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Influence of different parameters on calcium hexaluminate reaction sintering by Spark Plasma

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Abstract

Calcium hexaluminate ($CaAl_{12}O_{19}$) is the most alumina-rich intermediate compound of the $CaO–Al_2O_3$ system. The formation of this aluminate is produced by the reaction between calcium oxide and alumina. Intermediate compounds with lower alumina content ($CaAl_2O_4$, $CaAl_4O_7$,. . .) are formed during the synthesis of calcium hexaluminate with increasing temperature. With the aim to obtain dense and pure calcium hexaluminate by reaction sintering method using Spark Plasma Sintering (SPS) the variation of sintering parameters was studied. Final densities close to the theoretical and calcium hexaluminate formation rates over 93% were achieved by this method. Once the sintering parameters were optimized, a study of the flexural strength and the hardness of the samples were performed.
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Keywords: Calcium dialuminate (CA_2); Calcium hexaluminate (CA_6); SPS; Reaction sintering

1. Introduction

Cacium hexaluminate ($CaAl_{12}O_{19}$), or hibonite mineral, crystallizes in the hexagonal system with a space group $P6_3/mmc$ [1]. It has a magnetoplumbite ($PbFe_{12}O_{19}$) structure type consisting of spinel blocks and conduction layers, which are stacked alternatively to form a layered structure with a continuous order (*chhhcchhhc*), where *c* and *h* symbolize cubic and hexagonal close-packed layers, respectively. The cubic layers constitute blocks with spinel (S) structure that are sandwiched between hexagonal (R) blocks, accommodating Ca in anion positions in their central part [2]. The morphology of CA_6 grains shows preferential growth along their basal plane. Coupled diffusion of Ca^{2+} and O^{2-} ions from calcia-rich to alumina-rich phases is thought to control CA_6 formation [3,4]. Previous studies [5] have shown the following reaction sequence between $CaCO_3$ and Al_2O_3 to form CA_6:

$$CaCO_3 + Al_2O_3 \rightarrow CaO + Al_2O_3 + CO_{2(gas)}$$

$$CaO + Al_2O_3 \rightarrow CaO \cdot Al_2O_3(CA)$$

$$CaO \cdot Al_2O_3 + Al_2O_3 \rightarrow CaO \cdot 2Al_2O_3(CA_2)$$

$$CaO \cdot 2Al_2O_3 + 4Al_2O_3 \rightarrow CaO \cdot 6Al_2O_3(CA_6)$$

where the reaction temperature depends on the grain size of the initial product, powder dispersion, synthesis method, etc.

Pioneering studies on the formation of CA_6 were performed by Kohatsu and Brindley [6]. They analysed the solid state reaction between CaO and α-alumina at 1330 °C. In that study they found all the intermediate phases of the $CaO–Al_2O_3$ diagram oriented with their *c* axes parallel to the surface reaction. They concluded that this orientation was due to the preferential growth along the direction perpendicular to the *c* axes and not to a particular orientation of the alumina grains. The main migration corresponded to the diffusion of calcium ions into alumina.

Other authors have investigated some non-conventional CA_6 synthesis methods. Callender et al. [7] reported about the formation of crystalline CA_6 by a thermolysis process of calcium carboxylate and aluminoxane at 1400 °C. Cinibulk and Hay [8] initially studied the formation of calcium hexaluminate

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obtained from alumina sol containing calcium acetate and they found that after calcination at 1400 °C, a mixture of $CaO{\cdot}6Al_2O_3$, α-alumina and $CaO{\cdot}2Al_2O_3$ was formed at 1300 °C after 1 h.

So far, the formation of calcium hexaluminate has only been studied by conventional reaction sintering. This way, Dominguez et al. [1,9] obtained CA_6 by reaction sintering, mixing $CaCO_3$ and alumina in aqueous medium, and homogenized by attrition milling. The powder was pressed uniaxially under 75 MPa and it was heated at different temperatures (1200–1600 °C) to study the final density, the formation of different phases and the mechanical properties. Asmi and Low [10] applied the same method but instead of using an aqueous medium, they used propylene glycol as deflocculant and, in this way, they described the formation of phases at different temperatures. Vazquez et al. [11] also obtained calcium hexaluminate by reaction sintering by mixing alumina and $CaCO_3$, but with a pre-calcination step at 950 °C. After uniaxial pressing (200 MPa) they sintered at 1700 °C for 6 h and obtained CA_6 by this method.

