MODELLING STUDY OF THE PRODUCTION OF AlN NANOPARTICLES IN A NEW VERSION OF A PLASMA SYNTHESIS REACTOR

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Abstract

A theoretical study of the nucleation and growth of ultrafine particles is carried out as part of the development of a new version of a thermal plasma reactor for ceramic and metallic powder synthesis. Presently, the reactor is applied to the production of AlN powder. Considering the reaction between NH₃ and Al(ν) under controlled conditions, a two step two-dimensional laminar flow model that solves the gas-to-condensed phase transition is applied. First, the fields of velocity, temperature, and chemical species concentration in the reaction zone are determined. Following, it solves for the nucleation and growth of particles which form when hot gas carrying Al(ν) mixes with a cold jet of an Ar/NH₃ mixture. Two different geometries for reacting gas injection are analysed with respect to their influence on particles size and composition of operating parameters (temperature, Al(ν) concentration, and reacting gas flow rate).

1. Introduction

A new version of a thermal plasma synthesis reactor for ceramic and metallic ultrafine particles synthesis was built and is presently operational for the production of aluminium (Al) and aluminium nitride (AlN) fine powders. The description of the reactor as well as the experimental results obtained so far are presented in a parent paper.

The model developed for this system accounts for reaction both at the surface of embryos (surface reaction modified nucleation rate) and stable particles. Previous comparison between theoretical and experimental results were in good agreement. In the present work, a comparison is made between radial injection and centre line injection of same gas mixture. The analysis considers the influence on particle size of the following operating parameters: temperature, Al(ν) concentration, and reacting gas flow rate.

2. Numerical model

Considering the reaction between NH₃ and Al(ν) under controlled conditions, a two-dimensional numerical model is applied to this system. The many conservation equations describing both fluid flow conditions and phase transition phenomena are solved in two steps: (i) first, the fields for velocity, temperature, and chemical species concentration are calculated; (ii) following, the particle nucleation and growth process arising from the mixing of a hot gas flux carrying Al(ν) and a radial jet of a cold Ar/NH₃ gas mixture is determined.

The details of the development of this model for the AlN nucleation and growth is to be published. The geometry and dimensions for the reaction region are shown in Figure 1. Hot gas containing Al(ν) coming from an upper evaporation chamber enters a circular port of diameter De. Room temperature Ar/NH₃ gas mixture is fed through a circumferential gap 0.1 mm thick. The powder carrying gas is exhausted through a circular port of diameter Dc.

The following conservation equations are solved in the first step, assuming laminar axi-symmetric flow:
Continuity:
\[ \dot{V} \cdot (\rho \vec{u}) = 0 \]  
(1)

Moment conservation:
\[ \dot{V} \cdot (\rho \vec{u} \vec{u}) = \dot{V} \cdot (\mu \vec{\nabla} \vec{u}) - \dot{V} \cdot \vec{\nabla} \rho \]  
(2)

Chemical species conservation:
\[ \dot{V} \cdot (\rho \vec{u} \chi_i) = \dot{V} \cdot \left( \frac{\partial D_{i,Ar} \vec{\nabla} \chi_i}{\partial r} \right) + S_i \]  
(3)

Energy conservation:
\[ \dot{V} \cdot (\rho \vec{u} h) = \dot{V} \cdot \left( \frac{k}{C_p} \vec{\nabla} h \right) + \dot{V} \cdot \left[ \sum_{i} \left( \frac{k_i}{C_p^i} - \frac{k}{C_p} \right) \frac{\partial \chi_i}{\partial r} \right] + S_h \]  
(4)

Figure 1 - Geometry and dimensions adopted for the reaction region, with two possibilities of reacting gas injection: (i) radially through a 0.1 mm circumferential slot; and (ii) axially through a 15 mm diameter pipe.

The particle nucleation and growth problem is solved using the method of moments of the particle size distribution. It is assumed that particles are spherical and transported by convection, Brownian diffusion, and thermophoresis. It is also assumed that particles can grow by condensation and heterogeneous reaction and coagulation. The kth-moment conservation is written as:

\[ \frac{\partial M_k}{\partial t} + \dot{V} \cdot (\vec{u} + \vec{u}_a) M_k = \dot{V} \cdot (D_v \vec{\nabla} M_k) + v_{\text{eff}}^{-1} J - \int_{a}^{b} \frac{\partial}{\partial v} \left( (G_m) dv + (B - D) \right) dv \]  
(5)

A nucleation equation that considers the effect of heterogeneous reaction in the AlN system is included in the birth and death term:

\[ J = \frac{m(v, X)}{3S_{av}} \frac{B \times s_i}{\sqrt{\pi}} \left[ \exp \left( \frac{-4}{27 \left( \ln S_{av} - (1 - X) \right) \left( \frac{\Delta G_f}{k_B T} \right)} \right) \right] \]  
(6)

These two sets of conservation equations were written in the form of algebraic equations and solved using the SIMPLER computational method as developed by Patankar.

