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Densification behaviour of Ca-α-sialons

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Abstract

In this paper three methods of densification of Ca-α-sialon are compared. It is shown that both reaction hot pressing and reaction sintering are convenient methods to obtain densities close to theoretical values. For the densification of carbothermally prepared Ca-α-sialon powders the influence of the amount of CaO as a sintering additive has been shown to be significant. The highest density was reached with 15 wt.% CaO (~ 97% relative density). The 'mechanisms' of sintering using the three mentioned methods (reaction hot pressing, reaction sintering and sintering Ca-α-sialon powder with CaO as a sintering additive) appear to be similar. First a rearrangement of the particles takes place due to the presence of a liquid phase, followed by a solution/precipitation mechanism. The mechanism for liquid phase sintering of Ca-α-sialon is similar to that described in literature for other Ln-α-sialon (Ln = Y, lanthanide's) materials. © 2001 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

Keywords: A. Hot pressing; A. Sintering; D. Sialon

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1. Introduction

Silicon nitride has already been of interest as a ceramic material for quite a long time. The interest is due to the combination of several very good properties like high strength and fracture toughness, low thermal expansion, relatively high thermal conductivity and good oxidation/corrosion resistance at elevated temperatures in air [1,2]. Early work demonstrated that fully dense silicon nitride is hard to achieve and this is one of the major drawbacks of silicon nitride ceramics. However, with the development of β-sialon ($Si_{6-z}Al_zO_zN_{8-z}$) materials a new and very important approach for densification of silicon nitride based ceramics was taken [3]. To obtain fully dense silicon nitride based ceramic materials often the addition of alumina and / or yttria as sintering additives is applied, resulting in a liquid phase at the sintering temperature. The overall chemical composition and way of processing determine the microstructure and the mechanical properties of the final sialon materials [4,5]. Besides β-sialon also α-sialon material was discovered. This material with a similar structure as α-Si_3N_4 has the general formula: $M_{m/\mathrm{val}}Si_{12-(m+n)}Al_{m+n}O_nN_{16-n}$ where M = Li, Mg, Ca, Y or lanthanide, m,n are substitution coefficients and val = valency of the metal ion [6]. Since some 15 years these materials are intensively studied, especially the Y-α-sialon materials [7]. Last years also more effort is put in study of the lanthanide α-sialon materials [8–10]. On the contrary, only just recently more interest in Ca-α-sialon systems was displayed. Papers were published for the Ca-α-sialon materials concerning thermal stability [11] and more general dealing with phases, properties and microstructure [12]. The Ca-α-sialon system becomes even more interesting because it enables to incorporate other cations that were earlier thought to be impossible to substitute in the lattice [13]. Another application is adding luminescent cations [14]. From a scientific point of view one of the reasons to focus in our study on the Ca-α-sialon system is the still fairly large unexplored area of this system. Another reason from an application point of view is that Ca sources like CaO or $CaCO_3$ are much cheaper than yttria or lanthanide oxides. Also, we showed that the waste material fly ash could be used to prepare Ca-α-sialon materials with carbothermal synthesis [15].

In this paper a comparison is made between various sintering procedures of Ca-α-sialon materials viz.: 1. Reaction hot uniaxial pressing; this is an expensive method with inflexibility concerning shaping possibilities.

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On the other hand it is a very convenient route to prepare fully densified samples that can be used to determine the properties of dense ceramic materials. 2. Reaction sintering; the starting materials are the same as mentioned for the first route, but there is more flexibility in shaping possibilities like slip casting (as we have used for the preparation of β-sialon [16,17]). 3. Sintering of carbothermally prepared powders. Besides the advantage of the flexibility in shaping, another advantage of this method is the use of cheaper oxide starting materials [18] compared to the other methods mentioned above.

