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The Design of a Circulating Fluid Bed Reactor for the Carbothermal Synthesis of Silicon Nitride

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Abstract

A large reactor for the carbothermal synthesis of Si_3N_4 is discussed. It is shown that a circulating fluid bed (CFB) reactor with a capacity of at least 100 tons Si_3N_4 per year seems possible and suitable. The main disadvantage is the fact that the process is not a continuous one, but a batch process. This is due to the fact that 100% conversion of SiO_2 has to be reached.

Im folgenden wird ein großer, zur carbothermischen Synthese von Si_3N_4 konstruierter Reaktor beschrieben. Es wird gezeigt, daß es möglich ist, einen zirkulierende Wirbelschichtreaktor (CFB) mit einer jährlichen Kapazität von mindestens 100 Tonnen Si_3N_4 aufzubauen. Der entscheidende Nachteil jedoch ist, daß der Reaktor nicht kontinuierlich betrieben werden kann, sondern aufgrund der notwendigen 100% Konversion von SiO_2 im Batchweise betrieben werden muß.

Un grand réacteur pour la synthèse par carboréduction du Si_3N_4 est discuté. Nous montrons qu'un réacteur de type lit fluidisé circulant (CFB) permettrait d'assurer la production d'au moins 100 tonnes de Si_3N_4 par an. Le principal désavantage du procédé réside dans le fait qu'il s'agit d'une fabrication en batch et non en continu, ceci pour assurer la transformation complète (100 %) de la silice.

Notation

A	Surface (m^2)
Ar	Archimedes number, $g\ dp^3\ D_g(D_s\text{-}D_g)/\mu^2$
Cp	Specific heat (J/(kg K))
d	Thickness of the tube wall (m)
dp	Particle diameter (m)
D	Density (kg/m^3)
Dif	Coefficient of diffusion (m^2/s)
Dt	Inner diameter of the tube (m)
e	Porosity
Fr	Froude number, $u^2/(g\ dp)$
g	Gravity constant (m/s^2)
H	Energy per volume and time ($J/(m^3\ s)$)
k	Coefficient of mass transfer (m/s)
L	Length of the tube (m)
Nu	Nusselt number, $\alpha\ dp/\lambda$
Pr	Prandtl number, $\mu\ Cp/\lambda$
Re	Reynolds number, $D_g\ u\ dp/\mu$
Sc	Schmidt number, $\mu/(D_g\ Dif)$
Sh	Sherwood number, $k\ dp/Dif$
t	Reaction time (s)
u	Superficial velocity (m/s)
U	Overall coefficient of heat transfer ($W/(m^2\ K)$)
V	Volume (m^3)
α	Coefficient of heat transfer ($W/(m^2\ K)$)
ΔT	Temperature difference between heating elements and bed (K)
λ	Thermal conductivity (W/(m K))
μ	Dynamic viscosity ($N\ s/m^2$)

Subscripts

g	Gas
m	Minimum
s	Solid

1 Introduction

The carbothermal synthesis of fine Si_3N_4 powder offers the possibility of combining a good quality product with an economic and environmentally acceptable process. The carbothermal synthesis of Si_3N_4 on a laboratory scale is described in the literature.[1] The carbothermal synthesis is described by the following reaction:

$$3SiO_2 + 6C + 2N_2 = Si_3N_4 + 6CO$$

For a large-scale production one has to design a process. Most steps in the process are state of the art. However, the selection and design of the synthesis reactor is not state of the art. The process is shown in Fig. 1.

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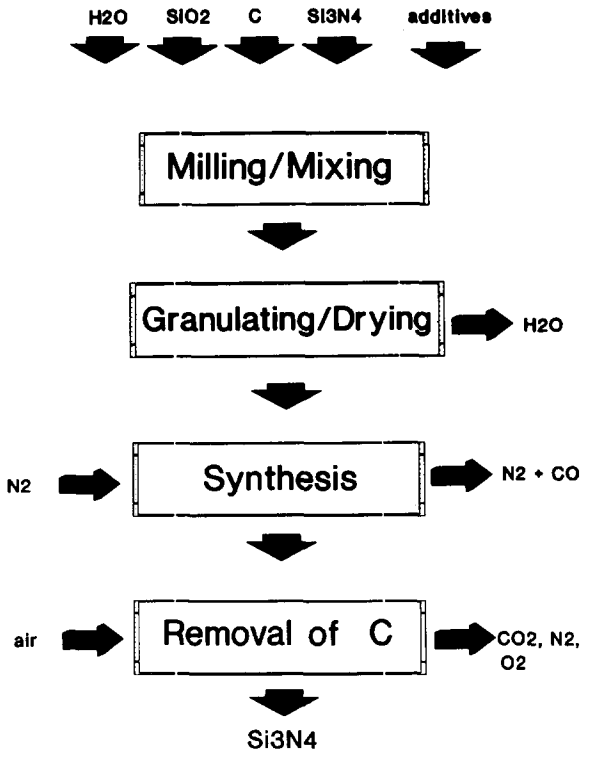

Fig. 1. Simple flow chart of the carbothermal synthesis process.