In this context, we investigated the calcium hexaluminate reaction sintering formation by Spark Plasma Sintering (SPS). This is the first time that the formation by reaction sintering of CA_6 is studied by means of SPS methods. Some attempts were reported in the literature for the reaction sintering of other compounds such as $MoSi_2$ or $Ca_3Co_4O_9$ [12,13], the CA_6 formation presented here shows the capability of complex oxide reactions to form binary compounds in a fast and simple technique, obtaining density, calcium hexaluminate formation values and flexural strength comparable to conventional methods and higher hardness than by conventional methods.

2. Experimental procedure

The starting powder used in the SPS experiments was formed by mixing alumina (Taimei TM-DAR) and two different types of commercial calcium carbonate (from Sigma–Aldrich and Asturcal) each in the percentage required for the fulfillment of the stoichiometry of the reaction and this takes place. The mixture made with Asturcal calcium carbonate was milled in two different ways: by attrition milling, where the mixture was ground in propanol for 1 h; and by ball milling, where the mixture was ground for 48 h. After milling, both powder mixtures were dried in an oven for 48 h. Fig. 1 shows the processing scheme.

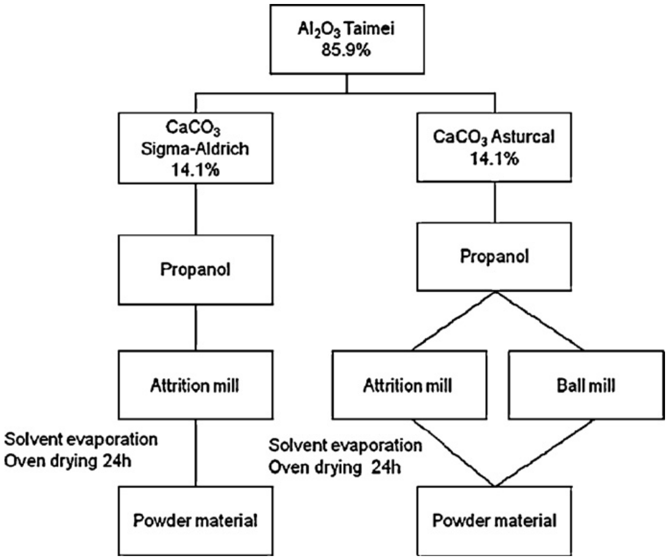

Fig. 1. Processing scheme.

The use of two different calcium carbonates and two milling methods was done in order to check the effect of the powder mixture grain size on the properties of the final material.

The resulting powders after mixing with alumina, by the methods described above, were sieved ($x \leq 63$ μm) and sintered by Spark Plasma Sintering (SPS) (model FCT_HP D 25/1) varying sintering parameters [14] such as sintering temperature, applied pressure, heating rate and dwell time at the highest sintering temperature, to study their influence on the densification and CA_6 formation in the process.

Sintering was performed between 1500 and 1700 °C, with an applied force between 5 and 20 kN, which corresponds to pressure values between 16 and 64 MPa for the 20 mm mould used. The samples were heated with rates of 10–100 °C/min and dwell times of 10–30 min. The estimation of the calcium hexaluminate formation obtained in the reaction sintering in the SPS was performed by X-ray diffraction followed by phase quantification by the Rietveld method, using Maud software [15]. The relative density values of the sintered samples were calculated from the apparent density data obtained by the Archimedes method taking as real values of density (theoretical density values, t.d. from now on in the text), the values obtained by helium pycnometry, for each ground and sintered sample. Hardness was measured by micro-indentation (Buehler Micromet 51 03) using a force of 2 kN and an indentation time of 10 s for each composite. Flexural strength was studied with a biaxial bending test (Instron E10000). The microstructures of the sintered samples were analysed by scanning electron microscopy (SEM) after thermally etching the polished surfaces by heat treatments at temperatures 100 °C below the reaction sintering temperatures.

3. Results and discussion

Different heat treatments in the SPS were performed to study density and CA_6 formation by reaction sintering using the mixture of alumina and Sigma–Aldrich calcium carbonate. With this mixture, the influence of sintering temperature, applied pressure, heating rate and dwell time on the densification and the formation of calcium hexaluminate during the sintering process were studied. Finally, the influence of grain size is described, using Asturcal calcium carbonate as well as the Sigma–Aldrich calcium carbonate with different grain size distributions.

