The Preparation of β Sialon from Kaolin by Carbonitrothermic Reduction

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ABSTRACT

The preparation of β -sialon from Turkish kaolin by carbothermic reduction under a nitrogen atmosphere has been described. The product of carbonitrothermic reduction at 1475-1500°C comprises principally β -sialon and minor amounts of another phase in the Si-Al-N-O system known as the 15R phase. The amount of each of these two phases strongly depends on reaction time. The colloidal stability behaviour of the ground carbothermal β -sialon in water was found to depend strongly on the pH. Slip casting of the β -sialon powder from the suspension followed by sintering at 1500 to 1600°C resulted in compounds with densities ranging from 94 to 99% of the theoretical value. The particle size of the β -sialon influences the densification achieved during sintering. The use of yttria in amounts of 5 and 10% as an additive to β -sialon to obtain higher densities by sintering works well for relatively coarser powder.

1. INTRODUCTION

β -Sialon is based on the β modification of silicon nitride in which aluminium partially replaces silicon and oxygen correspondingly replaces nitrogen. On account of its atomic arrangement, the physical and mechanical properties of β sialon are similar to those of Si_3N_4 and because of its composition, its chemical properties approach those of alumina /1/. β -Sialon has

high strength, good thermal shock resistance, resistance to corrosion and erosion and is superior to Si_3N_4 in sinterability and oxidation resistance /2,3/. It is generally synthesised by reaction sintering or reaction hot pressing of pure Si_3N_4 , Al_2O_3 , AlN and SiO_2 /4,5/. It is also possible to prepare β -sialon from a variety of naturally occurring materials like clay /6/, volcanic ash /7/, rice husk /1/ and kaolin /8/. The overall reaction for the preparation of β -sialon from kaolin by carbonitrothermic reduction may be written as

This reaction is thermodynamically favourable /8/ but the reaction mechanism and end products obtained depend on factors such as impurities in the kaolin and carbon used for the reaction. The impurities accumulate in the only solid product of the reaction, β -sialon, and may affect subsequent processing of β -sialon to form dense components. The actual composition of kaolin shows minor variations depending on the location, and the present investigation is concerned with the Turkish kaolin as the starting material and the processing of β -sialon prepared from it.

2. EXPERIMENTAL

Two kinds of indigenous kaolin, designated M1 and M6 (Matel A.S., Bilecik Turkiye), and carbon (Elftex 125, Cabot) were used as starting materials. The

analysis of these materials is given in Table 1. Calcium carbonate (Merck) was used as an additive to the kaolin-carbon charge to accelerate the carbothermic reduction.

Kaolin was dry milled in a hammer crusher. It was then mixed with calculated quantities of coal and calcium carbonate in a mixer. Water was then added as a binder and the damp powder was tumbled to obtain spherical granules which were sieved to separate a >2 mm, <4 mm size fraction.

Experiments with small charges were carried out in a horizontal tube furnace (Heareus). The pellets were placed in an alumina tube (25 mm diameter) in a packed bed and reacted with nitrogen in different batches under nitrogen flow varying from 6.25 lph to 50 lph. The temperature was varied from 1400 to 1500°C and the reaction time from 0 to 12 h.

Experiments with larger charges were carried out in a horizontal tube furnace which had a diameter of 50 mm and a hot zone length of 400 mm and was heated

by silicon carbide elements (Carbolite, Sheffield, England). About 500 g of non-fractionized pellets were used as charge, nitrogen flow was 35 lph and temperature was 1500°C.

The products were examined at different stages of the reaction by X-ray diffraction. After synthesis of the β -sialon, the granules were dry-milled in a hammer crusher and then heated to 750°C for 4 h in an air sintering furnace to remove any residual coal. The product was then milled in an attrition mill (HOD 1, Union Process, 0.75 l tefzel coated tank, 7 mm Si_3N_4 balls, with 5 and 10 wt% yttria as additive in some cases). Particle size and surface area were measured by using sedimentation and BET methods, respectively. Nitric acid or sodium hydroxide was added to the suspension to adjust the pH. Sedimentation experiments were performed to determine the conditions for a stable colloidal suspension. Ammonium polyacrylate (Dolapix CE 64, Zschimmer and Schwartz) was used as a deflocculant and a varying amount of deflocculant was

Table 1
Analysis of raw materials used for β -sialon preparation
(Values in wt% unless otherwise specified)

	Kaolin	
	M1	M6
Al_2O_3	38.86	36.30
SiO_2	48.14	47.36
Fe_2O_3	2.12	2.12
MgO	0.41	0.43
CaO	0.45	0.42
Na_2O	0.03	0.03
K_2O	0.33	1.38
TiO_2	0.34	0.95
LOI	9.32	11.01
d_{50} (μm)	0.49	0.31
BET m^2g^{-1}	21.17	17.10
Coal (Elftex 125)		
C	>98	
LOI	<0.1	
BET m^2g^{-1}	27	

added to the suspension with ultrasonic treatment /9,10/. Slip cast tablets, 33 mm in diameter and 3 mm in thickness, were prepared on plaster of Paris moulds using a suspension containing 70 wt% of solid at pH 10.5. After slip casting, the tablets were dried at room temperature for 5 h, then at 40°C for 10 h and at 100°C for 24 h. The dried tablets were then sintered at 1500 to 1600°C for 2 h under nitrogen at 1 atm using a nitriding furnace (KCE, Germany).

