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Journal of the European Ceramic Society 27 (2007) 743–747

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Effects of processing parameters on the production of β-SiAlON powder from kaolinite

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Abstract

In this study, the production of β′-$Si_{6-z}Al_zO_zN_{8-z}$ ($z = 3$) powders by the carbothermal reduction and nitridation of kaolinite ($Al_2O_3{\cdot}2SiO_2{\cdot}2H_2O$) of Turkish origin (Çan-Çanakkale) was investigated with different processing parameters. Temperature and gas flow rate had a great influence on the yield and amount of the final silicon aluminium oxynitride (SiAlON) phase in the product. Synthesis took place in the temperature range of 1400–1475 °C from the mixtures of kaolinite and reducing agent, i.e., solid carbon particles. Changes in gas flow rate had an influence on the final powder yield. Product after the process was mainly of β′-$Si_3Al_3O_3N_5$ powder along with small amount of Al_2O_3 and mullite phases were also present.

Keywords: SiAlON; Mullite; Silicate; Clays; Carbothermal

1. Introduction

Silicon aluminium oxynitride (SiAlON) ceramics are promising materials because of their potential in using them for various engineering applications. β-SiAlON ($Si_{6-z}Al_zO_zN_{8-z}$, $0 < z < 4.2$) ceramic materials exhibit high strength, good thermal-shock and corrosion resistance. They show excellence in sinterability and oxidation resistance compared to silicon nitride ceramics.[1,2] SiAlON is a solid solution of Si_3N_4 and Al_2O_3. Solubility of Al and O in β phase Si_3N_4 is high and determined by the "z" value in $Si_{6-z}Al_zO_zN_{8-z}$ composition. SiAlON ceramics are generally prepared by sintering mixtures of Si_3N_4, Al_2O_3 and AlN with some oxide additives (used as sintering aid) above 1500 °C.[3,4] SiAlON ceramics could also be produced readily in powder form by carbothermal reduction nitridation (CRN) of natural clay minerals, such as as-received kaolinite,[5,6] using carbon and N_2 gas following the chemical reaction below:

$$3[Al_2O_3{\cdot}2SiO_2{\cdot}2H_2O]_{(s)} + 15C_{(s)} + 5N_{2(g)} \Rightarrow 2Si_3Al_3O_3N_{5(s)} + 15CO_{(g)} + 6H_2O_{(g)} \quad (1)$$

and with the reaction below from the calcined mineral:

$$[3Al_2O_3{\cdot}6SiO_2]_{(s)} + 15C_{(s)} + 5N_{2(g)} \Rightarrow 2Si_3Al_3O_3N_{5(s)} + 15CO_{(g)} \quad (2)$$

Kaolinite as an aluminosilicate type of clay mineral provides a good source of the constituents necessary for the synthesis of SiAlON. Chemical formulae of kaolinite is $Al_2Si_2O_5(OH)_4$, where water is derived away in calcination before CRN process. A carbon source in discrete or monomer[7] form is used in the reaction to take the excess oxygen away with N_2-flow. Some other SiO_2 and Al_2O_3 rich clay minerals such as, vermiculite,[8] bentonite,[8] halloysite[10] and montmorillonite[6] have also been used as starting materials for synthesising SiAlON powders with small addition of Al or Al_2O_3 powders. So far, there has been limited investigation on the production of single-phase β-SiAlON from natural aluminosilicate minerals. In this study, however, Turkish origin (Çan-Çanakkale) kaolin was used as raw material to produce single-phase β-SiAlON powder by carbothermal reduction and nitridation. The influence of reaction temperature, holding time and N_2-flow rate on the formation of β-SiAlON powder has been investigated.

2. Materials and methods

Kaolinite, natural mineral used as a source for synthesising of SiAlON powders, was supplied by Kale Maden based on Çan

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doi:10.1016/j.jeurceramsoc.2006.04.062

Table 1
Chemical and mineral composition of kaolinite (designation code: Kaolen-143 M/63, Kale Maden) from Çan-Çanakkale, Turkey

Chemical composition										
Phases	SiO_2	Al_2O_3	Fe_2O_3	CaO	K_2O	TiO_2	SO_4	MgO	Na_2O	LoI[a]
Content (wt%)	52.12	33.83	0.55	0.15	0.13	0.45	0.13	0.05	0.01	12.58
Mineral composition										
Quartz		Feldspat			Kaolinite			Others		
13.59		0.88			83.85			1.68		

[a] Loss on ignition at 1000 °C.

