

## Carbothermal production of beta'-sialon

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## CARBOTHERMAL PRODUCTION OF $\beta'$ -SIALON

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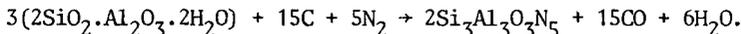
*It is shown that a  $\beta'$ -sialon powder  $\text{Si}_3\text{Al}_3\text{N}_3\text{O}_5$  can be produced from approximately stoichiometric mixtures of kaolin and carbon under a  $\text{N}_2$  flow at temperatures of 1400-1500°C. Reynolds number has to be low, otherwise mixtures of  $\text{AlN}$ ,  $\text{Si}_3\text{N}_4$  and  $\text{Al}_2\text{O}_3$  are formed. The reaction rate of the sialon formation is controlled by mass transfer.*

*La préparation de  $\beta'$ -sialon  $\text{Si}_3\text{Al}_3\text{N}_3\text{O}_5$  a été effectuée à partir des composés approximativement stoechiométriques de kaolin avec du carbone sous un courant d'azote à 1400-1500°C. Le nombre de Reynolds faut être bas, autrement une mélange de  $\text{AlN}$ ,  $\text{Si}_3\text{N}_4$  et  $\text{Al}_2\text{O}_3$  sera formée. La vitesse de la formation du sialon est déterminée par le transfert de la matière.*

*Es wird gezeigt das  $\beta'$ -Sialon Pulver  $\text{Si}_3\text{Al}_3\text{N}_3\text{O}_5$  geformt wird aus ein annäherend stoechiometrisches Gemisch van Kaolin und Kohlenstoff unter fließenden Stickstoff bei Temperaturen von 1400-1500°C. Die Reynolds Zahl soll niedrig sein, sonst werden  $\text{AlN}$ ,  $\text{Si}_3\text{N}_4$  und  $\text{Al}_2\text{O}_3$  entstehen. Die Reaktionsgeschwindigkeit von Sialon wird bestimmt durch den Massestransfer.*

### INTRODUCTION

According to the literature (1-5)  $\beta'$ -sialon can be produced from kaolin, carbon and nitrogen by the following overall reaction:



Since this reaction is very attractive because of the use of inexpensive raw materials, we have undertaken a further study.

Lee and Cutler (1) claim to have produced a  $\beta'$ -sialon within a few hours at temperatures below 1450°C. Above this temperature SiC is formed instead of sialon. It is assumed that iron has a catalytic effect on the reaction. However, Paris and Grollier-Baron (2) report that they were not able to reproduce the results of Lee and Cutler. Baldo c.s. (3) performed experiments with several types of clay, using temperatures below 1450°C. They observed that the gas flow influences the type of reaction products formed.

In this work we will describe the raw materials, experimental procedures, observed reactions and the powders which we obtained. We will also discuss the type of reactor and we will report on the thermodyna-

TABLE 1 - Chemical analysis of Monarch kaolin (wt.%)

SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O	K <sub>2</sub> O	CaO	MgO	Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	MnO <sub>2</sub>	ignition loss
45.60	38.60	---	0.06	---	---	0.34	1.37	---	13.88

mic changes of the raw materials and the impurities during the reaction. When we discuss the observed reactions we will examine the rate controlling step and the optimal reaction conditions.

#### EXPERIMENTAL DETAILS

##### Raw Materials

**Kaolin.** A pure kaolin is described the formula Si<sub>2</sub>Al<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>. In our experiments we used Monarch kaolin from Georgia. According to x-ray diffraction analysis this is a very pure kaolin. Table 1 shows the chemical analysis determined by x-ray fluorescence.

The specific area of the kaolin is 6.7 m<sup>2</sup>/g, as determined by N<sub>2</sub> adsorption in a "Ströhlein" areameter. The pycnometric density is 2.61 g/cm<sup>3</sup>. Curve D in Fig. 1 shows the particle size distribution measured with the aid of a "Micromeritics" SediGraph 5000D.

**Carbon.** As carbon source we chose carbon black because of the low ash content (< 0.1 wt%), low content of volatile matter (< 1 wt%) and its high specific surface. Our carbon black was obtained from CABOT BV. We used the types Elftex 125 and 575, with a specific area of 27 m<sup>2</sup>/g and 110 m<sup>2</sup>/g, respectively (Ströhlein Areameter). X-ray fluorescence showed that sulphur is the only impurity (< 0.5 wt%).

**Nitrogen.** The nitrogen gas used, was obtained by low temperature distillation of air. The gas contained 6 ppm of oxygen, as analysed with a zirconia oxygen gauge, and some water. Therefore it was dried over silicagel before entering the reactor.

