DESIGN OF COUNTER-CURRENT MOVING BED REACTOR FOR CVD COATING OF ULTRA-FINE PARTICLES

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Key Words: CVD, Coating, Ultra Fine Particle, Moving Bed, Counter Current

A new counter-current type of moving bed reactor was devised for AlN coatings of Si_3N_4 fine particles in the form of agglomerates by chemical vapor deposition. The influence of process parameters, such as reaction time and temperature, input concentration of gas precursor, and the agglomerate size, was investigated in relation to total quantity of deposited AlN inside the agglomerates. A simplified reactor model was used to analyze the deposition data. As a result, the conversion of Si_3N_4 particles to their composite with AlN increased with increasing temperature and concentration of AlCl_3 reaction gas and with decreasing agglomerate size. Thus, it has become possible to produce a sort of surface modified ultra-fine particle at certain coating ratios continuously.

Introduction

Recently, ultra-fine ceramic particles have been used for development of advanced materials for many novel applications such as space vehicles, micro-electronics, and ceramic heat engines, (Hlavacek and Puszynski, 1996). The performance of particles is strongly related to the structure of the surface layer. The coating of fine particles by chemical vapor deposition (CVD) is a promising technique for surface modification. The major advantage of preparing ceramic composites by CVD is that the desired properties of composites, such as thermal, electrical, mechanical, and chemical resistance to oxidation and corrosion, can be obtained by optimization of the CVD process. Then, the design of proper reactor geometry and the choice of operational conditions are important to obtain the required coating. Recently, different types of fluidized-bed CVD reactors were proposed for the coating of Si_3N_4 particles by AlN (Chiba *et al.*, 1996) and silicon deposition from silanes (Caussat *et al.*, 1995). The main disadvantages of the fluidized-bed CVD reactor are the necessity of the special design of the complicated gas distributor which is associated with the possibility of its plugging with deposited solids, and attrition of the agglomerates due to their frequent relative movements. In order to overcome these demerits a moving-bed reactor without gas distributor can be adopted.

In this study, a new counter-current type of

moving bed reactor was designed for the CVD coating of ultra-fine particles fed continuously with special attention to an efficient gas-solid contact reaction inside the solids layer and long stable operation. The performance of the moving bed reactor system was investigated for Si_3N_4 particles coated with AlN. The influences of process parameters, such as reaction temperature and gas precursor concentration, and of the size of Si_3N_4 agglomerates on the total quantity of the AlN deposit inside the agglomerates were analyzed on the basis of a simplified reactor model to be compared with the experimental data.

1. Device and Procedure

Coating of ultra-fine particles by chemical vapor deposition was carried out in a new counter-current type of moving bed hot-wall reactor from $\text{AlCl}_3\text{-NH}_3\text{-N}_2$ reactant mixtures under atmospheric pressure. This system consists of reagent supplying parts, the moving bed reactor, and an electrical resistance-heated tubular furnace, as shown in Fig. 1. The temperature was maintained at the desired level by using a programmable temperature controller which interfaced with the furnace power supply and a thermocouple placed near the reactor wall at the intermediate height of the furnace. It was regarded as the reaction temperature inside the thin tube reactor, which was nearly uniform in the radial and axial directions. The reaction temperature was varied from 1023 to 1123 K. The flow rates of NH_3 and N_2 were regulated with mass flow meters.

The sublimation of AlCl_3 powder was made in a vaporizer heated with a mantle heater. N_2 was used as a carrier gas. All gas lines were heated by using heater tapes at a temperature of 200°C in order to

* Received on October 3, 1996. Correspondence concerning this article should be addressed to K. Shinohara.

Presented at the 29th Autumn Meeting of the Society of Chemical Engineers, Japan, at Kyoto, September, 1996.

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Fig. 1 Schematic diagram of experimental setup

prevent the condensation of AlCl₃ vapor. The concentration of AlCl₃ gas was adjusted at the carrier gas flow rate 0.21/min by changing the vaporizer temperature from 170 to 240°C, corresponding to the sublimation rate in weight loss of AlCl₃ solids from $6.67 \cdot 10^{-6}$ to $1.58 \cdot 10^{-5}$ mol/s.