The effect of changing these parameters in the density and formation CA_6 using the same $CaCO_3$–Al_2O_3 mixture is discussed below:

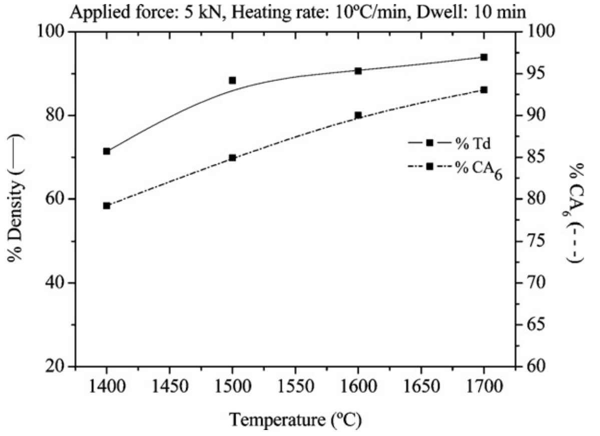

Fig. 2. Density and CA_6 formation as a function of temperature.

3.1. Sintering temperature

The influence of the temperature variation on CA_6 reaction sintering and densification of the material was first studied. For this study, the other parameters were kept constant as follows: applied force to 5 kN, heating rate to 10 °C/min and dwell time to 10 min. Fig. 2 shows the results of density and CA_6 percentage formation during sintering.

It can be seen that density increases with increasing temperature, varying from 70 to 93% t.d. values. In the same way, the percentage of calcium hexaluminate formed during sintering also increases with increasing temperature from 80 to 93%. This result follows the expected trend: as the temperature increases, the atomic diffusion increases and, therefore, the optimum conditions for calcium hexaluminate formation are achieved. According to previous studies, the formation of calcium hexaluminate by conventional reaction sintering takes place at 1600 °C [9,10], which is higher than the temperature needed for its formation by SPS reaction sintering. In addition, in those studies, XRD analysis showed some alumina diffraction maxima, which indicate that the transformation degree is lower than in SPSed powders at the same temperatures shown here. Also, diffraction peaks corresponding to calcium dialuminate and alumina are observed (see Fig. 3 for rietveld refinement of one of the samples) indicating that the reaction was not complete.

Density values of 95% t.d. at 1750 °C are obtained by conventional routes [1], values which are obtained at a lower temperature of 1500 °C by Spark Plasma Sintering. Moreover, at 1700 °C in the SPS, values of 99% theoretical density (t.d.) were reached after optimization of the other sintering variables as will be shown next.

Hibonite grains nucleate in the contact between Al_2O_3 and CA_2 grains. The incomplete reaction of formation of CA_6 has been observed in the microstructures (Fig. 4a and b), and some remnants of CA_2 and alumina are observed, with a smaller grain size compared with the growing CA_6 grains. Nevertheless, the volume of CA_6 observed in the studied microstructures is in agreement with the percentage of CA_6 formation estimated by XRD.

The morphology of CA_6 grains grown by reaction sintering was studied by Dominguez et al. [9]. CA_6 platelet grains are thought to be formed due to the preferential grown in the basal plane because diffusivity is enhanced in that direction. When the grain size, sample porosity and pores size are high, CA_6 grains have enough space to develop with high aspect ratios. On the other hand, when raw materials are well-dispersed, samples are denser and have small pores and CA_6 grains find their rapid growth direction bounded by other CA_6 grains before being able to develop high aspect ratios. As reaction progresses grain growth proceeds in other directions giving grains with lower aspect ratios and curved boundaries. As a consequence, it can be reported that the grain morphology is linked to calcium carbonate and alumina distribution in green specimens. Low green densities promote platelet CA_6 grains whilst high densities lead to the formation of elongated grains [9]. In our studies the presence of platelet like grains is restricted to some scarce nuclei (Fig. 4c and d). We have previously seen how reaction sintering by SPS enhances density and the microstructures obtained agree with that observation. Previous studies [16,17] showed that a transient glass phase formed during the CA_6 formation, can also be responsible for the platelet grains. This phase is not the only determining factor in microstructural development because platelet CA_6 grains cannot be formed if they have insufficient free space to develop in their preferential grown direction. This is because pressure has the effect of blocking the grain growth along the basal planes, producing equiaxial grains and the higher heating

