

Fabrication of low cost shrinkage-free porous sialon ceramics

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The possibility of fabricating shrinkage-free sialon ceramics from natural aluminosilicates by simultaneous carbothermal reduction and nitridation (CRN) was explored. X-ray diffraction studies confirmed that the products synthesized contained sialon as the major crystalline phase. The average linear shrinkage of sialon pellets produced by CRN at 1450 °C from bentonite and kaoline was about 9-18%. However, it is interesting to report that the study with kyanite led to an important discovery of the possibility of synthesizing sialon samples by CRN to have zero shrinkage after sintering. This has an important implication as many industrial applications demand close dimensional tolerance of fired ceramic bodies such as honeycomb structures. The volume expansion associated with the transformation of kyanite to mullite around 1350 °C is responsible for compensating the sintering shrinkage which would otherwise occur during CRN. The resulting porosity of sialon pellets was more than 60%.

Key words: Shrinkage free ceramics, Sialon ceramics, Kyanite, Carbothermal reduction and nitridation, Porous ceramics.

Introduction

Sialon ceramics have high potential to resolve a wide number of today's material challenges in many industries due to their attractive properties. Despite this, sialon ceramics are only used in a small percentage of applications in industry. Many manufacturers and end users are still reluctant to use these ceramics because of concerns about the high cost, difficulty of manufacturing articles with near net shape and reliability compared to competitive materials. In this study, the emphasis was therefore given to the above factors in the synthesizing of sialon ceramics.

The α and β sialons are solid solutions of α and β Si_3N_4 , in which Si and N are substituted by Al and O, respectively. β -sialons are expressed by the general formula $\text{Si}_{6-z}\text{Al}_z\text{O}_z\text{N}_{8-z}$, where, z is the Al substitution level and $0 < z < 4.2$ [1]. The stability of α -sialon however, requires the addition of some selected metal cations [2]. Different methods are known for fabricating sialon ceramics. Well known methods are (i) the direct synthesis by reaction sintering of a mixture of ceramic powders and (ii) simultaneous reduction and nitridation of aluminosilicate materials. For the direct synthesis, a mixture of powdered silicon nitride, aluminum nitride, silica, and alumina is compacted and is sintered at a very high temperature (1700 °C to 1800 °C). As stated already this method suffers from the drawbacks of using raw materials that are quite expensive, and of requiring sintering at very high temperatures. Previous investigations have shown

that sialon powders can be prepared from clay minerals by simultaneous carbothermal reduction and nitridation (CRN) [3-14]. For the reduction of aluminosilicates various reducing agents such as hydrogen, ammonia, carbon, etc. can be employed. A drawback of the carbon reduction methods lies in the difficulty of accurately controlling the carbon content, and thus the degree of reduction. Another drawback which results from the inclusion of carbon in the starting compound is that the resulting ceramic body is porous because of the inevitable evolution of carbon monoxide during reduction.

Previous studies of sialon synthesis by CRN

Lee and Cutler [3] were the first to report the carbothermal reduction and simultaneous nitridation of a kaolin/carbon mixture to form β -sialon powder. Since then several investigators [3-14] have studied various aspects of this method of synthesis of sialon powder using kaolin. Although, the reaction appears to produce very simple final products, in practice CRN can lead to complicated reactions resulting in SiC, AlN, Al_2O_3 and other sialon phases depending on the processing parameters such as the CRN temperature, the holding time, the carbon content, the nitrogen flow rate, the purity of starting materials, etc. Lee and Cutler [3] used kaolin and carbon black as starting materials to perform CRN at 1450 °C and obtained β -sialon powder with minor amounts of SiC and AlN phases. An excess of carbon resulted in the formation of Al_2O_3 and 15R phases in addition to sialon and they stressed the importance of controlling the carbon content. Lee *et al.* [5] observed the formation of β -sialon together with small amounts of Al_2O_3 , AlN, and 15R by performing CRN at 1350 °C for 10 h in a mixture of 80% N_2 plus 20% H_2 , using Korean kaolin and graphite as starting

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materials. Demir and Caliskan [10] obtained β -sialon with $z = 3$ by CRN of a mixture of Turkish kaolin and a stoichiometric amount of carbon black with 30% charcoal between 1400 °C and 1475 °C for 4 h. Cho and Charles [12] prepared β -sialon by CRN of kaolin and carbon mixtures at 1400 °C–1500 °C in flowing nitrogen. They observed that a single phase β -sialon powder is formed only when the kaolin/carbon ratio was accurately controlled. They also noted that the evaporation of SiO was an important factor in the reaction, strongly affecting the phase composition of the reaction products. Gilbert and Mosset [14] found that the preparation of β -sialon as a single phase was possible by CRN at 1400 °C with 30 wt.% of carbon. If the carbon content was too high (40 wt.%), SiC was formed in large amounts, whatever the temperature and the reaction time. Similar observations were made by Liu et al. [15] in CRN at 1450 °C for 6 hours under a N₂ flow of 2.5 l per minute. Xu *et al.* [16] reporting the optimum conditions for the formation of sialon, they stated that the clay mixture containing 20 wt.% of carbon should be sintered at 1500 °C for 6 hours in a nitrogen flow of 1.5 l per minute. Using Turkish kaolin, Tatli *et al.* [17] found that the holding temperature (1400 °C–1475 °C) and the gas flow rate (1.8 l per minutes) were important in determining the reaction rate and the yield of sialon. Vlasova et al. [18] were successful in performing CRN at 1450 °C–1600 °C on large quantities of powder samples up to 1.5 kg of kaolin/carbon mixtures. MacKenzie and Barneveld [19] carried out CRN to produce sialon powder using a mechanochemically activated precursor of raw materials fired at 1400 °C–1475 °C for 4 hours in a nitrogen gas flow of 100 ml per minute.