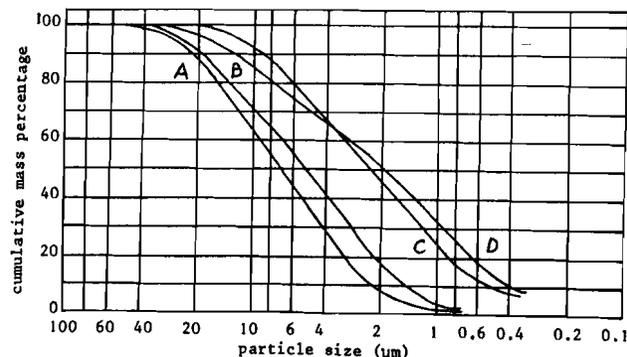


Fig. 1. Particle size analysis of powders. A. sialon formed at 1400°C, B. sialon formed at 1490°C, C. mixture of Si<sub>3</sub>N<sub>4</sub> and AlN formed at 1400°C, D. kaolin starting material.

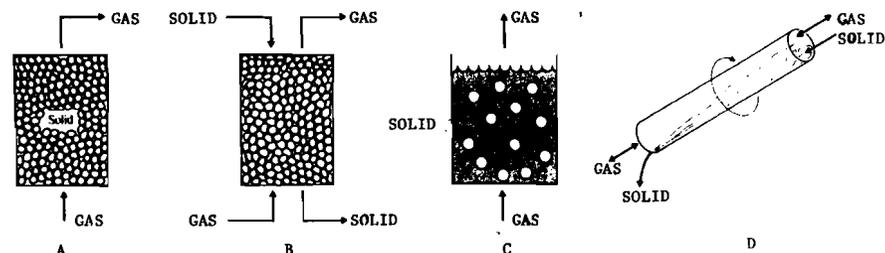


Fig. 2. Schematic picture of possible solid-gas reactors. a. Packed bed, b. moving bed, c. fluidized bed (batch or continuous), d. rotary kiln. Reproduced from J.J. Carberry, Chemical and Catalytic Reaction Engineering, Mc. Graw-Hill 1976.

##### The reactor

Fig. 2 shows four types of solid-gas reactors. For our experiments the packed bed reactor, type a, was chosen. However, type b, the moving bed reactor, is also suitable. We assume that both reactors can be described by the same kinetics. The other types are rejected because: in a continuous fluidized bed 100% conversion is not possible, in a fluidized bed extra nitrogen is needed due to the gas flow distribution, insight in the influence of the gas flow on the type of reaction is difficult to achieve. The rotary kiln is rejected because the gas flow between the pellets can not be controlled and therefore this type does not give full understanding of the reaction. A so-called dilute phase transport reactor is rejected because it is only useful for very fast reactions, which is not the case here. The reaction temperature in our reactor is maintained by direct heating through the reactor wall.

##### Experimental Procedure

Carbon black and kaolin were dry mixed in a ratio 1:0.235 (theoretical ratio 1:0.2326), using a ball mill to break down agglomerates. The mixture was pelletized with 20wt% water by means of a tumbling/rolling method, yielding a pellet porosity of 40%. The sieve fraction 1-2 mm was used for further experiments. After drying the pellets were poured into the reactor, consisting of a packed bed with a tube diameter of 2.5 cm. Each batch contained 30 ml of pellets. The reactor was heated in 4-6 hours at a total pressure of 1 atm, with a N<sub>2</sub> flow of 1 mm/s at room temperature. The reaction was followed with the aid of a CO-monitor.

##### THERMODYNAMIC CALCULATIONS

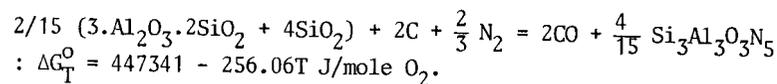
To get insight in the reaction describing the formation of β'-sialon and the possible side reactions we have performed some thermodynamic calculations. Using the JANAF thermochemical tables (6) the standard free energy changes for a number of reactions were calculated. Of course the validity of these calculations for our experiments is restricted, since the data hold for an equilibrium state. Though a continuous, but slow, nitrogen flow is used in our reactor, it can be shown that the equilibrium state is approached at least in the upper part of the reactor (7). Table 2 gives the standard free energy