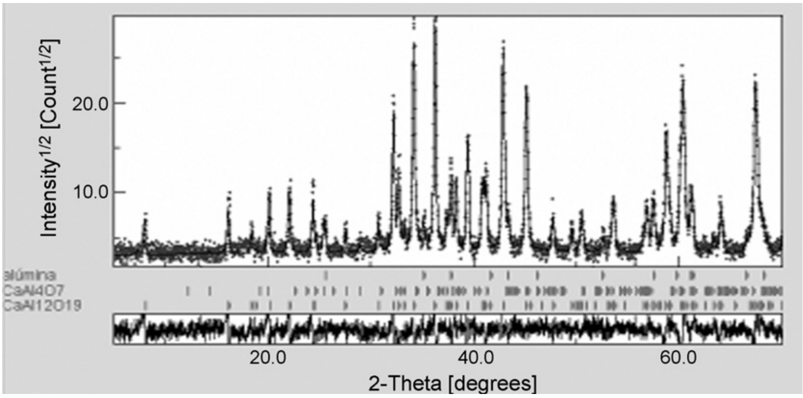

Fig. 3. Phase refinement by Rietveld method of a sintered sample at 1700 °C, 5 kN of applied force, 10 °C/min of heating rate and 10 min of dwell.

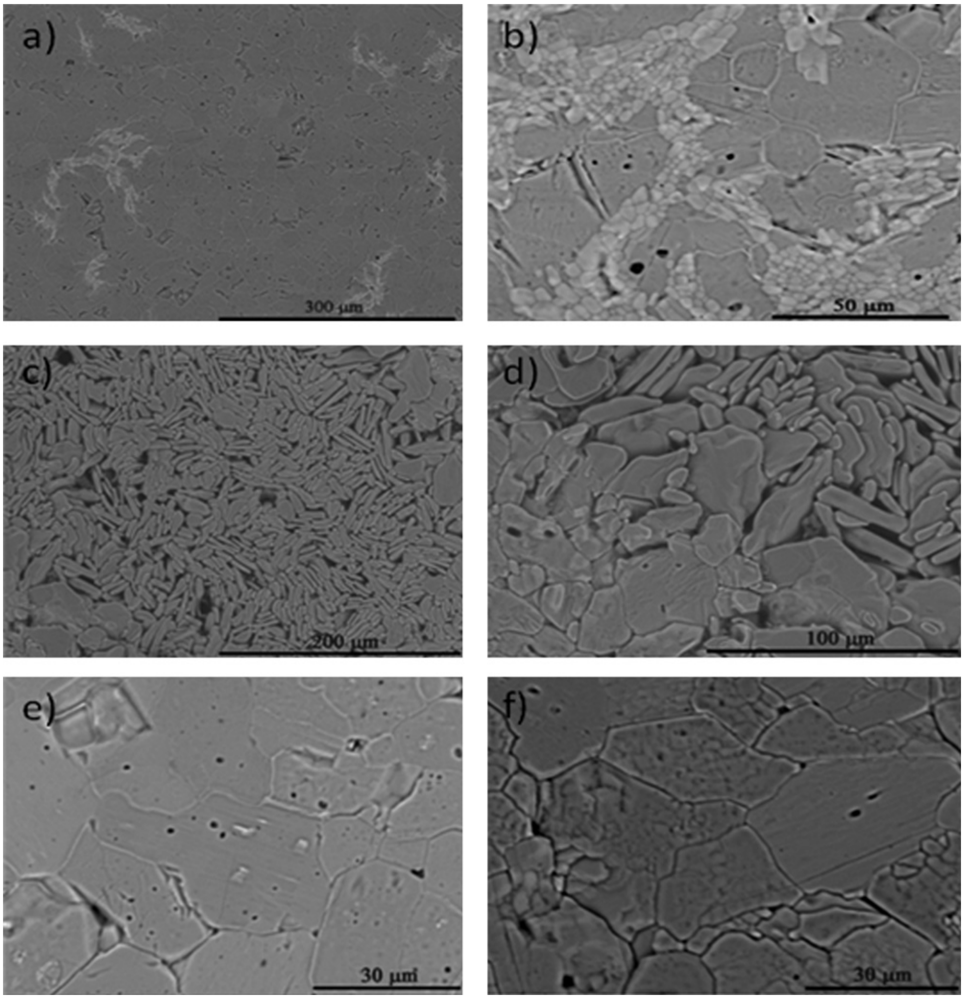

Fig. 4. Micrographs of sintered calcium hexaluminate at 1700 °C.: (a) and (b) 20 kN-100 °C/min-30 min, presence of CA_6, CA_2 and Al_2O_3 (500× and 2000× respectively); (c) and (d) 10 kN-10 °C/min-10 min, morphology (500× and 2000× respectively); (e) and (f) 10 kN-10 °C/min-10 min (2000×) perpendicular and parallel to the applied force.

rates applied in the SPS avoid the formation of the transient glass phase. The scarce nuclei of platelet grains have to be related with infrequent heterogeneities in the starting Al_2O_3–$CaCO_3$ powders that can be not perfectly homogenized in our starting material, even after milling.