The moving bed reactor consists of a feeding tank, a tubular reactor and two samplers, as shown in Fig. 2. The reactor is made of quartz glass tubing, 1 m long and 0.06 m inner diameter, and is composed of a lower gas supplying and solids withdrawing zone and an upper reaction zone 0.4 m long. The lower zone contains two coaxial gas paths, so NH₃ and AlCl₃-N₂ mixtures could be fed separately into the reaction zone. The reactor was designed with the purpose of preventing preliminary mixing of reagent gases and deposition of undesired intermediates, and of ensuring uniform free flowing of agglomerates without clustering. The solids discharge rate was controlled with differently sized nozzles placed inside the bottom sampler to attain uniform descending of agglomerates in the radial direction. The nonconverted reactant and product gases are removed from the reaction zone through an upper exhaust gas outlet where the cooling trap is set.

To enhance the flowability of Si₃N₄ raw particles of 0.75 μm (Nihon Cement Co.), they were agglomerated to size of 65 – 150 μm by using a Ro-Tap sieve shaker. The shaker imparts to the sieves both circular and tapping motions to allow for production of stable spherical agglomerates without any binder.

Fig. 2 Detailed diagram of counter-current moving bed CVD reactor

The SEM analysis revealed that the agglomerate size and shape did not change substantially during reaction cycles.

The presence of AlN in the agglomerate was confirmed by using an X-ray diffractometer with monochromatic CuK radiation operating at 40 kV and 30 mA. Then, to estimate the total amount of AlN inside the agglomerate, EPMA (electron probe microanalyzer, JEOL-8900M) analysis was carried out. The samples were prepared by casting in epoxy resin the collected agglomerates as a mixture through the two samplers during reaction, polishing and coating with gold in an ion sputtering device (JEOL JFC-1100E) to eliminate specimen charging. The total intensity of Al was measured over the cross-section of the agglomerate, corresponding to the quantity of AlN.

2. Analysis

The formation of AlN coatings over Si₃N₄ particles in the present CVD process from AlCl₃-NH₃-N₂ reactant mixture is assumed to proceed according to the following overall reaction

where $\text{Si}_3\text{N}_4(\text{s})$ is primary particles forming the agglomerates with the internal surface site on which the deposition occurs, and $\text{AlN-Si}_3\text{N}_4(\text{s})$ is the combined product of AlN deposit on the outer surface of $\text{Si}_3\text{N}_4(\text{s})$ inside the agglomerates. The chemical reaction rate is assumed to be first order in concentration of gas precursor AlCl_3 .

In order to evaluate the overall amount of deposit inside the agglomerate, a shrinking-core model was adopted, by analogy with gas-solid reaction, for a simplified mathematical description of the CVD reaction in the moving-bed. The agglomerate sphere (solid B) of radius r_s , which is made of primary Si_3N_4 particles, is in contact with AlCl_3 gas (gas A) with bulk molar concentration C_A . As the reaction proceeds, a layer of product $\text{AlN-Si}_3\text{N}_4$ (solid D) is formed around the unreacted inner core of solid B.

Based on the shrinking-core model combined with the chemical reaction step and diffusion in the product layer, the overall rate of reaction is determined in terms of solids conversion and is given by (Froment and Bischoff, 1979)

$$R_{VA}^{\text{glob}} = \left(\frac{3(1-x)^{2/3}}{r_s} \right) \cdot \left[\frac{C_A}{\frac{(1-x)^{1/3}r_s}{D_{eA}}[1 - (1-x)^{1/3}] + \frac{1}{k}} \right] \quad (2)$$

where R_{VA}^{glob} is the overall reaction rate of component A per unit agglomerate volume, x is the conversion of solid B into solid D, that is to be proportional to the total quantity of AlN deposited inside the agglomerate, D_{eA} is the effective diffusivity of gas A in the product layer, and k is the specific reaction rate constant. Thus, the first term on the right hand side of Eq. (2) indicates the specific reaction surface, and the first and second terms in the denominator of the second term correspond to the resistances to diffusion and reaction, respectively.