2. Experimental methods

2.1. Reaction hot-uniaxial-pressing and reaction sintering

The starting materials used were: Si_3N_4 (LC-12N, Starck, $\alpha/\alpha+\beta>95\%$, oxygen content ± 2 wt.%), AlN (Starck, grade C, oxygen content ± 2 wt.%), Al_2O_3 (AKP30, 99.9% α- Al_2O_3, Sumitomo) and $CaCO_3$ (Merck p.a.). The starting powders with the appropriate compositions (Table 1) were mixed for 48 h in iso-propanol (IPA) using Si_3N_4 balls (powder:balls ratio = 2:1) in a polythene bottle on a roller bench. As binder material a mixture of 1 wt.% of PEG 400 (Polyglykol 400 DAB8, Hoechst) and 1 wt.% PEG 8000 (Polyglykol 8000S DAB8, Hoechst) was added for obtaining a better running powder. Then the iso-propanol was removed by evaporation and the resulting powders were dried and fractionated by sieving ($0.5 < X < 1$ mm). Subsequently the powders were pressed uniaxially (10 MPa) followed by cold isostatic pressing at 250 MPa. Before hot pressing, the tablets were calcined at 900°C for 1 h in air in a special binder removal furnace to remove the binder and decompose the $CaCO_3$ into CaO. Finally the tablets were hot pressed at 1700°C for 1 h at 35 MPa in a nitrogen atmosphere. The shrinkage during reaction hot pressing was determined by monitoring the displacement of the piston. The hot-press used was a HP20 of Thermal Technology Ind. equipped with an Astro furnace model 100-4560-FP with graphite heating elements. The temperature was measured with a BGT-2 (graphite vs. B_4C) thermocouple. A graphite die (dia. 30 mm) and plunger were used. The heating rate was 10°/min and no pressure was used before 1700°C was reached. Cooling down was performed naturally which means 20–30°C/min from 1700 to about 1000°C. The reaction sintering experiments were carried out either in the dilatometer with bars or in a graphite resistance furnace with tablets. The tablets (dia. 12 mm) treated as described above, were heated in vacuum till 900°C, then nitrogen pressure (0.5 MPa) was applied. The sintering temperature was varied in the range 1700–1850°C and the heating rate was 10°C/min. In some experiments when the temperature had reached 1800°C, a high nitrogen pressure (10 MPa) was applied. The tablets were embedded in a powder bed consisting of a mixture of Si_3N_4 and BN. Cooling down was also performed naturally (20–30°C/min).

Table 1
Starting compositions of powders used for reaction hot-pressing (A, B, C) and reaction sintering (RS)

	m	*n*	$CaCO_3$ (wt.%)	Si_3N_4 (wt.%)	AlN (wt.%)	Al_2O_3 (wt.%)
A	2	1	15.5	65.4	19.1	–
B	2	1.5	15.5	61.8	20.1	2.6
C	1	2	8.3	69.7	13.6	8.4
RS	1.6	0.8	12.8	71.5	15.7	–

According to the phase behavioural diagram, the compositions A and B should give a single-phase α-sialon material and C should be an α/β-sialon composite material.

2.2. Sintering of carbothermally prepared Ca-α-sialon powder

Details with respect to the carbothermal preparation of Ca-α-sialon powder are given in Ref. [18]. The grain size of the powder (attrition milled) measured using the sedigraph method is less than 1 μm ($d_{50} = 0.96$ μm). To determine the optimal processing conditions for sintering carbothermally produced Ca-α-sialon powder (composition aimed at $m = 1.6$, $n = 0.8$ [18]) the influence of a number of variables was checked. An important parameter is the amount of sintering additive. This was studied using 10 and 15 wt.% CaO as a sintering additive. Three types of experiments were done in the dilatometer with bars (Section 2.3.):