CA_6 basal plains are perpendicular to the reaction front [9,18]. In those cases where platelets are observed in our case study, the reaction front seems to be perpendicular to the applied force in SPS, as we have platelet grains parallel to the applied force (Fig. 4d), as can be observed in some nuclei of platelet grains formation.

Fig. 4e and f shows the morphology of the grains observed in sections perpendicular and parallel to the applied force. In both cases the volume of CA_6 grains are equiaxed crystals and the differences in both sections are not as significant as the obtained by hot press (HP) [19]. The sintering mechanism in SPS and HP must be different as the effect of applied force in HPed samples led to platelet grain formation with the basal plane oriented perpendicular to the applied force, contrary to the equiaxial grain formation by SPS, and the scarce platelets oriented parallel to the applied force. Diffusion processes (crystal growth and reorientation) are favored in HP in relation with SPS because they are time-dependent kinetic processes.

3.2. Heating rate

Fig. 5 shows the influence of the heating rate on the density and calcium hexaluminate formation for three different sintering temperatures whilst the other parameters: temperature, applied pressure and dwell time are kept constant.

The density of the final material increases with the heating rate as observed in [20] for the sintering of alumina in SPS. The obtained density values are between 94 and 98% t.d. for the higher sintering temperature. That is an illustration of the advantages of the SPS: the possibility of obtaining higher final densities whilst using higher heating rates. This result is, *a priori*, not expected, since an increase of the heating rate reduces the total sintering time. However, a similar behaviour was observed by Chen and Mayo [21] in nanometer zirconia doped with yttria (3% molar) with heating rates between 2 and 200 °C/min. It was then shown that when the heating rate was increased, the final density was also higher for sintering

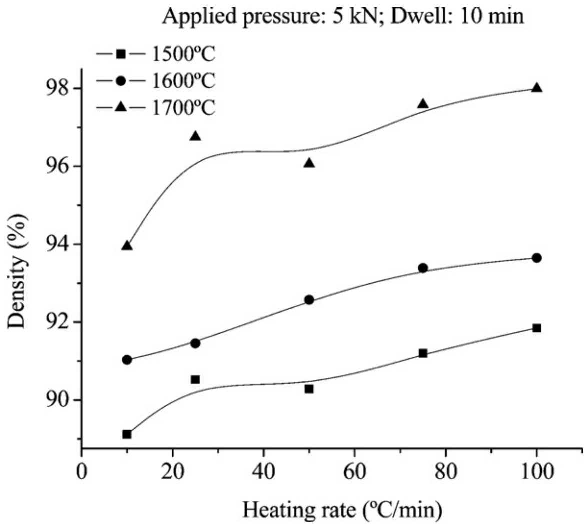

Fig. 5. Variation of density as a function of heating rate for different temperatures.

temperatures up to 1100 °C. This phenomenon is not general as in other studies, like Shen et al. [22], it was observed that the density of alumina decreases gradually with increasing heating rates from 350 to 600 °C. Therefore, it can be seen that the effect of densification with increasing heating rate depends on the system under study and on the processing conditions.

Regarding the calcium hexaluminate formation for different heating rates, the observed trend is the opposite, as shown in Fig. 6. With increasing heating rate the transformation degree decreases, with values of formed CA_6 decreasing from 91 to 75% for all of temperatures. This result was expected because the reaction time decreases with increasing heating rate. However, this may be offset by varying other parameters as discussed below.

3.3. Applied pressure

Sintering was carried out with an applied force between 5 and 20 kN, which corresponds to pressure values between 16 and 64 MPa for the 20 mm diameter moulds used. The heating rate was set to 100 °C/min and the dwell time to 10 min. Fig. 7 shows that higher forces increase the density since force stimulates compaction [23], helping to densification. Density strongly increases from 5 to 10 kN and increases only sligther from 10 to 20 kN. However, the calcium hexaluminate formation decreases from 95 to 89% when the applied force increases, as shown in Fig. 8. The reaction of calcium hexaluminate formation is an expansive process, involving an increase in volume. When the applied force is increased, the expansive process is impeded, reducing the CA_6 formation [24].