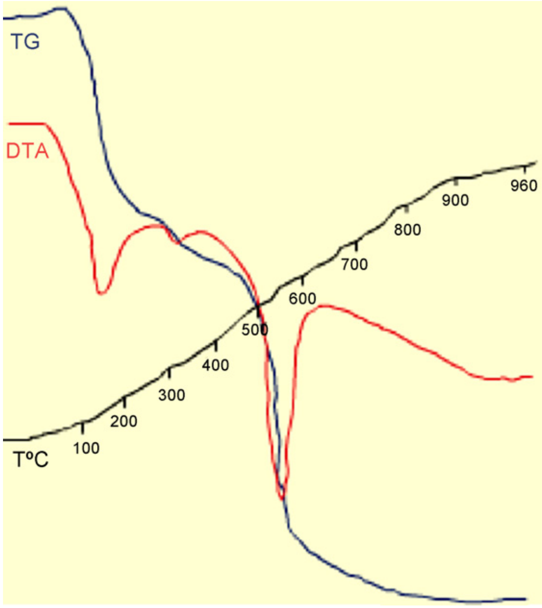

Fig. 1. TG-DTA analysis of as-received kaolinite mineral (designation code: Kaolen-143 M/63, Kale Maden).

region in Çanakkale, Turkey. Kaolinite ($Al_2O_3{\cdot}2SiO_2{\cdot}2H_2O$) is produced in the form of fine powder commercially available in different particle size fractions. Its chemical and mineral compositions are given in Table 1 (with supplier's data). As-received mineral in −63 μm size fraction was used in this work after calcination at 650 °C for 2 h for the removal of water molecules. The temperature for calcination was picked from the TG-DTA analysis of the mineral (Fig. 1). Two endothermic peaks shown in Fig. 1 around 150 °C and 570 °C were attributed to the loss of free and the bound water molecules, respectively.

Carbon black (Vulcan XC 72 from *CABOT*) was 99.7% pure and used as a reducing agent with a mean particle size of 5 μm and specific surface area of 110 $m^2\,g^{-1}$. Carbon black was added in the calcined kaolinite just above the stoichiometric amount of oxygen content in the mineral. The calculation of the stoichiometric amount was based on the data given in Table 1, assuming that the mineral was totally free from water molecules. In order to have a homogeneous mixture; constituents were mixed in an agate mortar using pestle in distilled water for 10 min by hand. After filtering the aqueous mixture, it is dried in an open air furnace for 24 h at 75 °C. Dried cake was then again taken to the mortar, where it was lightly grinded for making them in powders before taking them to the carbothermal reduction nitridation process. The carbothermic reduction was carried out using a tube furnace at temperatures 1400–1475 °C under the flow of nitrogen gas (99.99% pure). The products after CRN process were analysed using standard characterisation equipment for identifying their phase compositions (using XRD, Rigaku Dimaks 2200) and surface topography (using SEM, Philips).

3. Results and discussions

As-received kaolinite and carbon black mixture, in the form of fine powder, was weighted approximately 7 g and charged into an alumina tube furnace in a crystalline Al_2O_3 boat (Fig. 2(a)). Kaolinite powder (−63 μm) is light creamish in colour. When it is mixed with carbon clack, samples were covered fully in black colour. The mixture was hold in a tube furnace at different temperatures under constant nitrogen flow (1 l/min) for 4 h in a controlled N_2 atmosphere. Cooling down to room temperature, samples were taken out from the furnace for the next stage of residual carbon burning. Dark black colour of the charge has turned to a greyish white colour (Fig. 2(b)) after CRN. The surface of the sample was fully covered with a thin layer of white woolly overcoat. Beneath this cover, powders were loosely adhered and they were dark greenish black in colour (Fig. 2(c)).