1. Carbothermally prepared powder was mixed (Si_3N_4 balls, IPA, roller bench, 48 h) with $CaCO_3$ (to be decomposed to obtain CaO), pressed in bars and sintered, the decomposition of $CaCO_3$ was performed in vacuum at 900°C
2. To check the influence of residual carbon left after the carbothermal preparation the powder was first calcined at 700°C in air to remove the carbon, mixed as mentioned above with $CaCO_3$, pressed in bars and sintered, the decomposition of $CaCO_3$ was performed in vacuum at 900°C
3. To check the additional influence of granulation and fractionation, carbothermally produced powder (calcined at 700°C in air), $CaCO_3$ and PEG (see Section 2.1.) as binder were mixed as above, pressed in bars, binder removed and $CaCO_3$ decomposition at 900°C in air (as described in Section 2.1.), and sintered. In addition to the bars for the dilatometer experiments tablets (dia. 12

mm) were sintered in the same way as mentioned in step 3. All green tablets were sintered at 1700°C for 2 h in 0.5 or 10 MPa of nitrogen in a graphite resistance furnace with a heating rate of 10°C/min. The tablets were embedded in a powder bed consisting of a mixture of Si_3N_4 and BN to avoid decomposition of the starting materials. Cooling down was performed naturally (20–30°C/min).

2.3. Dilatometry

To determine the optimal sintering temperature several dilatometer experiments were performed. They were carried out with bars in a graphite resistance furnace in a static nitrogen atmosphere (0.5 MPa). Heating rate was 5°C/min to get a good separation of the shrinkage rate peaks (in contrast with the sintering experiments using tablets where 10°C/min was used), temperature was held constant at the maximum shrinkage rate and no soaking time was applied at the top temperature. In the dilatometry experiments no protective powder bed could be used, only a layer of BN. The dilatometer was set up to measure horizontal displacement. Mixtures for reaction sintering (Section 2.1.) and for sintering of carbothermally prepared powders (Section 2.2.) were pressed into bars (approximately $15\times5\times5$ mm^3), in some cases with the aid of PEG as a binder material (see above), first uniaxially (10 MPa) and then cold isostatically at 250 MPa. To remove the binder and decompose $CaCO_3$, the bars were carefully heated up in air to 900°C and soaked for 1 h.

2.4. Characterisation

To characterise the different phases present in the samples X-ray diffraction was used (Rigaku Geigerflex, Cu-K_α radiation). The ceramic samples were polished and placed in the sample holder of the diffractometer. The scanning angle ranged from 10° to 97° 2θ and the scan speed was 0.002°/s (0.01°/step, 5 s counting time). The density of the samples was measured using the Archimedes method by immersion in water. If the samples had still open porosity the density was determined from size and weight of the samples. The theoretical density is about 3.22 g/cm^3 [19].

3. Results and discussion

3.1. Phase composition

During sintering no significant decomposition took place (weight loss < 2 wt.%) for all three methods. From the X-ray diffraction pattern it was determined that both reaction hot pressed samples A and B were single-phase Ca-α-sialon. Sample C was multi-phase, besides Ca-α-sialon also traces of a β-sialon with low z-value and 12H were observed. This phase composition is in agreement with the results found by Hewett et al. [18], Wood et al. [20] and our own results [21]. From the diffractograms the cell parameters of the materials were calculated. With the equation given in Ref. [22] the m-values were calculated to be $m=1.5$ for A ($a=0.7851$ nm, $c=0.5713$ nm), $m=1.4$ for B ($a=0.7844$ nm, $c=0.5708$ nm) and $m=0.9$ for C ($a=0.7813$ nm, $c=0.5682$ nm). For the single-phase Ca-α-sialon material (samples A and B) this means that about 75% of the amount of calcium is incorporated in the α-sialon matrix. This is in close agreement with the results found by Huang et al. [23]. They found an incorporation of nearly 70% of the Ca amount on the line $m=2n$. For sample C the calculated m-value (0.9) resembles the m-value belonging to the weight-out composition (1.0). This, together with the observation of some β-sialon phase in sample C, is in agreement with the fact that the composition is near the border between the single-phase α and two phase α/β regions.