In the present moving bed reactor, the solid phase or the agglomerates of Si_3N_4 fine particles move downwards under gravity in counter-current with an upward flowing gas stream, that is, a mixture of ammonia, AlCl_3 vapor and nitrogen. The main assumptions used in the reactor model formulation are: 1) steady-state isothermal operation, 2) plug flow for both solid and gas phases, 3) uniform structure of the moving bed, 4) ideal gas behavior, and 5) constant physical properties. **Figure 3** illustrates the notation adopted for the reactor model.

Fig. 3 Notation of moving bed model

Assuming one-dimensional piston flow of the solids, the mass flow rate of the solids per reactor cross-sectional area at the entrance, F_0 , is written as

$$F_0 = U_S \rho_{ag} (1 - \varepsilon_r) \quad (3)$$

where U_S is a constant descending velocity of the solids, ρ_{ag} is an apparent density of agglomerates and $(1 - \varepsilon_r)$ is the fraction of reactor volume occupied by the agglomerates. Then, the residence time of the solids, t_s , is given by

$$t_s = \frac{L \rho_{ag} (1 - \varepsilon_r)}{F_0} \quad (4)$$

The mass balance for the solid phase at a certain depth, z , is expressed as

$$F_0 \frac{dx}{dz} = M_B \cdot R_{VA}^{\text{glob}} (1 - \varepsilon_r) \quad (5)$$

where M_B is the molecular weight of Si_3N_4 .

The mass balance for the bulk concentration of gas component is

$$U_G \frac{dC_A}{dz} = R_{VA}^{\text{glob}} (1 - \varepsilon_r) \quad (6)$$

where U_G is the upward axial volumetric flow rate of gas mixture per unit cross-sectional area of reactor.

Introducing the following dimensionless variables

$$y = \frac{C_A}{C_{A0}}; \quad l = \frac{z}{L} \quad (7)$$

and combining Eqs. (2) – (7), the change in conversion

x with dimensionless length of the reactor l , is derived as

$$\frac{dx}{dl} = \frac{3(1-x)^{2/3}t_s M_B C_{A0} k}{r_s \rho_{ag}} \left[\frac{y(l)}{\frac{(1-x)^{1/3} r_s k}{D_{eA}} [1 - (1-x)^{1/3}] + 1} \right] \quad (8)$$

The boundary condition for this differential equation is

$$x = 0 \text{ at } l = 0 \quad (9)$$

The relationship between the dimensionless bulk concentration of reactant A, y , and conversion of the solids at any intermediate axial position, $x(l)$, is obtained from Eqs. (5) and (6)

$$y(l) = 1 - \frac{F_0}{U_G M_B C_{A0}} (x_L - x(l)) \quad (10)$$

where x_L is the conversion of solid B leaving the reactor and C_{A0} is the concentration of gas A in the feed.

An iterative solution of the differential equation of Eq. (8) with Eq. (10) for the boundary condition of Eq. (9) is used for calculation of the desired solid conversion x_L at the bottom outlet of the counter-current moving-bed reactor as a function of operating conditions.

3. Results and Discussions

Computer simulation of the AlN coating of Si_3N_4 particles in the present CVD reactor was carried out on the basis of the mathematical model developed in the previous section. The typical values of parameters used for the simulation are summarized in **Table 1**. The specific reaction rate constant k was given as a function of temperature T based on the Arrhenius equation:

$$k = k_0 \exp \left[\frac{E}{R_G T_0} \left(1 - \frac{T_0}{T} \right) \right] \quad (11)$$

where the activation energy E is taken from the literature data (Kim *et al.*, 1991) and the reaction rate constant k_0 at reference temperature T_0 was chosen to correspond to our experimental data.