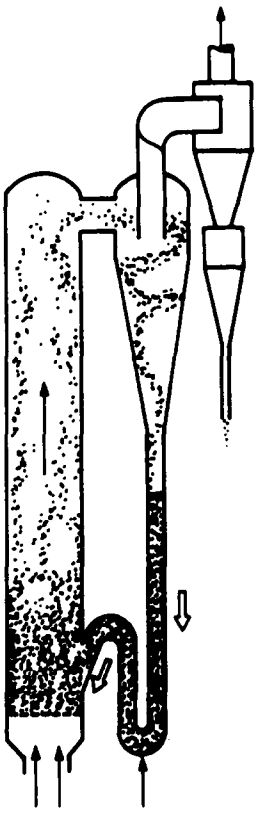

Fig. 2. A circulating fluid bed reactor.[4]

The milling/mixing process is done with a polyurethane lined stirred ball mill, using Ottawa sand as milling media. This processing step is water based and additives such as binder, dispersant, antifoaming agent, etc., are added.

The drying/granulating step is spray drying, resulting in a granulate with a diameter between 0·05 and 1 mm. This size of the granulate prevents limitation of the reaction rate by (Knudsen) gas diffusion.[2]

For the synthesis one should select a type of reactor which meets the following criteria: (1) excellent interaction between gas (N_2) and solid (SiO_2–C granulate); (2) excellent heat transfer; (3) continuous operation; (4) 100% conversion of the silica. A CFB reactor, in batch operation, has excellent heat transfer, excellent interaction between gas and solid, is suitable for small granulates, is capable of obtaining 100% conversion of the SiO_2, but is not continuous. When the CFB reactor is operated in a continuous way, one can not reach 100% conversion of the SiO_2. Problems may be anticipated concerning dust and blocking of the gas outlet by condensation of SiO at colder parts of the reactor. A small laboratory-scale fluid bed reactor (non-circulating) with an inner tube diameter of 75 mm was operated. Excellent results were obtained[3] and no dust problems were encountered. Figure 2 shows a CFB reactor.[4]

After synthesis excess free carbon has to be removed from the product. A batch operating CFB reactor seems suitable to do this job as well. The operating temperature is 650°C.[5] The gas used to remove the free carbon is oxygen (air). By cooling and circulating most of the exhaust gases, the gas used for the removal of the free carbon contains about 5 wt% oxygen. In this way the temperature of the exothermic reaction between C and O_2 can easily be controlled as the heat generated by the reaction is used to heat the gases. When the temperature is too high, oxidation of the fine Si_3N_4 will occur.

After removal of free carbon, the product is fine Si_3N_4 powder in a granulated form. These granulates are weak and can easily be deagglomerated, for instance by using a polyurethane-lined stirred ball mill and sintered Si_3N_4 balls.

A large scale reactor is the most challenging equipment in the carbothermal synthesis process of silicon nitride (and other nitrides). Hardly any literature on this subject is available. Especially, the use of a circulating fluid bed reactor for this synthesis is new. This paper describes the design of a circulating fluid bed reactor for the carbothermal synthesis of silicon nitride. The goal of this paper is to show whether such a reactor is suitable for this carbothermal synthesis.

2 Physical Data and Dimensionless Numbers

The physical data of the gases and granulate are needed for the design of a reactor. As both CO and N_2 have a molecular weight of 28, they have about similar physical properties. Table 1 gives the

Table 1. Physical properties of N_2 at 1 atm

T (K)	D_g (kg/m^3)	Cp (J/(kg K))	$Dif(\times10^{-6})$ (m^2/s)	$\mu(\times10^{-6})$ (N s/m^2)	$\lambda(\times10^{-3})$ (W/(m K))
273	1·251	1 012	17·4	16·6	27·9
1 273	0·268	1 161	234	47·0	86·0
1 473	0·232	1 191	298	51·6	95·9
1 673	0·204	1 221	371	56·1	106
1 873	0·182	1 251	449	60·7	117
2 073	0·165	1 281	531	64·4	126

physical data for N_2 and Table 2 gives the physical data for CO, both as a function of temperature. Table 3 gives the data for the granulate before and after synthesis. A molar ratio of SiO_2:C of 1:2·1 is used. The data are based on Perry *et al.*[6] and Turkdogan.[7] The Prandtl number for CO and N_2 at 1 bar is about 0·65 and the Schmidt number is about 0·75.