For the reaction sintered specimens the composition was a single-phase Ca-α-sialon material with an estimated m-value of 1.2 (calculated from $a=0.7830$ nm, $c=0.5694$ nm with the equation of [22]) while a value of $m=1.6$ was weighed out. This means an incorporation of±75% of the calcium, the same as found for samples A and B.

The sintering of the carbothermally prepared Ca-α-sialon powders with 10 and 15 wt.% CaO as sintering additive resulted in about the same m-value of the α-sialon. The m-value calculated for the starting powder is 1.4±0.2 [22] (indicating an incorporation of 75% Ca) whereas for the ceramic samples $m \approx 1.2$ and $m \approx 1$, respectively. For addition of CaO to Ca-α-sialon ($m=2n$), formation of $2CaO{\cdot}Si_3N_4$ in equilibrium with Ca-α-sialon with a higher m-value is expected according to Huang et al. [23]. In our work neither $2CaO{\cdot}Si_3N_4$, nor an increase in the m-value was observed, indicating non-equilibrium conditions.

3.2. Densification mechanism

The 'mechanism' of sintering appears to be rather similar for the three methods used. For our reaction hot pressing experiments it is not possible to determine the temperature of liquid phase formation due to the set up of the experiment. For the densification rate during reaction hot pressing of the materials no information was obtained before the pressure was applied at the top temperature of 1700°C. The shrinkage behaviour of the three different compositions can be qualitatively compared with each other at that temperature. The order in decreasing densification rates is: sample B ($m=2$, $n=1.5$) $\approx$ C ($m=1$, $n=2$) $>$ A ($m=2$, $n=1$). The rate difference between sample B and C is very small but the rate difference of these two is significant compared to the densification rate of sample A (B $\approx$ C $>$ A). This is in agreement with what is expected if the rate is controlled by the oxygen content. Sample A is on the line $n = m/2$ and has the lowest amount of oxygen compared to the other two, moreover the intentionally added oxygen originates only from CaO. Samples B and C meet the requirement $n > m/2$, the oxygen is present due to CaO and the addition of extra Al_2O_3. This means a larger amount of liquid phase which causes a faster densification compared to sample A. The density of the reaction hot pressed tablets (3.20, 3.18 and 3.19 g/cm^3 for samples A, B and C, respectively) was about 99% of the theoretical density.

The densification during reaction sintering of the composition $m = 1.6$, $n = 0.8$ as followed by dilatometry shows two major peaks in the shrinkage rate (Fig. 1). The first peak can be ascribed to particle rearrangement due to the formation at about 1350°C of a eutectic liquid phase from CaO and the oxide layers on the surface of the nitride starting materials. Between 1400 and 1500°C solution/precipitation of the nitride starting materials is believed to take place. This temperature is in agreement with the results reported by Hewett et al. [24] for reaction hot pressing Ca-α-sialon where they found an increasing fraction of liquid phase due to redissolution of gehlenite to support densification. This gehlenite formation/redissolution is also observed with X-ray diffraction in our reaction sintering experiments [25]. Besides these major peaks some smaller peaks can be recognised. At ±1560°C a small but clear peak is visible. Less pronounced peaks can be observed at ±1610°C and ±1660°C. Menon et al. [26] suggested several reactions to occur during densification of Ca-α-sialon by reaction hot pressing based on the shrinkage curves. The temperatures of the reactions identified in their study are in good agreement with the values we have found:

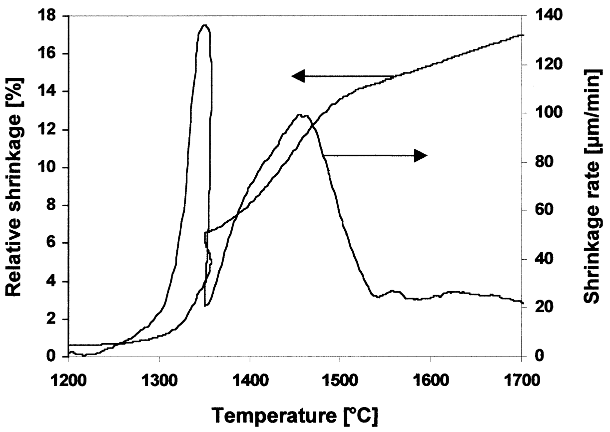

Fig. 1. Dilatometer curve of reaction mixture of CaO, Si_3N_4 and AlN with a composition $Ca_{0.8}Si_{9.6}Al_{2.4}O_{0.8}N_{15.2}$. The kink in the shrinkage curve at the holding temperature of 1350°C (15 min) is a result of an overshoot when it is reached. Final density of this sample is 95% of the theoretical density.

1. 1360°C, the eutectic formation [26] as in our case.
2. 1410–1450°C, ascribed to wetting of Si_3N_4 [24] corresponding with the start of the solution/precipitation mechanism.
3. 1550°C assigned to the formation of the final Ca-α-sialon phase [26], corresponding with a similar reaction in our reaction scheme proposed for reaction sintering [25]. In results recently reported by Zhou et al. [27] for hot pressed Ca-α-sialon ceramics the gehlenite phase has disappeared at a similar temperature (1500°C) as in our experiments and they find the same trend of densification. Moreover, their results indicate that nearly full densification can be obtained at 1600°C and higher [27], in agreement with figure 1 and the densities we have obtained for the sintered tablets (95%, [25]).

The influence of the different processing parameters (as the burn out of residual carbon and granulation) on the densification of carbothermally prepared Ca-α-sialon powders with 10 wt.% CaO as sintering additive is shown in Fig. 2. Without treatment the powder hardly densifies. The relative density of the green samples is about 50% and the final relative density is about 65%. After only burn out of the residual carbon the relative density increases from 52% (green density) to 68% (ceramics). No oxygen is consumed anymore by the carbon during sintering resulting in a larger amount of liquid phase. A full treatment, meaning carbon removal as well as granulation (green density 55%), gives a relative density of 73% (ceramics). It is clear that both removal of residual carbon as well as granulation have a positive effect on the density of the Ca-α-sialon material. The granulation makes the density of the green body higher and consequently that of the sintered product. Densification goes drastically better if more sintering additive is used. The maximum density of the dilatometer samples achieved with 10 wt.% CaO is 2.34 g/cm^3 whereas for 15 wt.% CaO a density of 3.06 g/cm^3 is obtained. These values correspond to 73% and 95% of the theoretical density, respectively (ceramics). These densities are obtained for dilatometer samples and are always lower than densities obtained with tablets using a protective powder bed. When applying a higher pressure or a protective powder bed mixture as is the case in the furnace experiments for sintering carbothermally prepared powders the density becomes 3.11 g/cm^3 ($\sim$97%) for samples with 15 wt.% CaO as sintering additive. This value is obtained by a not yet optimised sintering process. Recently, another possibility was suggested to increase the densification by using dual cation sialons [28].