Other researchers have used SiO₂–Al₂O₃ compositions [20], silicate or aluminosilicate minerals such as talc, halloysite [19, 21, 22], diatomaceous [23], diatomite, bentonite [24, 25], mullite, andalusite, cyanite, different clays, pyrophyllite [25] and zeolite [26]. Taking the above findings into consideration, in particular the processing parameters of CRN, the present research study on synthesis of sialon was planned. The main emphasis was given to produce low shrinkage, low cost sialon ceramics from cheap natural aluminosilicates such as kaolinite (Al₂O₃·2SiO₂·2H₂O), bentonite (Al₂O₃·4SiO₂·H₂O) and kyanite (Al₂O₃·SiO₂) using activated carbon as the reducing agent.

Experimental Procedure

As already mentioned, kaolin, bentonite (Particle size = 0.1 – 4 μ m; Sigma-Aldrich Korea) and kyanite (Calcined; 35–200 mesh, Dong. Kuk. Rhs Company, Korea) were used as natural aluminosilicates and activated carbon (surface area = 130 m² per gram, particle size = 22 nm, apparent density = 160 kg m^{–3}; Grand Chemical & Materials Co., Ltd, Korea) was used as the reducing agent. Since the particle size of the as-received kyanite powder was large, the kyanite powder was further crushed down using a mortar and a pestle before the ball milling process.

The appropriate amounts of aluminosilicates and the carbon powder to form sialon were mixed and milled in a rotating polyethylene bottle in ethyl alcohol with silicon nitride balls as the milling media. The amounts of reactants in the mixture were calculated according to the stoichiometric compositions of the expected sialon product (Si_{6–z}Al_zO_zN_{8–z}; $z = 2, 3$ or 4) depending on the Si/Al ratio of the starting aluminosilicate composition. The precursor charge was 50 grams and the milling time was about 60 hours. The milled wet powder mixture was sieved through a 38 μ m grid and then dried. The dried powder was cold isostatically pressed (CIP) at 200 MPa to form disc shaped pellets (diameter–16 mm) and square pellets (10 × 10 mm). Pellets as well as powder mixtures kept in alumina boats were simultaneously corbothermally reduced and nitrified in a horizontal alumina tube furnace. The holding temperature was kept at 1450 °C, for 6 hours in nitrogen with a flow rate of 500 ml per minute. The heating and cooling rates were 10 K minute^{–1} and the samples were allowed to heat as well as cool under flowing nitrogen to avoid oxidation. The synthesized samples were subsequently heated in air at 700 °C for 6 hours to burn out any remaining carbon. Before and after each experimental step the pellet samples were weighed and the dimensions of the pellets were measured accurately in order to calculate the shrinkage and the density. Sialon samples synthesized from kaolin, bentonite and kyanite were also post sintered using gas pressure sintering (GPS) at 1600 °C and 1900 °C in a graphite crucible in a carbon resistance furnace under a static nitrogen gas pressure of 0.9 MPa. The phase composition of the reaction products was identified by X-ray diffraction (Rigaku D/Max 2200, Japan) with Cu–K α radiation using the powder as well as pellet forms. The porosity was determined using a mercury porosimeter (Micrometrics AutoPore IV 9500, U.S.A.) and was also compared with observations in a scanning electron microscope (JEOL JSM-5800, Japan).

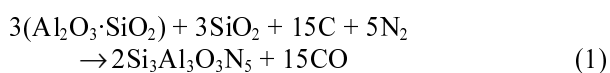
Results and Discussion

The as-prepared powder mixture of kaolin and carbon was black in color and the samples turned into a grey color after CRN reactions at 1450 °C, for 6 hours in nitrogen with a flow rate of 500 ml per minute. This observation was similar for bentonite as well as for kyanite after the CRN reactions. The XRD analysis confirmed the formation of β -sialon after CRN and GPS.

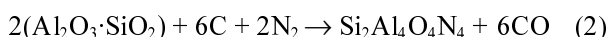
The average linear shrinkage of sialon pellets produced by the CRN of kaoline was about 18%. The post sintering by GPS resulted in more shrinkage up to 20% with an improved density. The sialon pellets produced by CRN of bentonite showed a slightly lower sintering shrinkage of 14% than that of kaolin samples. As highlighted earlier the occurrence of a low sintering shrinkage is an important factor and desirable in fabricating structural components for many applications. Since the shrinkage

is never exactly uniform throughout the ceramic body, there is always a certain amount of warpage or distortion. Usually when sialon ceramics are prepared from the direct route the sintering shrinkage is typically around 15-20% depending on the sintering conditions and fabricating parameters. The shrinkage occurs during firing due to the elimination of pores via diffusion of matter to reduce the surface energy. In addition, the ceramic raw materials used can undergo a chemical or a crystalline transformation during sintering. If the transformed ceramic is of a greater density and of a lesser volume than the raw ceramic ingredients, then this also contributes to the shrinkage. The opposite of this second process can be used to control the shrinkage. In other words if the raw materials undergo a transformation during firing to form materials having a low density with a greater volume, the firing shrinkage due to densification can be compensated to result in a low shrinkage ceramic body.

