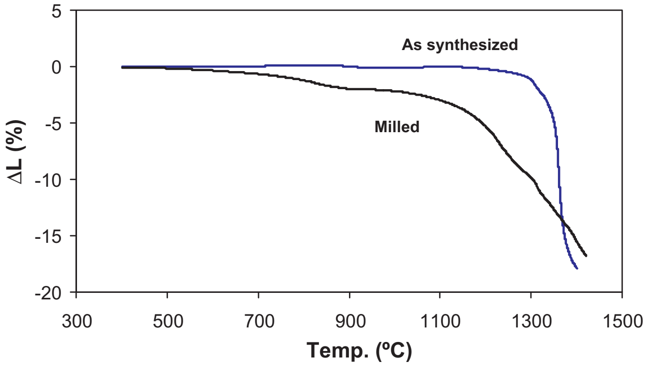

Fig. 5. RCS measurements of the combustion products ($n = 1$) before and after milling.

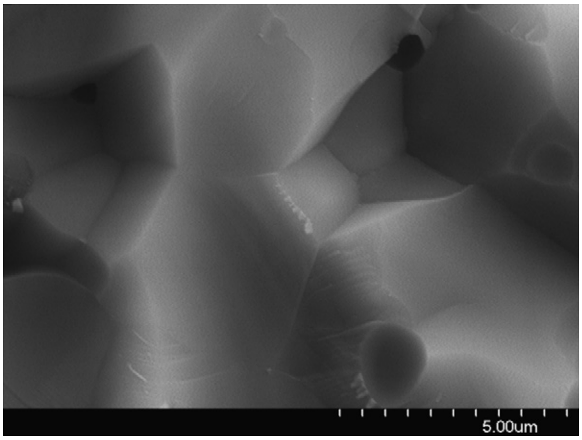

Fig. 6. FESEM micrograph of the sintered sample at 1390 °C.

was introduced in the attritor. In order to avoid the effect of crushing the particle size distribution was determined after 7 min milling. The average particle size was 7.9 µm. The further milling was accompanied with gradual decrease in particle size. After 4 h of milling the average particle size of the product becomes 1.4 µm. The behavior of the particle size distribution can be clearly observed in Fig. 4. Two points are noticeable first is that not a steady state have been reached, and it is possible decrease more the size only increasing time and secondly the great decrease in the value of d_{90}, from 32 µm to 2.6 µm. Finally it is noticeable that any change in the specific surface has been observed in the sample after milling. It can be explained due to the milling effect is more related to a deagglomeration process, that to a real milling.

Rate controlled sintering (RCS) was carried out to study the sinterability of obtained powders before and after milling to obtain dense $CaAl_2O_4$. The upper temperature limit for sintering was fixed at 1400 °C.

In Fig. 5 dilatometric study of the rate controlled sintering of the combustion product at $n = 1$ compacted with a green density of 49% is presented. The sample started to be heat at a nominal rate of 5°/min up. At the beginning a weak thermal expansion is determined until 1100 °C. Above this temperature the sample shrinks slightly up to 1300 °C. Above this temperature the shrinkage rate increases reaching to a maximum value at 1360 °C. It has no sense to increase temperature higher than 1400 °C as the lowest invariant point of the Al_2O_3–CaO system is around that temperature.

When the study is carried out on the milled sample a very different behavior is observed. There is a first shrinkage effect centered at 850 °C. It could be due to the shrinkage of nanometric particles deagglomerated during milling. Above this temperature the sample shrinks slightly up to 1100 °C, after that the shrinkage rate increases reaching a maximum at 1320 °C. The sintering of combustion product obtained at $n = 1$ is accompanied without any phase transformation.

Studying the sintering of the milled sample, the pressed samples were heated in the above described way. The densities after sintering are different. When the sintering temperature was 1370 °C the final density was 2.69 (91%) g/cm^3, while when the maximum temperature was 1390 °C the density was 2.83 (96%) g/cm^3. In Fig. 6 the fracture of the sample sintered at 1390 °C can be observed. Increasing in the grain size is observed, but not so much and, probably, the final size is defined by the agglomerate size after milling. With this experiment the sinterability of the combustion product obtained material has been shown.

4. Conclusions

From the undertaken studies it was concluded that the amount of urea has a big influence on the morphological characteristic and phase composition of the product obtained by solution combustion synthesis. At low quantity of urea different calcium aluminates were obtained. Although, the system comes to the equilibrium and pure monocalcium aluminate forms using stochiometric amount of urea ($n = 1$). The sintering behavior of the combustion products was studied by rate controlled sintering method based on which a thermal schedule was designed improving the sintering.

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