The data are also based on measurements carried out in the laboratories of Alusuisse-Lonza, using a small fluid bed reactor (non-circulating) and the papers 1 and 3. The inner diameter of the small reactor was 75 mm.

3 Modelling of the Reactor

The advantage of a CFB reactor over a normal fluid bed reactor lies in the higher ratio of wall: volume of the CFB reactor. This is important for reasons of heat transfer. The reactor will be indirectly heated, for instance by heating elements outside the reactor tube. Heat has to be transferred from the heating elements, through the reactor tube, to the bed for the reaction, which is endothermic, and for heating the granulate and the N_2. As a construction material for the high-temperature part of the reactor, graphite seems ideal. In order to improve the abrasion resistance, the graphite may be coated with SiC. It is assumed that the reactor is not cooled between the processing of the batches, but the granulate is fed to and taken from the hot reactor. It is also assumed that graphite is used as material for the heating elements. The reactor should operate under normal pressure.

Table 2. Physical properties of CO at 1 atm.

T (K)	D_g (kg/m^3)	Cp (J/(kg K))	$Dif(\times10^{-6})$ (m^2/s)	$\mu(\times10^{-6})$ (N s/m^2)	$\lambda(\times10^{-3})$ (W/(m K))
273	1·250	1 035	17·4	16·6	28·3
1 273	0·268	1 214	240	48·1	90·5
1 473	0·232	1 250	305	52·8	101
1 673	0·204	1 286	375	57·2	112
1 873	0·182	1 322	454	61·8	123
2 073	0·165	1 357	541	66·4	135

Table 3. Physical properties of the granulate before and after synthesis.

	D_s (kg/m^3)	Cp (J/(kg K))	*Pore diameter* (nm)
Before	1 000	1 600	40
After	900	1 200	200

The minimum superficial fluidization velocity, u_m is calculated according to eqn (1).

$$(D_s - D_g)g = 150(1-e)\mu u_m/(dp^2e^3) + 1{\cdot}75D_g u_m^2/(dpe^3) \quad (1)$$

The coefficient of heat transfer between the heating elements and the outer tube wall, α_1, is 900 to 1200 W/(m^2 K).[8] The thermal conductivity of graphite, λ, at 1500°C is 30 W/(m K).[8] The coefficient of heat transfer between the inner tube wall and the bed, α_2 is at least 500 W/(m^2 K).[4,9] The overall coefficient of heat transfer, U, is calculated according to eqn (2).[8]

$$1/U = 1/\alpha_1 + 1/\alpha_2 + d/\gamma \quad (2)$$

The heat balance of the synthesis is given in eqn (3) with $A = \pi Dt\ L$ and $V = \pi\ Dt^2\ L/4$:

$$UA\ \Delta T = H\ V \quad (3)$$

The porosity of a normal fluid bed is taken as 0·5 and the porosity of a CFB is taken as 0·8. The pressure drop over the gas distributor should be about 50% of the pressure drop over the bed. The pressure drop over the bed is equal to the weight of the bed.

The heat transfer between gas and solid is calculated according to eqn (4)

$$Nu = 0{\cdot}03\ Re^{1.3} \quad \text{for } Re < 1 \quad (4a)$$

$$Nu = 2\ Re^{0.5} \quad \text{for } Re > 10 \quad (4b)$$

The mass transfer between gas and solid is calculated according to eqn (5)

$$Sh = 0{\cdot}03\ Re^{1.3} \quad \text{for } Re < 1 \quad (5a)$$

$$Sh = 2\ Re^{0.5} \quad \text{for } Re > 10 \quad (5b)$$

4 Example

With substitution of dp = 0·5 mm and e = 0·5 in eqn (1), one finds that u_m = 0·03 m/s and Re_m = 0·045 at 1600°C and u_m = 0·11 m/s and Re_m = 4 at 0°C.