It is known [27, 28] that when kyanite or cyanite ($\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$) is heated at high temperatures around 1350 °C it is converted to mullite, ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) and free silica with a considerable increase in volume. Kyanite has a triclinic crystal structure with an average density of $3.6 \times 10^{-3} \text{ kg m}^{-3}$ and mullite has an orthorhombic crystal structure with an average density of $3.0 \times 10^{-3} \text{ kg m}^{-3}$. A simple calculation shows that the volume increase is about 18% during the transformation of kyanite to mullite and silica. In the present study this interesting property of kyanite was successfully used to fabricate shrinkage-free sialons. Kyanite has two polymorphs, andalusite and sillimanite and both are anhydrous aluminosilicate minerals unlike kaolin and bentonite. Kyanite has the highest density and can be distinguished from the other two polymorphs by its physical properties. Kyanite has the lowest Si/Al ratio ($\text{Si/Al} = 0.5$) compared to that of kaolin ($\text{Si/Al} = 1$) and bentonite ($\text{Si/Al} = 2$). Therefore by adding the appropriate amounts of SiO_2 to a stoichiometric powder mixture of kyanite and carbon, β -sialons having different z values can be synthesized by CRN. For example by adding 3 moles of SiO_2 to 3 moles of kyanite, and making $\text{Si/Al} = 1$, $z = 3$ β -sialon can be produced by CRN as given by the following reaction:



Using only kyanite and carbon can also produce a β -sialon having $z = 4$ by CRN according to the following chemical reaction:



In the present study both the above CRN reaction compositions were used to convert kyanite to β -sialons. A stoichiometric powder mixture of kyanite, silica and carbon was prepared according to the first chemical equation (1) above to give a β -sialon by CRN at 1450 °C for 6 hours in nitrogen with a flow rate of 500 ml per minute. Pellet samples were prepared by CIP (200 MPa) with

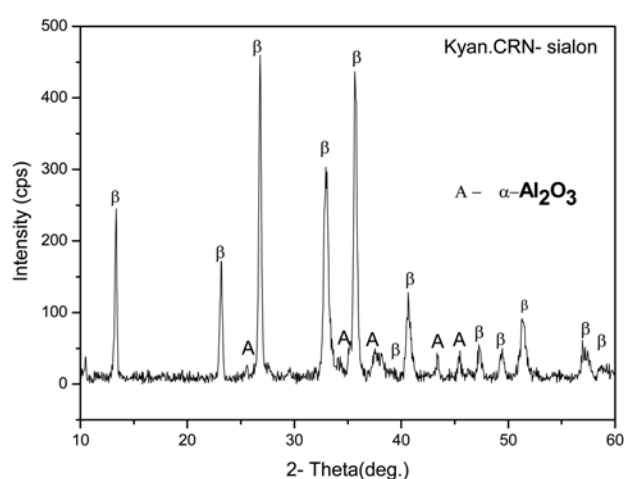


Fig. 1. XRD pattern of a sample prepared by CRN of kyanite, silica and carbon at 1450 °C for 6 hours in nitrogen with a flow rate of 500 ml per minute. β -sialon is present as the major phase. Small $\alpha\text{-Al}_2\text{O}_3$ peaks are also present as a minor phase.

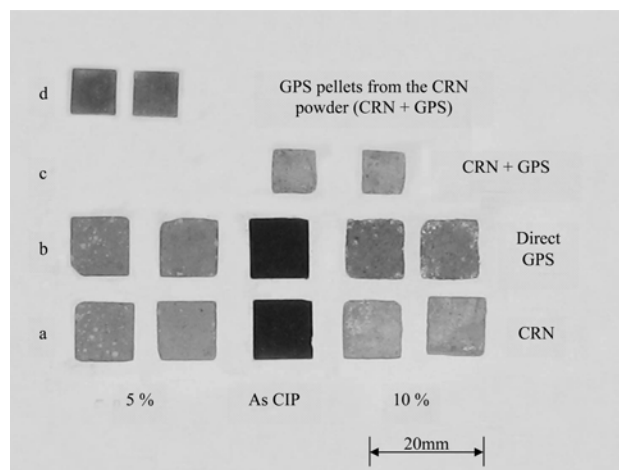


Fig. 2. Photographs of sialon samples prepared from kyanite, silica and carbon with 5 wt.% and 10 wt.% Y_2O_3 showing (a) the retention of the size with almost zero sintering shrinkage after CRN at 1450 °C (b) having almost zero sintering shrinkage even after direct GPS at 1600 °C for 4 hours (c) 24% shrinkage of the pellets previously undergone CRN at 1450 °C and subsequently subjected to GPS and (d) 21% shrinkage of the pellets prepared by CIP from the sialon powder obtained from CRN with 3 wt.% Y_2O_3 as a sintering additive.

(5 wt.% and 10 wt.% Y_2O_3) and without a sintering additive. The X-Ray Diffraction (XRD) analysis (Fig. 1) confirmed the formation of β -sialon as the major phase. The XRD pattern shows the presence of very small peaks from Al_2O_3 .