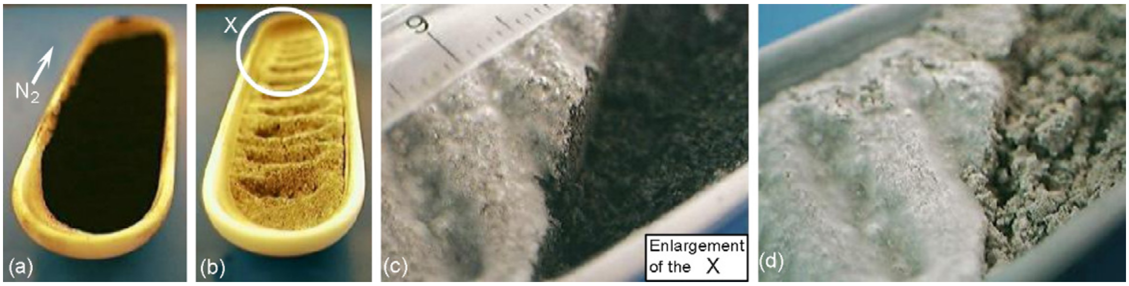

Fig. 2. Colour changes of the reactants after each stage: (a) a mixture of constituents before the CRN stage, (b) after reacting the samples at 1400 °C for 4 h in 1800 ml/min N_2-flow, (c) enlargement of X in "b" (surface was cut to show the colour beneath) and (d) same as "c" after excess carbon burning (900 °C, 1 h) stage.

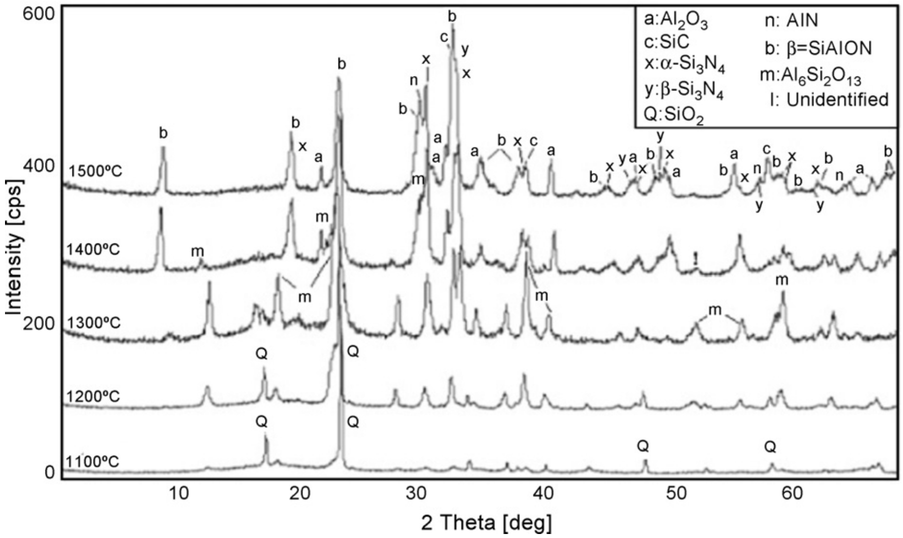

Fig. 3. XRD pattern of samples after CRN in various temperatures (1100–1500 °C). N_2-flow rate (1800 ml/min), time (4 h) and heating/cooling rate (300 °C/h) were kept constant for all runs.

After the residual carbon burning in an open air chamber furnace at 900 °C for an hour, surface coat in the boat got whiter and beneath this black colour has disappeared leaving behind a greyish green colour (Fig. 2(d)). In order to record changes and to calculate the yield, before and after each stage, samples were weighted using a digital balance with a sensitivity of 0.0001 g.

The colour and the data from weight measurements roughly tell about the success of the process. Samples, for example, remained black in colour or if there was an insufficient weight loss after CRN process, it was understood that the process was unsuccessful and there was an incomplete reaction. Nevertheless, the XRD analysis is necessary to evaluate the product for their crystalline phases formed after CRN.

The powder mix was reacted at high temperatures (1100–1500 °C) under constant nitrogen flow (1800 ml/min) for 4 h in order to determine transmission temperature for kaolinite to SiAlON ceramic. XRD patterns of these samples were sequentially replaced in one graph (Fig. 3) to follow the phase transformations. As shown in Fig. 3, only quartz phase exist and no β-SiAlON peak is found in the sample reacted at 1100 °C. As the temperature increases, mullite forms from the silica and alumina equilibrium reactions and no nitridation phase has been observed in between 1200 and 1300 °C. As a result of reduction and nitridation of the mullite phase, silicon nitride based β-SiAlON $z = 3$ ceramic powders occur between 1400–1500 °C as described in Eq. (1). As mullite phase is not completely disappeared at 1400 °C, silicon carbide and others secondary phases start to form at 1500 °C. For that reason, accurate CRN optimisation is carried out at temperatures between 1400–1500 °C.

Fig. 4 shows XRD patterns of the samples run under identical testing conditions using different temperatures (1400–1475 °C). β′-SiAlON ($z = 3$) was a dominant phase at all temperatures.