It is assumed that $L = 20D$, that t = 18000 s and that 10 kg N_2 are used for 1 kg of Si_3N_4. The reaction enthalpy is 9320 kJ per kg Si_3N_4.[7] Based on the present size of the market, a reactor with a capacity of 100 tons Si_3N_4 per year seems to be a

'large' reactor. 100 tons Si_3N_4 per year requires a reactor volume of 0·6 m^3, which results in D = 0·35 m and L = 7 m. The energy needed for the synthesis is 52 kJ/(m^3 s). The energy needed to heat the N_2 is 100 kJ/(m^3 s). The energy needed to heat the granulate is 27 kJ/(m^3 s). Therefore, the capacity of the reactor, without heat losses, must be more than 110 kW.

It is assumed that $d = 0{\cdot}03$ m, $\alpha_1 = 1100$ W/(m^2 K) and α_2 = 600 W/(m^2 K). According to eqn (2), this leads to U = 300 W/(m^2 K). Substitution of the data in eqn (3), with $H = 100 + 52$ kJ/(m^3 s) results in a value for ΔT, the temperature difference between heating elements and bed, of 40°C.

The superficial gas velocity, u, is calculated to be 1·8 m/s and Re is calculated to be 3 for dp = 0·5 mm and at 1500°C. Ar, for the example given, is about 70 at 1500°C. Fr, for the example given, is about 0·10 at 1500°C.

Per batch the input into the reactor is: 80·5 kg SiO_2, 35·5 kg C, 4 kg Si_3N_4, 625 kg N_2, 3 kg volatile matter and at least 540 kWh of electricity. Per batch the output out of the reactor is: 66·5 kg Si_3N_4, 3·5 kg C, 75 kg CO, 600 kg N_2, 3 kg volatile matter, energy in form of hot gases 338 kWh and in form of hot solids 35 kWh.

With eqn (4), with Re = 3 and dp = 0·5 mm, the height of a heat transfer unit can be calculated. According to this calculation the gas is heated within about 10 mm. This indicates that the gas is heated by passage through the bottom plate of the reactor or at the entrance of the fluid bed by the granulate.

With eqn (5), with Re = 3 and dp = 0·5 mm, the height of a mass transfer unit can be calculated. According to this calculation the nitrogen is 'saturated' with CO within about 10 mm, when mass transfer would be a rate limiting step of the reaction rate. As the nitrogen leaving the reactor is not 'saturated' with CO, a reaction rate limited by mass transfer can be excluded.

5 Discussion

From a chemical engineering point of view a 'large' CFB reactor for the carbothermal synthesis of Si_3N_4 seems possible and suitable. A temperature difference between the heating elements and the bed of 40°C seems acceptable. Firstly the granulate is heated to the reaction temperature, then the reaction proceeds. It seems of importance that measurement and control of temperature is done *in* the bed, in order to prevent temperatures over 1500°C of the granulate and formation of SiC. The reactor has a capacity of about 100 tons Si_3N_4 powder per year.

The preheating of N_2, especially by the flue gases leaving the reactor, would not only save energy, it would also reduce the heat transfer 'problem' substantially. One should note that in the example given, more energy is needed for heating the N_2 than for the reaction itself. Per kg of Si_3N_4 8·6 kWh of energy are needed. From this 8·6 kWh, only 2·5 kWh are needed for the reaction and 5 kWh are needed for heating the N_2.

The model used to describe the heat transfer is a simple model. It is anticipated that the N_2 is mainly heated at the entrance of the reactor, for instance during its passage through the bottom plate.

When the reaction time is shorter than 5 h, the heat transfer and the gas flow must be increased. Because one has the granulate size to play with, between 0·05 and 1 mm, this seems possible. Of course, the temperature difference between heating elements and bed would increase. The conversion can be monitored by measurement of the amount of CO in the flue gases leaving the reactor.

From the example, one can see that the superficial velocity is higher than the minimum superficial velocity. The use of a smaller sized granulate decreases the minimum superficial velocity, the Reynolds number and the Archimedes number and increases the Froude number. This indicates that with a smaller sized granulate one would still operate the granulate in the CFB regime according to the Reh-diagram.[9]

Electricity is not only needed for the synthesis reactor but also for the production of N_2, by cold distillation of air, and for the milling of the raw material. Therefore, the best location for a plant with a very large capacity seems a location with cheap electricity, which means hydro-electric power. Such locations are also advantageous for aluminium plants, Acheson plants, etc.

6 Conclusion

From a chemical engineering point of view, a CFB reactor seems suitable and possible for the carbothermal synthesis of Si_3N_4. It seems possible to construct a reactor with a capacity of at least 100 tons Si_3N_4 per year. The main disadvantage lies in the fact that the reactor has to be operated batchwise in order to obtain 100% conversion of the SiO_2.

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