As anticipated the sintering shrinkage of sialon pellet samples was almost zero after CRN at 1450 °C. Fig. 2(a) (bottom line) shows a photograph of the retention of the size of the samples without a change. This was true for the samples prepared with (5 wt.% and 10 wt.% Y_2O_3) and without a sintering additive. For comparison, an as-CIP sample (without CRN) is also included in the photographs. The average linear shrinkage of the sides

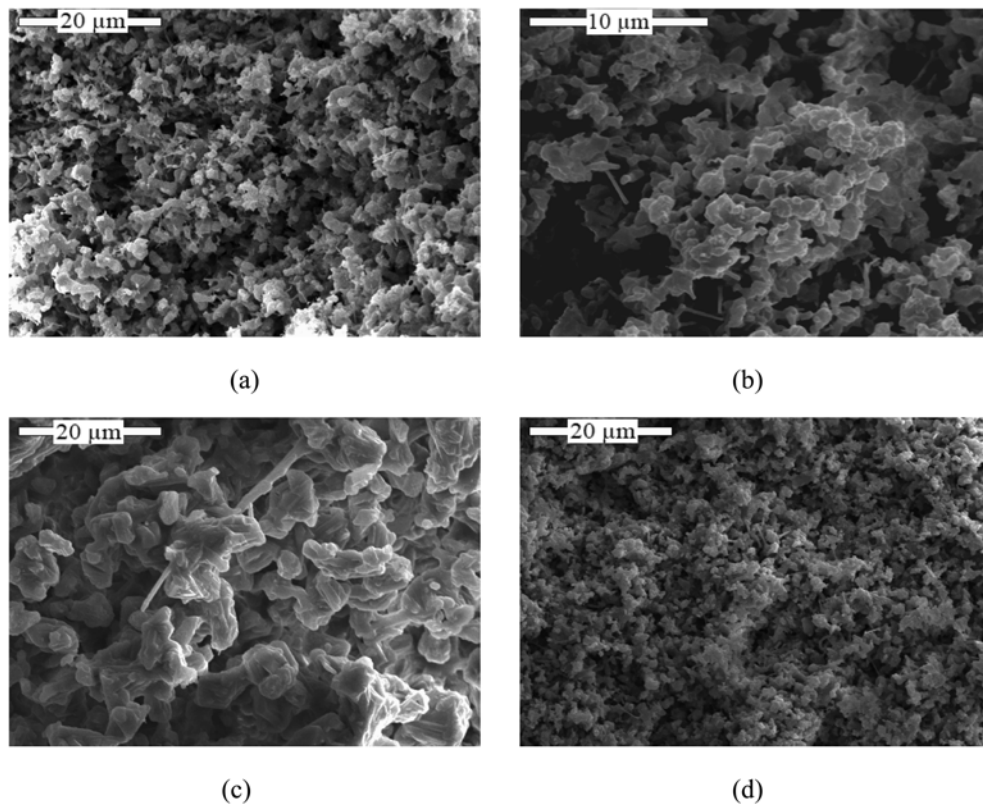


Fig. 3. SEM micrographs of fracture surfaces of sialon samples showing the porous structure. Samples of (a) & (b) were prepared from kyanite, silica and carbon with 5 wt.% Y_2O_3 by CRN. The average grain size is about 2 μm . (c) Similar porous structures of the samples prepared by GPS at 1600 °C. The average grain size has increased due to the higher sintering temperature. (d) Samples prepared from kyanite, and carbon with 5 wt.% Y_2O_3 by CRN (no silica).

Table 1. The pellet samples prepared under different conditions to study the low shrinkage behavior of the sialon formation from kyanite

Sample Type		Process Description	Linear Shrinkage	Density $kg\ m^{-3}$
1	Direct GPS	Direct GPS of pellet samples prepared from the stoichiometric powder mixture of kyanite, silica and carbon with (5 wt.% and 10 wt.% Y_2O_3) by CIP (200 MPa)	0.2%	1000
2	CRN + GPS	The pellets had previously undergone CRN at 1450 °C (with 5 wt.% and 10 wt.% Y_2O_3) and were subsequently subjected to GPS	24%	2100
3	GPS pellets from the CRN powder	Pellets prepared by CIP (200 MPa) from the sialon powder obtained from CRN with 3 wt.% Y_2O_3 as a sintering additive	21%	3000

of square samples with 5 wt.% Y_2O_3 was about 0.7%. In the direction of thickness a slight expansion was observed and the average value was about 0.5%. As expected the density was very low and the average value was about $0.83 \times 10^{-3}\ kg\ m^{-3}$. The observation of similar low values of the shrinkage and the density of the samples without additives and with 5 and 10 wt.% Y_2O_3 indicates a small effect of sintering additives in the over all shrinkage. However, for a better mechanical strength, sintering additives should be added.

The experimental weight loss of samples was about 42% which is about 9% more than the calculated value. As mentioned earlier, escape of volatile SiO is likely to be the reason for the difference. The porosity of pellets was about 55% and the average pore size was about 5 μm . However, the calculated porosity is about 75% based

on the bulk density value of CRN pellets and the theoretical density. The closed pores present in the ceramic which are not sensitive to the mercury porosimeter measurements may account for the balance of 20% porosity predicted by the density calculation. The porous structure was also observed in the scanning electron microscope (Fig.3(a) and 3(b)). The average grain size is about 2 μm .