TABLE 2 - Standard free energy changes in J/mole O<sub>2</sub>

A	$2/3 \text{ Al}_2\text{O}_3 + 2/3 \text{ N}_2 = 4/3 \text{ AlN} + \text{O}_2$	$\Delta G_T^0 = 688741 - 63.85T$
B	$\text{SiO}_2 + 2/3 \text{ N}_2 = 1/3 \text{ Si}_3\text{N}_4 + \text{O}_2$	664557-70.50T
C	$\text{SiO}_2 + \text{C} = \text{SiO} + \text{CO}$	687264-343.80T
D	$2/3 \text{ Al}_2\text{O}_3 + 2/3 \text{ N}_2 + 2\text{C} = 4/3 \text{ AlN} + 2\text{CO}$	459960-235.39T
E	$\text{SiO}_2 + 2/3 \text{ N}_2 + 2\text{C} = 1/3 \text{ Si}_3\text{N}_4 + 2\text{CO}$	435776-242.04T
F	$\text{SiO}_2 + 3\text{C} = \text{SiC} + 2\text{CO}$	604002-339.41T

changes for a number of possible reactions.

The calculated values of  $\Delta G_T^0$  are shown graphically in Fig. 3. From this figure it is obvious that carbon has a strong influence on the free energy changes. At  $P_{\text{CO}} = 0.1$  atm the SiO pressure at high temperatures is still low. Above about 1450-1500°C the possibility that SiC is formed should be considered. We can compare  $\Delta G_T^0$  for reaction E with the value for the formation of  $\beta'$ -sialon (8,9) according to the reaction



It is seen that there is hardly any difference in  $\Delta G_T^0$  for the formation of  $\beta'$ -sialon and  $\text{Si}_3\text{N}_4$ .

With increasing temperature the CO pressure will rise. The nitrogen, flowing through the reactor, not only reacts with the oxides, it also serves to remove the CO. At higher temperatures therefore less nitrogen is needed to remove the carbon monoxide.

As was shown in Table 1, kaolin contains a number of impurities. These impurities can play an important role both during the reaction and during the subsequent sintering process. Also the properties of the sintered product will be influenced.

From the thermodynamic equilibrium considerations we find that Ca and Mg will be present as an oxide after the reaction; Ti will be

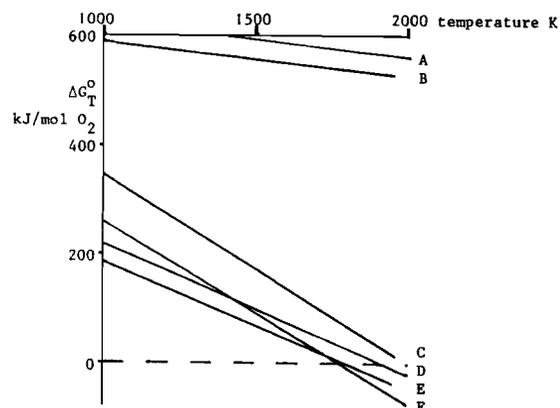


Fig. 3. The standard free energy change for the reactions given in Table 2.

present as TiN. Iron can form Fe or iron carbide at temperatures below 1200°C, and iron silicide at higher temperatures. Mn impurities will cause manganese carbide or silicide. Sodium and potassium are likely to disappear as metallic vapour from the pellets (10).

## RESULTS

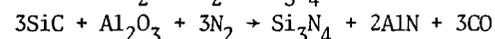
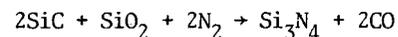
### Observed Reactions

The only way to get the desired reaction is by using a low gas flow, approximately a superficial gas velocity of 1 mm/s at room temperature. This means that the reaction takes place at a low Reynolds number (Re), based on particle diameter. The reaction takes about 40 hours at 1400°C and 20 hours at 1490°C.

When we use high Reynolds numbers ( $\approx 2$  at room temperature) we obtain a mixture of silicon nitride, aluminium oxide and aluminium nitride. Iron has a strong catalytic effect on the rate of the latter reaction and the reaction time decreases to a few hours. When we use more carbon we obtain a mixture of  $\text{Si}_3\text{N}_4$  and AlN.

For low values of Re ( $\approx 0.1$  at room temperature) we obtain a  $\beta'$ -sialon powder. Under these reaction conditions Fe does not show a catalytic effect. If we stop the reaction before it is finished, we do not see any sign of inhomogeneous reaction of the pellet. This means that diffusion does not control the reaction rate. Together with the fact that iron does not show any effect on the reaction rate we conclude that the rate is controlled by mass transfer.

Despite reports in the literature (1,11) we could not find any SiC in the pellets when the reaction took place at temperatures from 1450° till 1600°C. This is also in contradiction with our thermodynamic calculations, but can be well explained by considering the following reactions



Because we find some blue SiC at the cooler parts of the reactor we assume the forming of SiO takes place. In that case the following reaction may occur:  $\text{SiO} + \text{CO} = \text{CO}_2 + \text{SiC}$ . The weight loss of the pellets however is less than 0.5 wt%. It is observed that the presence of the impurities plays an important role in this process.