The effective diffusivity, D_{ei} , was estimated by Eq. (12) (Wakao and Smith, 1962):

$$D_{ei} = \frac{\varepsilon_{ag}^2}{\left(\frac{1}{D_{Ki}} + \frac{1}{D_{mi}} \right)} \quad (12)$$

Table 1 Parameters used for simulation

Parameter	Std. value	Variation range
L [m]	0.4	
R [m]	75×10^{-6}	32.5×10^{-6} , 75×10^{-6}
F_0 [$\text{kg m}^{-2} \text{s}^{-1}$]	0.51	0.255, 0.51
U_G [m s^{-1}]	2.95×10^{-3}	
ε_{ag} [—]	0.6	
ε_r [—]	0.4	
ρ_{ag} [kg m^{-3}]	0.632×10^3	
C_{A0} [mol m^{-3}]	3	2.5–4.5
T [K]	1073	1023–1123
k_0 [m s^{-1}]	1.4×10^{-6}	0.57×10^{-6} – 3.16×10^{-6}
$E/R_G T_0$ [—]	18.3	($T_0 = 1073$ K)
D_{eA} [$\text{m}^2 \text{s}^{-1}$]	9.9×10^{-6}	8.6×10^{-6} – 1.1×10^{-5}

Fig. 4 Profiles of gas concentration and solids conversion in reactor for different residence time of agglomerates

where ε_{ag} is an internal void fraction of agglomerate, D_{mi} is the gas phase diffusion coefficient for component i in the carrier gas and D_{Ki} is the Knudsen diffusion coefficient for species i . The diffusion coefficient for the binary gas system was estimated by the Chapman-Enskog formula, and the Knudsen diffusivity is calculated by using the correlation resulting from the kinetic theory of gases (Froment and Bischoff, 1979).

Figure 4 illustrates the typical axial profiles of gas reactant concentration and solid conversion inside the reactor. Due to the counter-current mode of operation, the reactant gas introduced at the bottom of the reactor ($z=L$) is consumed in the ascending period. On the other hand, the solids were fed from the top of the reactor ($z=0$) and thus the quantity of deposit (solid conversion) inside the agglomerates increases as the solids move downwards. The increasing residence time of the agglomerates, t_s , also gives rise to the higher conversion of solids leaving the reactor, as shown in **Fig. 4**. It can be adjusted by changing the descending velocity of agglomerates or the reactor length. Thus, these are favorable to more deposition of AlN inside the agglomerates.

Fig. 5 Variation of solids conversion and total intensity with reactor temperature for different agglomerate size

Fig. 6 Variation of solids conversion and total intensity with input concentration of gas

The influence of reaction temperature on solid conversion is shown in Fig. 5 for different agglomerate sizes. The effect of input AlCl_3 gas precursor concentration on the solid conversion is demonstrated in Fig. 6. These are the main operational parameters with which we can adjust the deposition rate of the CVD coating. In these figures the solid line corresponds to the calculated solid conversion which is assumed to be proportional to the total quantity of AlN deposit inside the agglomerate. The circles are the experimental points as the total normalized intensities obtained from EPMA analysis on the aluminum distribution inside the agglomerate. The characteristic intensities are roughly proportional to the mass fraction of the emitting element of Al. The total intensities within the agglomerate were normalized with beam current and with agglomerate cross-sectional area.

Three kinds of reaction temperature were examined and the experimental data revealed that the quantity of AlN deposit increases with temperature within the present temperature range. The calculated solid conversion also increases with temperature. This is because of the following two

reasons. The reaction rate increases according to the Arrhenius exponential dependence of Eq. (11). And, the effective diffusivity of the gas precursor is also increased in proportion to the $(T)^{3/2}$ for ordinary diffusivity (D_{mi}) and $(T)^{1/2}$ for Knudsen diffusivity (D_{Ki}). However, according to literature data on the temperature dependence of CVD deposition of AlN films, there is a trend where further increasing temperature above 1273 K will lead to the homogeneous gas phase nucleation mechanism of AlN production and formation of AlN fines, in other words, decreasing the rate of coating. Figure 5 also depicts the influence of agglomerate size on solids conversion. With increasing agglomerate size the solid conversion decreases due to the lower rate of diffusion of gas A through the product layer inside the agglomerate.