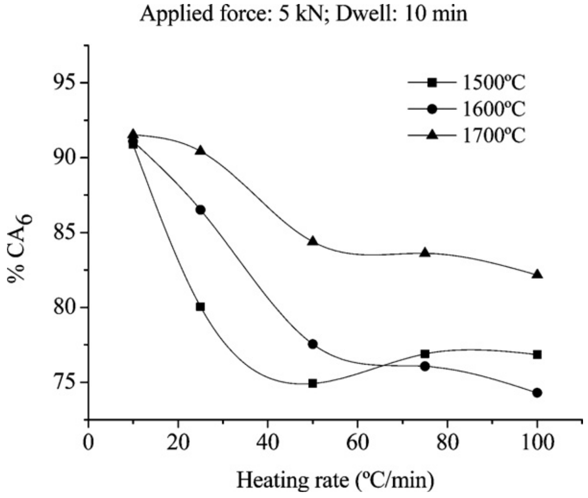

Fig. 6. CA_6 formation as a function of the heating rate for the working temperatures.

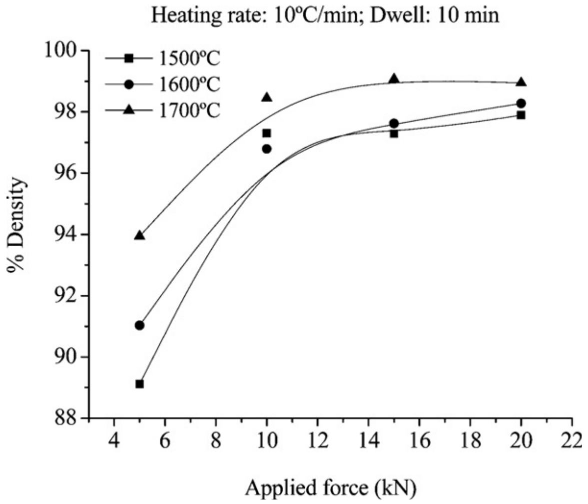

Fig. 7. % Density as a function of applied force.

3.4. Dwell time

As for the rest of variables, the applied force was set to 20 kN (equivalent to a pressure of 64 MPa) and the heating rate to 100 °C/min. The results obtained for the density and CA_6 formation at different dwell times are shown in Table 1. By

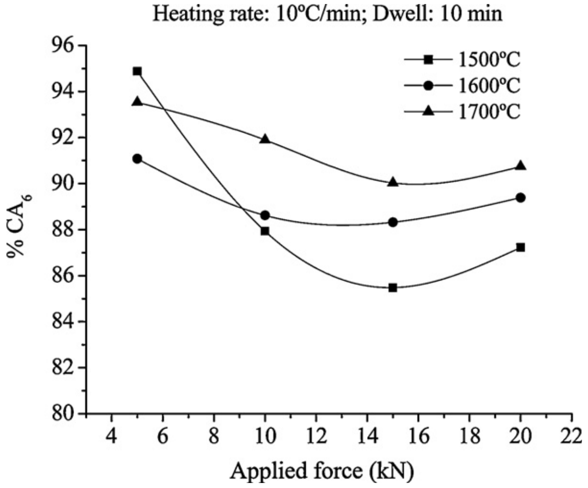

Fig. 8. % CA_6 formation as a function of the applied force.