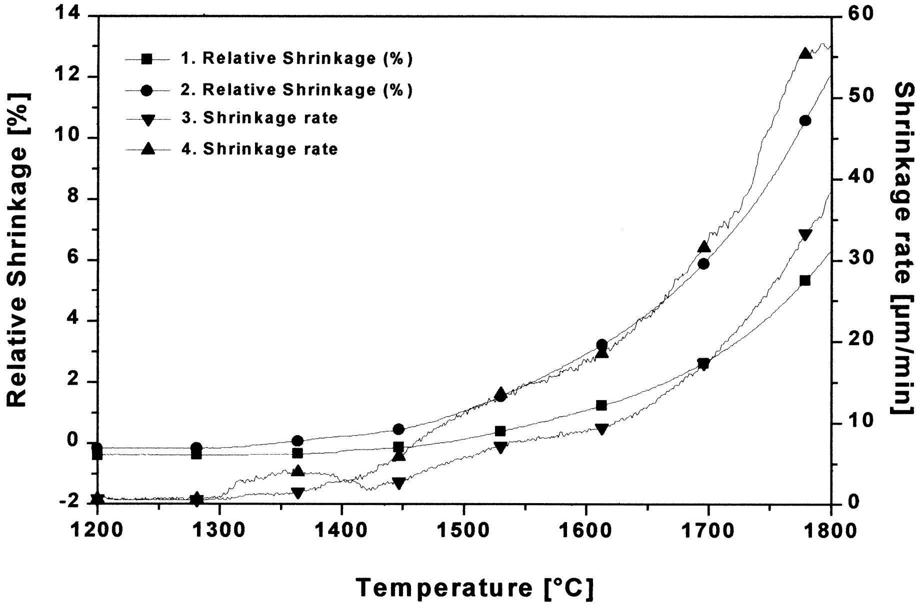

Fig. 2. Comparision of dilatometer curves of carbothermally prepared Ca-α-sialon powders with 10 wt. CaO as sintering additive; not processed (1, 3) and processed (2, 4: i.e. calcined at 700°C in air to remove residual carbon and granulated before pressing).

If the dilatometer curves obtained with carbothermally prepared powder (Fig. 2) are compared to the curve obtained for reaction sintering (Fig. 1) several similarities and differences can be recognised. The formation of the eutectic liquid (first peak) is at the same temperature (1350°C) as in reaction sintering, this is obvious because the same melt is formed from of CaO and Al–Si–O compounds present at the surface of the nitride or sialon starting materials. The wetting of the sialon starting material inducing the solution/precipitation mechanism (peak 2), however, takes place at a significantly higher temperature indicating a higher wetting temperature for sialon material (1500–1550°C) as compared to Si_3N_4 (1450°C). In the curves also other minor peaks are recognisable at±1650–1700°C. It seems that here also an intermediate phase dissolves similar to the reaction sintering route. As a final remark, we want to mention that the shapes of the measured sintering curves (carbothermal powders and reaction sintering) are similar to shrinkage curves reported for other α-sialon materials (containing lanthanide's or Y) for both low pressure reaction sintering [29] as well as for reaction hot pressing [26]. This indicates similar densification mechanisms for all these materials.

4. Conclusions

Reaction hot pressing is a very efficient and convenient method to obtain almost fully dense Ca-α-sialon materials (~99% relative density). Reaction sintering is also a good method to achieve almost full densification (> 90% relative density). The influence of the amount of CaO as a sintering additive on the densification of carbothermally prepared Ca-α-sialon powder has been shown to be significant. The highest density was reached with 15 wt.% CaO (~ 97% relative density). It was shown that removal of residual carbon and granulation has a positive effect on the final density of the material. Use of a protective powder bed and higher nitrogen pressures further improves densification. The mechanisms of liquid phase sintering using the three mentioned methods (reaction hot-pressing, reaction sintering and sintering of carbothermally prepared Ca-α-sialon powder with CaO as a sintering additive) are similar to each other. First a rearrangement of the particles takes place due to liquid formation at about 1350°C followed by a solution/precipitation mechanism at 1450–1550°C depending on the starting materials. The mechanism for sintering Ca-α-sialon is similar to the mechanism described in literature for other Ln-α-sialon (Ln = Y, lanthanide's) materials.

Full densification of the material can be accomplished by either higher nitrogen pressure or addition of more sintering additives. The former has the disadvantage of higher processing costs while the latter could influence the high temperature properties in a negative way, although this is not so significant for the Ca-α-sialon ceramics. Combination of Ca with other cations may further increase the density or ease the processing conditions.

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