In order to study more about the low shrinkage behavior of the sialon formation from kyanite, pellet samples prepared under different conditions (Table 1) were sintered using gas pressure sintering (GPS) at 1600 °C for 4 hours under a static nitrogen gas pressure of 0.9 MPa. The corresponding shrinkage and densities are given in Table 1. Fig. 2(b), 2(c) and 2(d) show photographs of the pellets processed and sintered under different conditions as indicated in Table 1. It is evident from the photograph of Fig. 2(b)

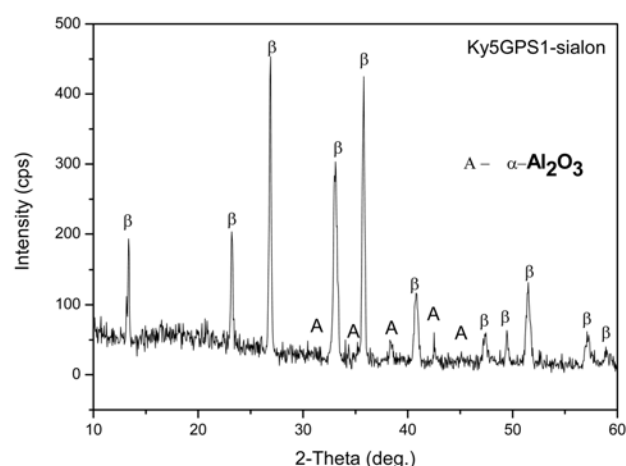


Fig. 4. XRD pattern of a sample prepared by GPS of kyanite, silica and carbon at 1600 °C, for 4 hours. β -sialon is present as the major phase and α - Al_2O_3 is present as a minor phase.

that the size has been maintained with almost zero sintering shrinkage even after direct GPS at 1600 °C for 4 hours of the pellet samples. The geometrical measurement of dimensions before and after GPS also confirmed this extremely low shrinkage (0.2%) of the direct GPS samples (Table 1: samples processed under the condition 1-direct GPS). The XRD analysis (Fig. 4) confirmed the formation of β -sialon after direct GPS at 1600 °C for 4 hours. It was observed by SEM (Fig.3c) that these samples also have a similar porosity to that of CRN samples. The low density of GPS samples is an additional indication of the high porosity. However, the average grain size has increased due to the higher sintering temperature. The samples processed under conditions 2 and 3 in Table 1 showed the typical sintering shrinkage associated with these ceramics (Fig. 2(c) and (d)). The pellet samples prepared from the CRN powder and subsequently subjected to GPS (Table 1: condition 3) showed the highest density. This is not surprising since the as- CIP pellets from CRN powder had a high initial compact density ($1.48 \times 10^{-3} \text{ kg m}^{-3}$) compared to that prepared under condition 2 (initial density- $0.83 \times 10^{-3} \text{ kg m}^{-3}$).

Process involved in the formation of shrinkage-free sialon

In order to understand the process involved in the formation of shrinkage-free sialon a series of CRN studies were performed at 1100 °C, 1200 °C, 1300 °C, 1350 °C, 1400 °C, 1450 °C and 1500 °C. Pellet samples pressed (CIP-200 MPa) from the stoichiometric powder mixture of kyanite, silica and carbon were used in this investigation. The linear shrinkage, the density/mass reduction and the phase composition of the resulting CRN samples were determined. Fig. 5 and 6 show the variation of the density and the shrinkage respectively of pellets sintered at different CRN temperatures. As the carbon content in the sample is continuously eliminated as carbon monoxide, the mass of the sample reduces gradually with heating.

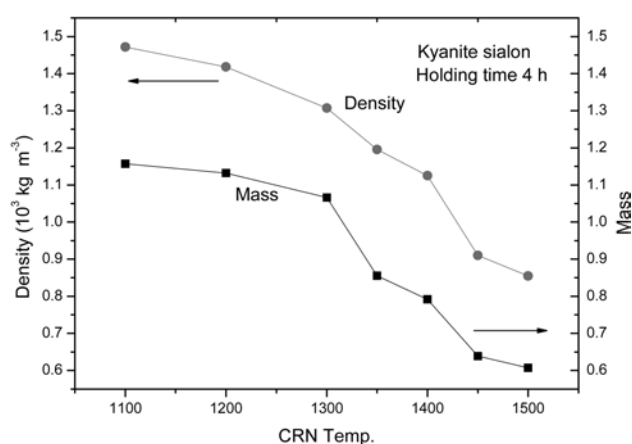


Fig. 5. Variation of the density and mass of pellets sintered at different CRN temperatures.

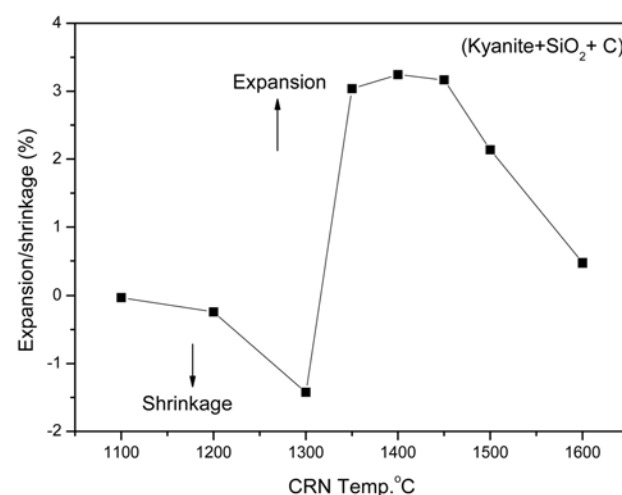


Fig. 6. Variation of the sintering shrinkage of pellets sintered at different CRN temperatures.