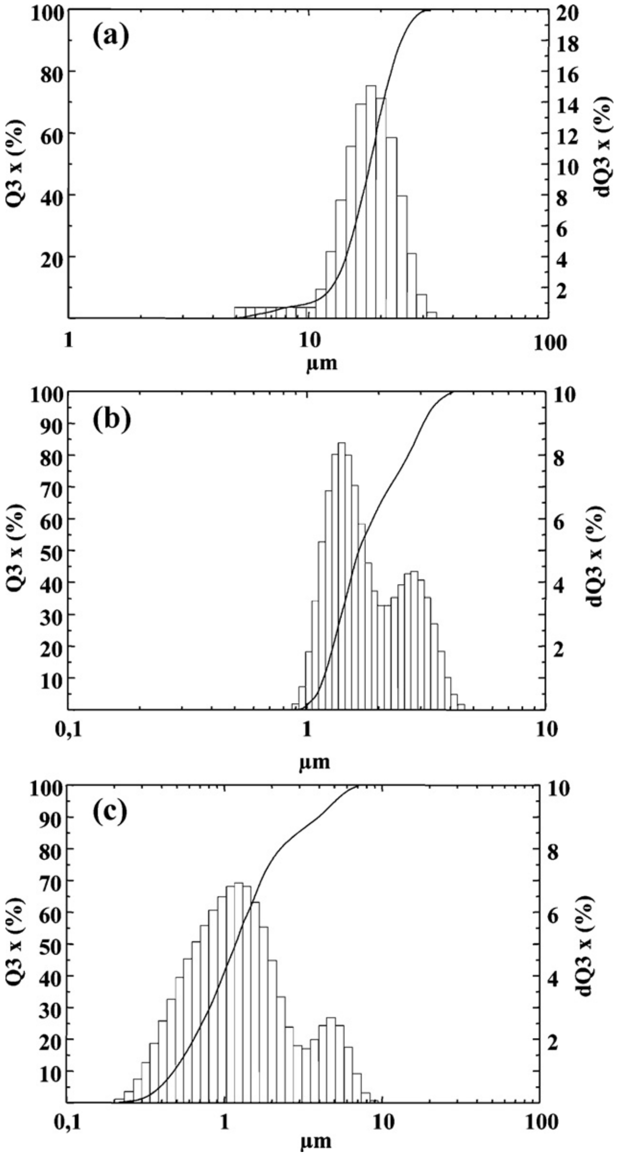

Fig. 9. Grain size of: (a) alumina-$CaCO_3$ Sigma Aldrich by attrition milling; (b) alumina-$CaCO_3$ Asturcal by attrition milling; (c) alumina-$CaCO_3$ Asturcal by ball milling.

increasing the dwell time, the final percentages of density and calcium hexaluminate formation are enhanced, from 98 to 99.5% for density, and from 83 to 93% for the CA_6 formation. It was previously shown that an increase on the applied force and on the heating rate led to a decrease on the calcium hexaluminate formation. It is possible to offset this reduction in the transformation using a longer dwell time, as observed in the Table 1. This way, by increasing the dwell time from 10 to 30 min and a high applied force (20 kN), high heating rates can be used, minimizing the total duration of the sintering cycle (50 min), especially when compared to conventional sintering cycles which last between 5 and 48 h for the CA_6 formation [25]. On the other hand, if required, the sintering temperature can be decreased to 1500 °C, and still transformation values similar to those obtained at 1700 °C with smaller applied forces and heating rates can be achieved.

3.5. Grain size distribution

Finally, the influence of the grain size of the raw materials used in the reaction sintering of calcium hexaluminate in the SPS is considered. Fig. 9 shows the particle size distribution of attrition milled alumina-$CaCO_3$-Sigma Aldrich (Fig. 9a) and both attrition milled (Fig. 9b) and ball milled (Fig. 9c) alumina-$CaCO_3$–Asturcal mixtures. As it can be seen, the mixture made with Sigma–Aldrich calcium carbonate has a larger grain size (d_{50}) than the mixture made with Asturcal calcium carbonate, being of 18 and 1.5 μm respectively. However, the milling method does not significantly affect the grain size, since both methods tested on the mixture made with Asturcal calcium carbonate lead to a similar final grain size (1.5 μm). By ball milling the particle size takes values from 0.2 to 10 μm whereas by attrition milling it has a narrower distribution, taking values from 1 to 5 μm. With these mixtures, the influence of the particle size distribution on the densification and CA_6 formation will be studied.

To analyse the influence of grain size and milling method, the temperature was set to 1700 °C, the applied force at 5 kN, the heating rate was set to 10 °C/min and the dwell time 10 min. Fig. 10 shows the results for the mixtures made with two calcium carbonates and for the different milling methods.

Both, density and the calcium hexaluminate formation improve, by decreasing grain size by attrition milling, from 94 to 95.5% for the former and from 91 to 93% for the latter. However, the most important change takes place with the Asturcal calcium carbonate, although there is no difference in the average grain size for both milling methods. However, the bimodal distribution present in the ball milled Asturcal calcium carbonate seems to play a key role in these results. This distribution makes the compaction of the particles easier, which helps increasing the density and the calcium hexaluminate formation, increasing from 95.5 to almost 100% for the density

Table 1
% Density and % CA_6 transformation as a function of the dwell time for the sintering temperatures.