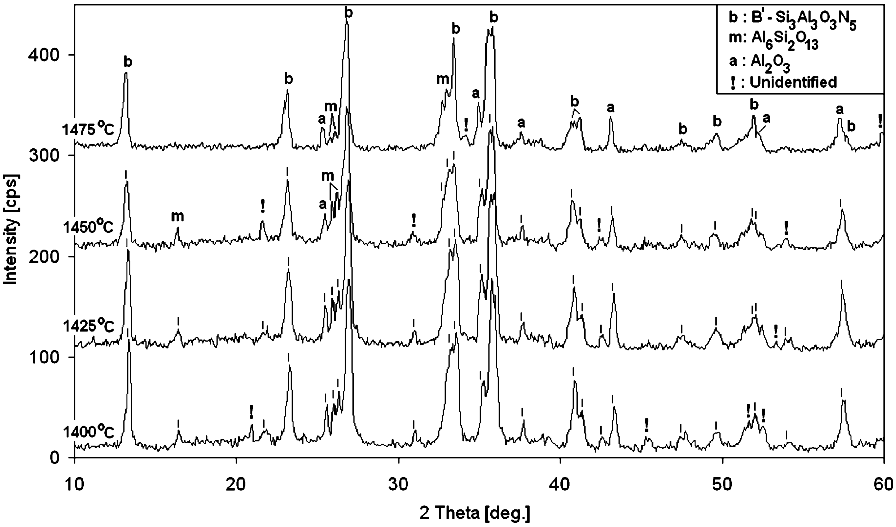

Fig. 4. XRD pattern of samples after CRN in various temperatures (1400–1475 °C). N_2-flow rate (1000 ml/min), time (4 h) and heating/cooling rate (300 °C/h) were kept constant for all runs.

Table 2
Representing the phase formation for the comparison of the testing parameters

Code	Parameters	Variables	Constants	Phases (relative)
CRN 1-1	Temperature	1100 °C	Time, N_2-flow, reactants	Quartz_{vs}
CRN 1-2		1400 °C	Time, N_2-flow, reactants	SiAlON_{s}–$\mathrm{Mullite}_{w}$–$\mathrm{Alumina}_{w}$
CRN 1-3		1475 °C	Time, N_2-flow, reactants	SiAlON_{vs}–$\mathrm{Alumina}_{w}$–$\mathrm{Mullite}_{vw}$
CRN 1-4		1500 °C	Time, N_2-flow, reactants	SiAlON_{vs}–SiC_{s}–$\mathrm{Alumina}_{w}$
CRN 2-1	N_2-flow	0.6 l/min	Temperature, time, reactants	SiAlON_{s}–$\mathrm{Mullite}_{w}$–$\mathrm{Alumina}_{w}$
CRN 2-2		1.8 l/min	Temperature, time, reactants	SiAlON_{vs}–$\mathrm{Alumina}_{w}$–$\mathrm{Mullite}_{vw}$

Intensities: vs, very strong; s, strong; w, weak; vw, very weak.

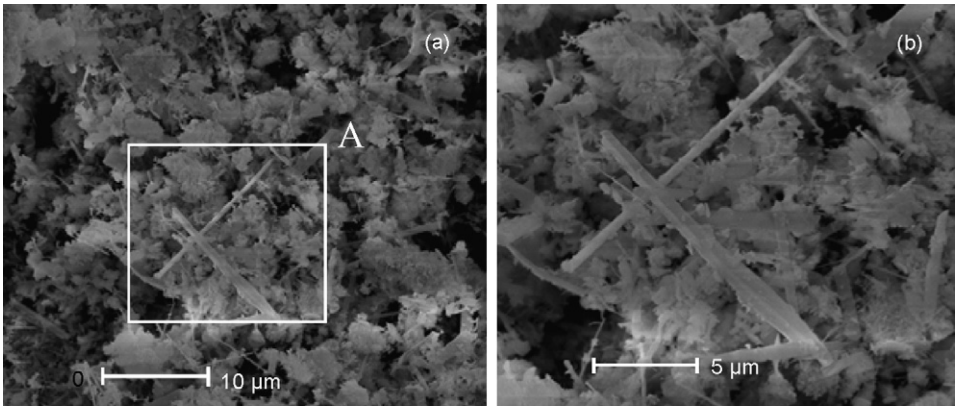

Fig. 5. SEM micrographs of sample run at 1475 °C for 4 h in 1000 ml/min N_2-flow. General view is given in 'a' and 'b' is the enlargement of the rectangular area A in 'a'.