This gradual mass reduction was observed and is shown in Fig. 5. Since the volume of the sample remains virtually the same due to the low shrinkage, the density reduction follows in a similar manner to the mass reduction. It can also be seen (Fig. 6) that initially there is a very small shrinkage from 1100 °C to 1300 °C and then expansion (swelling) up to 1350 °C and again shrinkage from 1450 °C after having a plateau region (no dimensional change). However, it is important that the extent and the rate of shrinkage are dependent on the sintering temperature and the holding time. The observation of the expansion of samples around 1300 °C is also an indication of the onset of transformation of kyanite to mullite around 1300 °C. This was further confirmed by the phase evaluation of samples sintered at different temperatures. The relevant composite XRD patterns are shown in Fig. 7. For comparison the XRD pattern of the starting stoichiometric powder mixture of kyanite, silica and carbon is also included. It is clearly evident from Fig. 7, that at 1350 °C, the disappearance of kyanite and silica phases occurs with the formation of mullite,

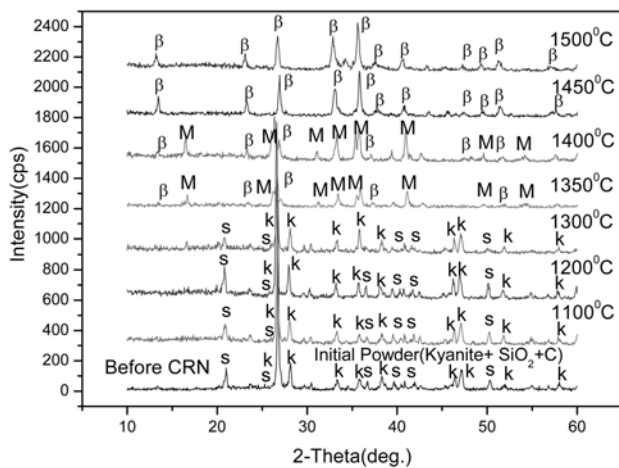
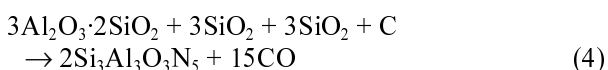
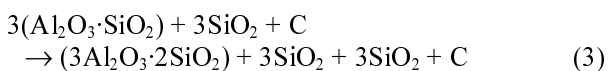


Fig. 7. XRD patterns of samples prepared by CRN of kyanite, silica and carbon at different CRN temperatures. It is evident that at 1350 °C, the disappearance occurs of kyanite (k) and silica (s) phases with the formation of mullite (M), and also the initiation of the conversion to sialon (β).

and also the initiation of the conversion to sialon. At this reaction temperature, the major phase present was mullite and β-sialon was present as a minor phase. It is interesting to note that the silica phase which may have formed during the transformation of kyanite as well as the silica deliberately added initially to the powder mixture was not detected in the XRD patterns. A similar observation has been reported in the literature [28]. The most likely reason for silica not being detected in XRD is due to the formation of a silicate liquid phase at this reaction temperature with the impurity oxides present in the original raw kyanite as well with the sintering additive. As a result the silica content is present as an amorphous phase at the end of the CRN process.

As seen in Fig. 7, when the CRN temperature was raised to 1400 °C the proportion of β-sialon increased. At 1450 °C and above, the β-sialon phase has become the dominant product and a complete disappearance of mullite was observed. Furthermore, the presence of the plateau region from 1350 °C to 1450 °C in Fig. 6 is additional evidence for the compensating of sintering shrinkage by the volume expansion associated with the kyanite to mullite transformation. The chemical reactions taking place in the temperature range from 1300 °C to 1450 °C, can be written as follows:



As pointed out earlier, the kyanite and carbon mixture (without silica) can also produce β-sialon with $z = 4$ by CRN according to the reaction (2).

Pellet samples pressed with 5 wt.% Y_2O_3 were prepared by CRN using a stoichiometric powder mixture of kyanite

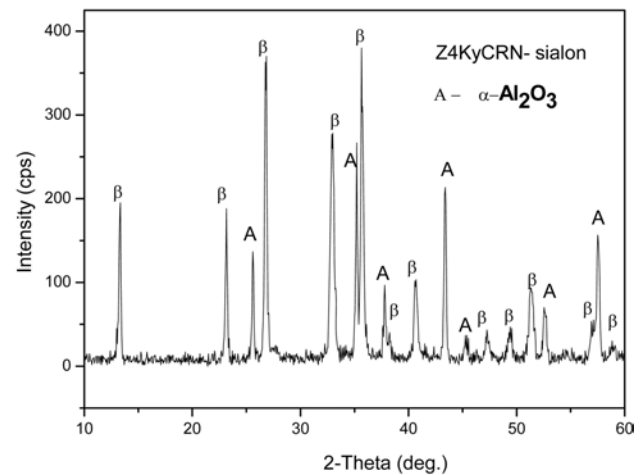


Fig. 8. XRD pattern of a sample prepared by CRN of kyanite and carbon at 1450 °C, for 6 hours in nitrogen with a flow rate of 500 ml per minute. β-sialon is present as the major phase and α- Al_2O_3 is present as a minor phase.

and carbon under similar experimental conditions given previously for CRN. The XRD analysis (Fig. 8) confirmed the formation of β-sialon as the major phase. However, the amount of the minor phase, α- Al_2O_3 was observed to be more in the XRD of this second composition, compared to that of the first composition. Escape of SiO has probably reduced the Si/Al ratio in the kyanite composition hence resulting in an increase of the Al_2O_3 concentration. This was not prominent in the first composition as there was extra silica added to the initial powder mixture.