The fact that we need slightly more carbon than predicted is due to impurities in nitrogen, carbon and kaolin. Extra carbon leads to the presence of 15R phase in the powder and a shortage in carbon leads to the presence of  $\alpha\text{-Al}_2\text{O}_3$ . The type of carbon black does not influence the reaction rate. A prolonged nitrogen flow leads to oxidation of the pellets. By use of x-ray diffraction we were able to determine titanium as TiN, iron as a mixture of  $\alpha\text{-Fe}$  and  $\text{Fe}_x\text{Si}$  (and iron carbide) and manganese as  $\text{Mn}_x\text{Si}$  after the reaction. Sodium, potassium and sulphur are not present in the product after the reaction. This was determined by x-ray fluorescence. Calcium and magnesium are not present as crystalline phases after the reaction. It is likely that they are present as a glassy phase.

### Powder Characterisation

The  $\beta'$ -sialon powder from the reaction at 1400°C has a specific surface of 1.1 m<sup>2</sup>/g. The  $\beta'$ -sialon powder from the reaction at 1490°C has a specific area of 1.5 m<sup>2</sup>/g. This difference is probably due

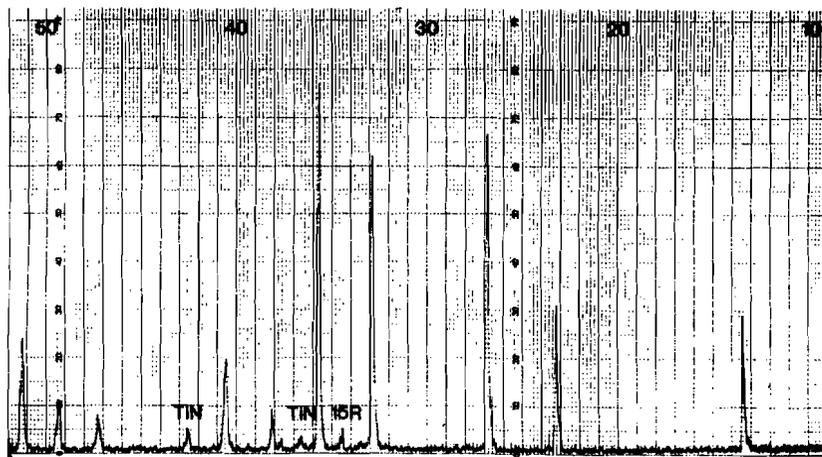


Fig. 4. X-ray diffractogram of a sintered sample of  $\beta'$ -sialon;  $\text{CuK}\alpha$  radiation.

to the shorter reaction time needed at the higher temperature.

The powder mixture of  $\beta'$ - $\text{Si}_3\text{N}_4$  and  $\text{AlN}$  from the reaction at  $1400^\circ\text{C}$  has a specific surface of  $5 \text{ m}^2/\text{g}$ . In Fig. 1 a comparison is given between kaolin, the mixture of  $\text{Si}_3\text{N}_4$  and  $\text{AlN}$  and the  $\beta'$ -sialon powders.

The reacted pellets are not strong and are easily milled. Despite it we have to conclude from Fig. 1 and the specific surface of the powder that some sintering of the  $\beta'$ -sialon pellets does occur.

Studies of the sinterability of our powders have just been started. Fig. 4 shows an x-ray diffractogram of a sample sintered at  $1725^\circ\text{C}$ , during 14 hrs.  $\text{TiN}$  is visible as an impurity; also some traces of the 15R phase are present.

#### CONCLUSIONS

A  $\beta'$ -sialon  $\text{Si}_3\text{Al}_3\text{N}_3\text{O}_5$  can be produced from kaolin/carbon mixtures under a nitrogen flow when Reynolds numbers are low and when approximately the stoichiometric kaolin: carbon ratio is used. Under these conditions the reaction rate is controlled by mass transfer.

When excess carbon is used, a mixture of  $\text{AlN}$  and  $\text{Si}_3\text{N}_4$  is produced. At high Reynolds numbers only a mixture of  $\text{AlN}$ ,  $\text{Si}_3\text{N}_4$  and  $\text{Al}_2\text{O}_3$  is formed. This reaction is accelerated in the presence of iron.

Reaction at temperatures of about  $1500^\circ\text{C}$  is favourable because the reaction time is shorter, less nitrogen is needed and the resulting  $\beta'$ -sialon powder has a higher specific surface. With the reactor used in our experiments, which has a limited height, no  $\text{SiC}$  is formed above  $1450^\circ\text{C}$ .

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