Temperature (°C)	Applied force (kN)	Heating rate (°C/min)	Dwell time (min)	% Density	% CA_6
1500	20	100	10	98	83
			30	>99	87.6
1600	20	100	10	97.5	84
			30	99.5	88.3
1700	20	100	10	98	89.3
			30	>99.5	92.6

Table 2
Hardness and flexural strength of the samples by SPS in comparison with different conventional methods.

Samples	SPS		[1]		[26]	[19]	
						//	⊥
Sintering temperature (°C)	1600	1700	1600	1700	1700	1600	
Flexural strength (MPa)	215 ± 4	227 ± 11	206 ± 16	219 ± 23	159	593 ±50	612 ± 35
Hardness (GPa)	13.4 ± 1.5	14.8 ± 0.6				13.1 ± 0.1	13.4 ± 0.1
Density (%)	99	99.5					
Phase transformation (%)	90	91.5					

and from 93 to 99.5 for the CA_6 formation, i. e, density values close to the theoretical and almost pure CA_6 formation are obtained.

3.6. Mechanical properties

Once the conditions for obtaining dense samples with high transformations have been optimized, the study of the mechanical properties was performed. Flexural strength and hardness were studied for selected sintering temperatures. Table 2 shows the most relevant results obtained for 1600 and 1700 °C. Samples with the best values of density and the greater phase transformation were chosen for comparison. In this case for 1600 °C density values of 99% were obtained and CA_6 content of 90%. For 1700 °C, density values are 99.5% and CA_6 content of 91.5%.

In Table 2, the results of our study are shown together with the mechanical properties obtained for reactive sintering by conventional methods in other studies [1,19,26]. As it can be seen, hardness values are very similar to those reported so far by hot press (13 GPa). For the flexural strength values, there are more differences as a function of the sintering temperature in the different studies. The values obtained by reactive sintering at 1600 °C by SPS (215 MPa) are similar to those obtained by conventional methods (206 MPa); however the values obtained at 1700 °C by reactive sintering by SPS (217 MPa) are higher than some obtained by conventional methods (159 MPa) at this temperature. In the case of hot pressed CA_6 [19], the obtained values are approximately 600 MPa. These amazingly high strength values have to be related with the microstructures obtained by hot press, in which platelet CA_6 crystals form a reinforced interlocked and highly dense microstructure.

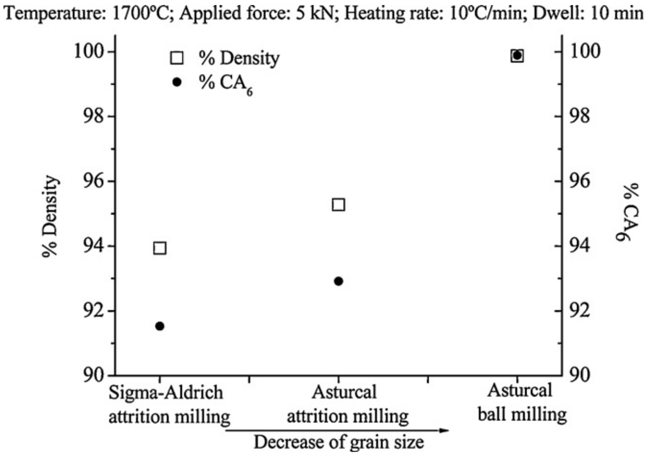

Fig. 10. Variation of density and CA_6 formation as a function of the grain size and the milling method.

4. Conclusion

Dense calcium hexaluminate was obtained by reactive Spark Plasma Sintering. It has been shown that, by this technique, it is possible to reduce the time of sintering cycles compared to conventional methods. Calcium hexaluminate formation rates over 93% were achieved with densities close to the theoretical values. It has been shown that the particle size significantly affects the reaction sintering of CA_6 leading to larger final densities and greater CA_6 formations when a smaller particle size is used. Microstructures obtained are equiaxied CA_6 grains in agreement with high densities achieved at early stages of crystal growth. In addition, in those cycles in which the best rates of calcium hexaluminate and densities close to the theoretical value have been obtained, the mechanical properties achieved are similar to those obtained by conventional reactive sintering CA_6. These results open the possibility of obtaining dense materials with improved mechanical properties in short periods of time in multi component systems.

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