The average linear shrinkage of the CRN pellets from the second composition was slightly higher and was about 5 %. The density was about $1.23 \times 10^{-3} \text{ kg m}^{-3}$ which is also higher than that of the pellets sintered from the first composition. However, it is noted that the initial packing density ($1.67 \times 10^{-3} \text{ kg m}^{-3}$) of as-CIP pellets of the second composition was higher than the packing density ($1.54 \times 10^{-3} \text{ kg m}^{-3}$) of as-CIP pellets of the first composition. Since the density of the carbon nanopowder is extremely low, the volume fraction added to the first composition is much more than what was added to the second composition. Since the carbon powder content is less in the second composition, the frictional resistance imposed by the large surface area of the carbon nanopowder against packing is less, to give a relatively high initial packing density for the pellets compacted from the second composition. There can be another possibility for the slightly higher sintering shrinkage observed in pellets pressed from the second composition. If the average particle size of the kyanite powder in the second composition is smaller than that in the first powder composition, it can give rise to a better packing density of CIP pellets. Moreover, finer particles of kyanite reduce the volume expansion associated with the transformation of kyanite to mullite due to better packing and hence giving rise to a higher

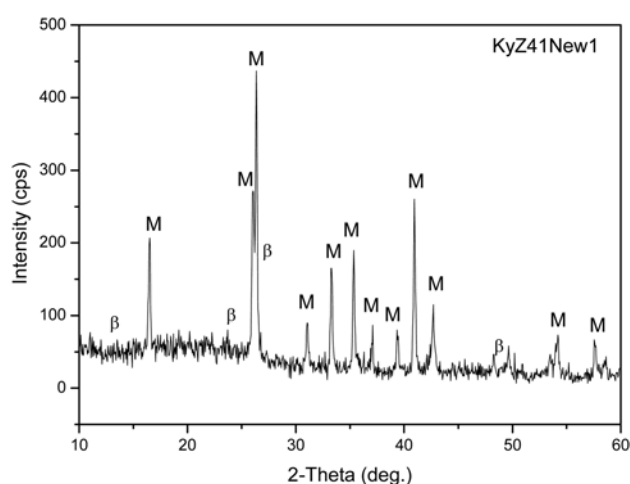


Fig. 9. XRD of a pellet sample(kyanite + carbon) heated up to 1450 °C under CRN conditions and the furnace switched off instantly without having a holding time.

shrinkage. As reported by Bradt *et al.* [29] the particle size of kyanite has a drastic effect on the volume expansion during the transformation of kyanite to mullite. From the dilatometric measurements of attrition milled kyanite powders they observed a total elimination of volume expansion with the reduction of particle size down to the nanorange. However, it is very unlikely to have any significant variation of particle size of the powder mixtures prepared in the present study under similar experimental conditions.

It has been reported [27] that the transformation of kyanite to mullite begins around 1180 °C and to almost 100% completion within 30 minutes at 1340 °C. Moreover, the dilatometric and XRD measurements showed [28] that the complete conversion of kyanite into mullite and the resulting expansion (a linear expansion of about 12%) are taking place in the temperature range 1320 °C to 1420 °C. Therefore at 1450 °C, the CRN-holding temperature of the present study, the transformation of kyanite to mullite and hence the volume increase have to be completed nearly 100% at the beginning of the holding period. In order to witness this behavior in the present system (kyanite under CRN condition), the pellet samples were heated at a rate of 10 K per minutes up to 1450 °C and the furnace switched off instantly without having a holding time. The square pellets showed a maximum of 9% linear expansion along the direction of the thickness due to the transformation. However, along the sides of the pellets the average linear expansion was lower and was about 4%. The XRD analysis of the pellets showed the transformation to mullite and disappearance of kyanite (Fig. 9). Appearance of very small peaks corresponding to β -sialon indicates the initiation of CRN reactions. However, it is difficult to identify the main β -sialon peaks as most of the main β -sialon peaks coincide with the mullite peaks. The observation of about 10% mass reduction of pellets during the above heating process also suggests the initiation of the CRN reaction. The above findings can be illustrated

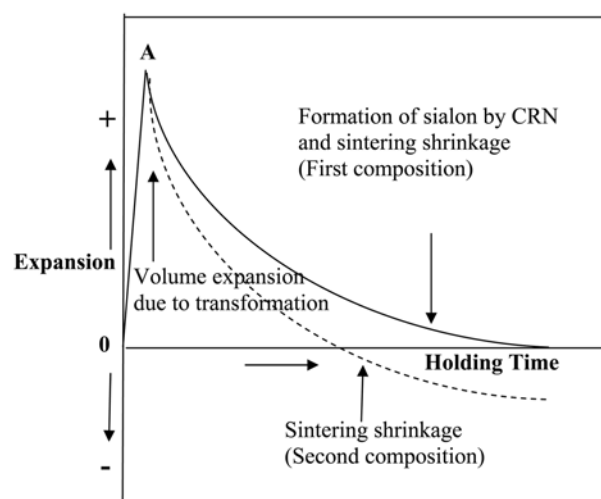


Fig. 10. Based on experimental evidence, illustrating the possible processes involved in formation of shrinkage-free sialon.

as shown in the Fig. 10. However, the densification of sialon from kyanite under CRN conditions (from kyanite via mullite transformation) may not be a simple process as the carbon content escapes as CO during the CRN reactions. The dotted line in the illustration (Fig. 10) represents a relatively higher sintering densification observed in the pellets sintered from the second composition and hence giving rise to a small residual shrinkage. The initial densification point marked (A) in Fig.10 may not be the same for the both compositions as they had different initial packing densities.