3. RESULTS AND DISCUSSION

Carbonitrothermic reduction experiments on small charges carried out at different temperatures and nitrogen flow rates showed an optimum reaction temperature of 1475°C and a nitrogen flow rate of 12.5 lph. The composition of the products obtained at this temperature and flowrate for a 30 g charge of >2 mm <4 mm pellets prepared from M1 kaolin is shown as a function of reaction time in Fig. 1. When the pellets had reached 1475°C, the reduction and nitridation had already started and approximately 9% β -sialon had already formed. At the same time, the product contained a large amount (about 60%) of mullite and other phases like Al_2O_3 , X-phase and SiC. At the beginning of the reaction some X-phase is formed which disappears after three hours. The maximum

sialon content of about 88% is reached after 9 h of reaction time, and the other component in the product is the 15 R phase. If the reaction time is longer than 9 h, the β -sialon content of the product decreases and the 15 R phase content increases.

The products formed during the course of reaction as shown in Fig. 1 generally conform to the known behaviour of kaolin on heating /8/. When kaolin is heated, at about 500°C dehydration occurs resulting in the formation of an amorphous material known as metakaolin and at 1200°C nucleation of mullite occurs. When the reaction temperature of 1475°C is reached, kaolin has already broken down to a mixture of mullite and pure silica and silica reacts with carbon to form silicon carbide, SiC. The reactions may be represented as:

and

Silicon carbide reacts subsequently with mullite to form β -sialon

Fig. 1: Composition of the product as a function of the reaction time at 1475°C in a nitrogen flow of 12.5 lph (for M1 kaolin).

The products referred to as X and 15 R in Fig. 1 are phases found in the Si-Al-O-N behaviour diagram at high temperatures.

The products obtained in the carbothermic reduction of kaolin to β -sialon are influenced by the constituents in the kaolin and their relative concentration. This is brought out by the results of larger scale experiments. A product containing 85% of β -sialon and 15% of R is obtained by reacting 500 g of the M1 pellets at 1500°C for 28 h in a nitrogen flow of 35 lph. At the same temperature and nitrogen flow, 95% of β -sialon and 5% of 15 R is produced using M6 pellets for 25 h.

The attrition milling curve of carbon removed β -sialon product is shown in Fig. 2. Even though 8 h of attrition milling was applied to both β -sialon (M1 and

Fig. 2: Attrition milling curve for M1 and M6 β sialon powders.

M6) powders, they could not be milled to submicron size. To obtain smaller particle size, a higher rotation speed was also tried during attrition milling. The d_{50} value indeed decreased and was determined as $1.65 \mu\text{m}$ after 5 h of attrition milling at 600 rpm.

The results of sedimentation experiments are presented in Figs. 3 and 4. Fig. 3 shows that the sediment volume for diluted suspensions, obtained after several weeks, is lowest indicating the lowest degree of flocculation, i.e., highest degree of stability at pH 10-11. The effect of deflocculant addition on sedimentation at pH 10.5 is shown in Fig. 4. It may be seen that

Fig. 3: Sediment volume as a function of pH for diluted β -sialon suspension.

Fig. 4: Sediment volume as a function of deflocculant concentration for diluted β -sialon suspension.

addition of more than 1 mg Dolapix/g of sialon has no significant effect on the sediment volume.

The sintering experiment on dried slip cast tablets prepared from coarser powder (milled at 400 rpm for 4 h) and containing 5 wt% Y_2O_3 was carried out at 1500°C for 2 h. This resulted in a density of 3.03 g cm^{-3} ($\rho_{\text{rel}} = 94\%$). Increasing the sintering temperature to 1550°C and 1600°C improved the density to 3.14 g cm^{-3} ($\rho_{\text{rel}} = 97.5\%$) and 3.15 g cm^{-3} ($\rho_{\text{rel}} = 97.82\%$). Under similar conditions tablets containing 10 wt% yttria reached densities of 3.11 g cm^{-3} ($\rho_{\text{rel}} = 94.81\%$), 3.18 g cm^{-3} ($\rho_{\text{rel}} = 96.95\%$) and 3.24 g cm^{-3} ($\rho_{\text{rel}} = 98.78\%$) at 1550 and 1600°C , respectively. Tablets prepared from fine powder (milled at 600 rpm for 5 h) containing 5 and 10 wt% Y_2O_3 were sintered at 1600°C for 2 h. The density of tablets containing 5 wt% Y_2O_3 was 3.13 g cm^{-3} ($\rho_{\text{rel}} = 97\%$). The tablets containing 10 wt% Y_2O_3 cracked due to evaporation of gaseous products. There was approximately 9% weight loss in these samples.

Ball on ring test was applied to samples which contained 5 wt% Y_2O_3 and had been sintered at 1600°C . Average BOR strength was $182 \pm 42 \text{ MPa}$ ($n = 11$).

4. CONCLUSIONS

Starting from two varieties of Turkish kaolin, β

sialon has been prepared by carbonitrothermic reduction at 1475°C. The reaction proceeds through the formation of mullite and silicon carbide and an X phase, all of which disappear in about 8 h of reaction time and only β -sialon and a 15R phase remain. Depending on the kaolin used, the product contains 85 to 95% β -sialon and the remainder is 15R.

The β -sialon product obtained could be milled to micron size powder but not to submicron size even after 8 h of attrition milling. The colloidal stability of the suspension prepared from milled powder is strongly pH dependent, the stability being highest at pH 10-11. Slip cast tablets prepared from this suspension, with 5 to 10% yttria, could be sintered to high densities at 1500 to 1600°C in a nitrogen atmosphere. The densities range from 94 to 99% of the theoretical value. The particle size of the β -sialon influences the densification achieved during sintering. The 10% Y_2O_3 as an additive works well with relatively coarser powder, resulting in nearly 99% of theoretical density after sintering for 2 h at 1600°C.

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