Figure 6 illustrates that the quantity of AlN deposit or the solid conversion increases with concentration of gas precursor AlCl_3 . The calculated curve is a straight line, because the kinetic expression implied for simulation is in the first order with respect to the concentration of the gas precursor. Some deviation of experimental points from the linear dependence can be ascribed to both an experimental error and more complicated kinetics of CVD deposition of AlN from $\text{AlCl}_3\text{-NH}_3$ than used for simulation. For example, Lee *et al.* (1995) proposed a Langmuir-Hinshelwood type of expression for description of dependency of kinetics on gas reactant concentration.

Conclusion

A new counter-current type of moving bed reactor was devised and applied to the continuous production of AlN coatings of Si_3N_4 ultra-fine particles by chemical vapor deposition from a $\text{AlCl}_3\text{-NH}_3\text{-N}_2$ system. The influences of process parameters, such as reaction time and temperature, input concentration of gas precursor AlCl_3 , and agglomerate size of Si_3N_4 particles, on the total quantity of deposited AlN were investigated experimentally, and theoretically by using a reactor mathematical model. As a result, the quantity of AlN deposited on Si_3N_4 primary particles increased with increasing reaction time, temperature and AlCl_3 input gaseous concentration and with decreasing agglomerate size.

Acknowledgment

The authors are grateful to Dr. Kazuo Kondo, Messrs. Yasushi Ohyama and Kazuyuki Harima for their experimental assistances and useful suggestions. It was possible to construct the present CVD moving bed reactor through a Grant-in-Aid for Scientific Research, Japan.

Nomenclature

C_A = molar concentration of gas reactant A in unit volume of reactor [mol m⁻³]

C_{A0}	= initial molar concentration of gas reactant A in unit volume of reactor	[mol m ⁻³]
D_{eA}	= effective diffusivity of gas A within product layer inside agglomerate	[m ² s ⁻¹]
D_{Ki}	= Knudsen diffusion coefficient for species i	[m ² s ⁻¹]
D_{mi}	= gas phase diffusion coefficient for component i in carrier gas	[m ² s ⁻¹]
E	= activation energy	[J kmol ⁻¹]
F_0	= mass flow rate of solids per unit cross-sectional area at entrance of reactor	[kg m ⁻² s ⁻¹]
I	= total normalized intensity	[—]
k	= specific reaction rate constant	[m s ⁻¹]
k_0	= specific reaction rate constant at reference temperature T_0	[m s ⁻¹]
L	= length of reaction zone	[m]
l	= dimensionless reaction distance	[—]
M_B	= molecular weight of Si ₃ N ₄	[kg kmol ⁻¹]
r_s	= $R(1-\varepsilon_{ag})^{1/3}$ initial radius of spherical agglomerate in shrinking-core model	[m]
R	= agglomerate radius	[m]
R_G	= ideal gas law constant	[J kmol ⁻¹ K ⁻¹]
R_{VA}^{glob}	= overall reaction rate of component A per unit agglomerate volume	[mol m ⁻³ s ⁻¹]
t_s	= residence time of solids agglomerate	[s]
T	= temperature inside reactor	[K]
T_0	= reference temperature	[K]
U_s	= axial velocity of solids	[m s ⁻¹]
U_G	= upward axial volumetric flow rate of gas mixture per unit cross-sectional area of reactor	[m ³ m ⁻² s ⁻¹]
x	= conversion of solid B, that is composite solid volume per agglomerate solid volume	[—]

x_L	= conversion of solid B leaving reactor	[—]
y	= dimensionless gas concentration inside reactor	[—]
z	= axial coordinate from top of reactor	[m]
ε_r	= void fraction among agglomerates inside moving bed reactor	[—]
ε_{ag}	= internal void fraction of each agglomerate	[—]
ρ_{ag}	= $\rho_s(1-\varepsilon_{ag})$ apparent density of agglomerate	[kg m ⁻³]
ρ_s	= solid density of Si ₃ N ₄	[kg m ⁻³]

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