Other phases of $Al_2Si_2O_{13}$ and Al_2O_3 were also formed in varying amounts at different temperatures. However, these secondary phases of $Al_2Si_2O_{13}$ and Al_2O_3 reduce in amount when the temperature increases. Some unidentified peaks seen at all product powders may be attributed to the complex intermediate phases of oxides. Sample run at 1475 °C for 4 h under 1000 ml/min N_2-flow rate gave better products in terms of the SiAlON phase. The amounts of intermediate phases were low in this run compared to others with lower temperature runs (Table 2).

Examination of the surface topography by SEM analysis revealed a product consisting of a mixture of nano sized fine particles, short and tangled whiskers and relatively thick fibres. A typical general view of the sample product, run at 1475 °C (in Fig. 4), is shown in Fig. 5(a). Needle-like region is magnified to examine cross-section of grains in Fig. 5(b). In addition to irregular powder shape, rectangular cross-sectioned long grains are also formed. If the irregular powder form is closely examined, small needle-like powders can also be observed. Because

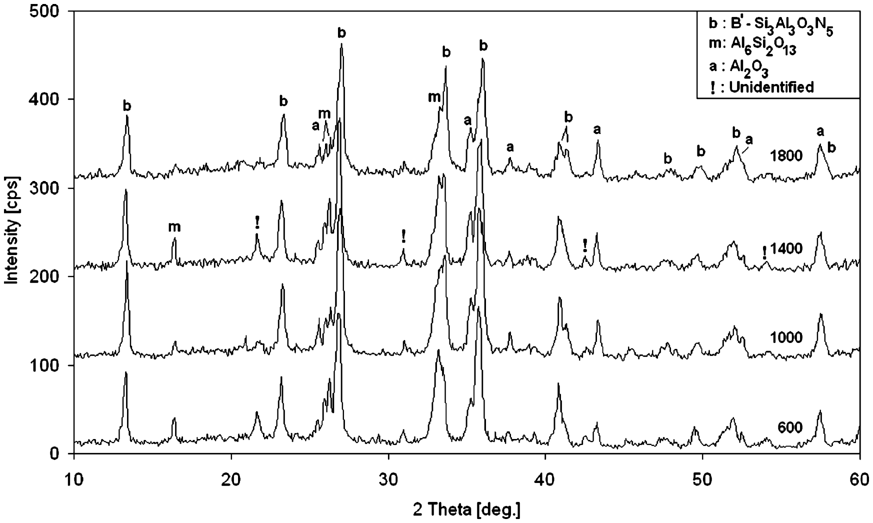

Fig. 6. XRD pattern of the samples run at different N_2-flow rate (600–1800 ml/min). Temperature (1400 °C), holding time (4 h) and heating/cooling rate (300 °C/h) were kept constant for all runs.

of this particle morphology, resulting β-SiAlON can be used for ceramic composite fabrication, and tougher composites might be obtained.

High SiAlON phase could also be achieved increasing the N_2-flow rate from 1000 ml/min to 1800 ml/min even lowering the temperature from 1475 °C to 1400 °C. Fig. 6 shows the effect of N_2-flow rate on the formation of SiAlON phase. The XRD pattern of a sample run at 1400 °C with 1800 ml/min N_2-flow rate in Fig. 4 is identical with the sample run at 1475 °C with 1000 ml/min N_2-flow in Fig. 6. Although main reaction phases are shown in Figs. 4 and 6, the crystallinity of the products is not very high as seen on the background noise of the XRD patterns. There must have some unidentified crystalline phases present as well small amount of amorphous components.

4. Conclusions

SiAlON powders of $z = 3$ have been produced successfully in relatively short time (4 h) compared to previous works[9,10] using Turkish origin −65 μm size fraction as-received kaolinite natural mineral and carbon black at 1400 °C under 1800 ml/min N_2-flow in a controlled atmosphere. Temperature and gas flow rate were found important in determining the reaction rate and yield of the product phases. β′-SiAlON was the dominant product with small amounts of Al_2O_3 and mullite for all the samples in this work.

Acknowledgments

Authors would like to thank the DPT (State Planning Organisation of Turkey) for their financial support (Grant No. DPT-2003K120970). Our thank also go to Kale Maden for their generous support in providing us with raw materials.

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