Conclusions

Shrinkage-free porous β -sialon ceramics were prepared by simultaneous carbothermal reduction and nitridation (CRN) of kyanite at 1450 °C, for 6 hours in nitrogen with a flow rate of 500 ml per minute. As anticipated, the volume expansion associated with the transformation of kyanite to mullite and free silica around 1350 °C, compensates the sintering shrinkage which would otherwise occur during CRN. However, it is important to maintain the particle size of kyanite powder in the micrometre range in order to obtain the advantage of the volume expansion connected with the transformation. Furthermore, the extent and the rate of shrinkage depend on the sintering temperature and the holding time.

The development of shrinkage-free ceramics has an important consequence in opening up the possibility of designing complicated sialon ceramic structural components such as honeycomb structures with high porosity and zero shrinkage. Adding appropriate amounts of silica to the initial kyanite and carbon powder mixture, shrinkage-free β -sialon ceramic bodies with different Al substitutions may be fabricated by CRN. Using gaseous reducing agents and hence avoiding mass reduction due to the carbon escape from the sintering body during CRN, a

greater flexibility in the sintering as well as the porosity may be achieved.

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References

1. K.H. Jack and W.I. Wilson, *Nature*, 238 (1977) 28-29.
2. S. Hampshire, H.K. Park, D.P. Thompson, and K.H. Jack, *Nature*, 274 (1978) 880-882.
3. J.G. Lee and I.B. Cutler, *Am. Ceram. Soc. Bull.* 58[9] (1979) 869-871.
4. J. Mukerji and S. Bandyopadhyay, *Adv. Ceram. Mater.* 3[4] (1988) 369-373.
5. H.L. Lee, H.J. Lim, S. Kim, and H.B. Lee, *J. Am. Ceram. Soc.* 72[8] (1989) 1458-1461.
6. J.C.T. Van der Heijde, R.A. Terpstra, J.W.T. van Ruten, and R. Metselaar, *J. Eur. Ceram. Soc.* 17 (1997) 319-326.
7. J. Zheng, and B. Forslund, *J. Eur. Ceram. Soc.* 19 (1999) 175-185.
8. A.D. Mazzoni, E.F. Aglietti, and E. Pereira, *Appl. Clay Sci.* 12 (1993) 407-420.
9. F.K. Van Dijen, R. Metselaar, and C.A.M. Siskens, *J. Am. Ceram. Soc.* 68 (1985) 16-19.
10. A. Demir and F. Caliskan, *Mater. Sci. Forum*, 554 (2007) 85-89.
11. M. Hoch, and K.M. Nair, *Am. Ceram. Soc. Bull.* 58 (1979) 191-193.
12. Y.W. Cho, and J.A. Charles, *Mater. Sci. Technol.* 7 (1991) 399-406.
13. P.K. Panda, L. Mariappan, and T.S. Kannan, *Ceram. Int.* 26 (2000) 455-461.
14. J.E. Gilbert and A. Mosset, *Mater. Res. Bull.* 32 (1997) 1441-1448.
15. X.-J. Liu, X.W. Sun, J.J. Zhang, X.P. Pu, Q.M. Ge, and L.P. Huang, *Mater. Res. Bull.* 38(2003) 1939-1948.
16. Li-H. Xu, F. Lain, H. Zhang, Y.B. Bi, K. Cheng, and Y.B. Qian, *Mat. and Design*, 27 (2006) 595-600.
17. Z. Tatli, A. Demir, R. Yilmaz, F. Caliskan, and A.O. Kurt, *J. Eur. Ceram. Soc.* 27(2007) 743-747.
18. M. Vlasova, V.B. Vinokurov, O.N. Grigorev, A.D. Panasyuk, N.D. Bega, M. Kakazey, J.C. Gonzalez-Rodriguez, G.Dominguez-Pantino, and M. Dominguez-Pantino, *Mat. Sci. Eng.*, A366 (2004) 325-331.
19. K.J.D. MacKenzie and D.V. Barneveld, *J. Eur. Ceram. Soc.* 26 (2006) 209-215.
20. I.J. Davies, T. Minemura, N. Mizutani, M. Alzawa, and K. Itatani, *J. Mat. Sci.* 36 (2001) 165-172.
21. J. Y.Qiu, J. Tatami, K. Komeya, K. Watari, and T. Meguro, *J. Ceram. Soc. Of Japan Supplement, PacRim5 Special Issue*, 112[5] (2004) S1148-S1152.
22. C. Zhang, K. Komeya, J. Tatami, T. Meguro, and Y. B. Cheng, *J. Eur. Ceram. Soc.*, 20(2000) 1809-1814.
23. B. Matovic, A. Saponjic, and S. Boskovic, *J. Serbia. Chem. Soc.* 71 (2006) 677-683.
24. A.D. Mazzoni and E.F. Aglietti, *Applied Clay Science*, 17 (2000) 127-140.
25. A.D. Mazzoni and E.F. Aglietti, *Applied Clay Science*, 17 (1998) 447-461.
26. F.J. Li, T. Wakihara, J. Tatami, K. Komeya, and T. Meguro, *J. Eur. Ceram. Soc.*, 27 (2007) 2535-2540.
27. H. Schneider and A. Majdic, *Ceramurgia International*, 6 (1980) 61-66.
28. M.A. Sainz, F.J. Serrano, J. Bastida, and A. Caballero, *J. Eur. Ceram. Soc.*, 17 (1997) 1277-1284.
29. R.C. Bradt, J.A. Santillana, and H.B. Ramirez, *J. Ceram. Processing Res.* 6[4] (2005) 271-275.