3. Simulation results

Considering the hot gas flow rate of 30 lpm, and an inlet temperature of 2200 K, a study was carried out to determine the minimum inert gas flow rate which radially injected with 3 lpm of NH₃ would produce full conversion to AlN in both cold gas injection geometries. The results
presented in Figure 2 show that conversion is proportional to Ar flow rate, and that full conversion is attained at a flow rate of 20 lpm with the radial injection and above 15 lpm with the axial injection. These flow rates adopted (flow rate of Ar mixed with NH₃ of 20 lpm, in both radial or axial injection), the specific surface area (SSA) of the powder evaluated at the reactor outlet for different combinations of temperature and a saturated Al(v) concentration are shown in Figure 3. A 100% conversion was verified in all situations plotted in this figure. It can be observed at the temperature range studied that for the same operating conditions, larger particles (smaller SSA) are in general produced with the axial injection. In case of radial injection, a larger dependence exists of particle size with respect to temperature; powders with greater particle size result at higher temperatures. Yet with respect to temperature, little change is observed in case of the center line injection with the tube positioned at the 175 mm distance from hot gas port. Positioning the tube farther downstream (at 225 mm from the hot gas inlet port) results in powders with smaller particle size and, contrary to the tendency observed in the radial injection, an ascending dependence of SSA with respect to temperature is predicted. The larger particles produced with the 175 mm distance are seen as the result of a longer residence time of particles in the reacting zone which is provided in this situation.

![Graph](image1)

![Graph](image2)

(a) radial injection  
(b) axial injection

Figure 2 – Percentage of AlN converted as a function of Al(v) mole fraction and a mixture of cold gas mixture of Ar/NH₃ radially and axially injected for a hot gas flow rate of 30 lpm and 2200 K at inlet; NH₃ flow rate kept constant at 3 lpm. Axial injection at 175 mm from hot gas port.

The fields of temperature, nucleation rate, average BET particle diameter, and particle number density observed for a temperature of 2000 K at the hot gas entrance port are shown in Figures 4 to 7, respectively. Because of axial symmetry, only half plot is shown in these figures. The zero coordinate for the axial distance refers to the point where the circumferential slot for radial injection is positioned (75 mm downstream of the hot gas port, located at the left; gas outflow is to the right). In Figure 4 it is observed that the center line injection results in a steeper temperature gradient near the hot gas entrance, and smaller nucleation rates (Figure 5) as compared to radial injection. The average BET particle diameter distribution (Figure 6) shows larger particles over the entire chamber in the center line injection case. This observation is fully compatible with a smaller number density of particles also predicted by
the model (mass conservation), shown in Figure 7. In the radial injection situation, particle number density is at least one order of magnitude higher than the centre line injection over the entire calculation domain.

![Graph showing specific surface area (SSA) vs temperature](image)

Figure 3. Specific surface area predicted for different inlet hot gas temperatures for different gas injection geometries: RD – radial; CL-175 – centre line injection at 175 mm from hot gas entrance; CL-225 – centre line injection, 225 mm from hot gas entrance; saturated concentrations of aluminum. Flow rates: plasma gas ~ 30 lpm, \( \text{NH}_3 \) ~ 1 lpm, and Ar mixed with \( \text{NH}_3 \) ~ 20 lpm.

4. Conclusions

A study based on the numerical simulation of the nucleation and growth of ultrafine AlN particles in a new concept of synthesis reactor has been carried out to analyse two different cold gas injection configurations (radial and centre line injection). For both geometries, it is verified that full conversion should be attained for the operating range of hot gas temperature, up to the Al(\( \gamma \)) saturation concentration (in case of the dimensions and gas flow rates conditions adopted). For the saturation Al(\( \gamma \)) concentration, the simulation results show that particle size increases with temperature in the radial injection and that it practically does not change in the centre line case where cold gas is injected at a shorter distance from hot gas entrance (175 mm). For a larger distance (225 mm), particle size slightly decreases. The simulation results also show that longer residence times (provided by the axial injection at the 175 mm distance) produces larger particles. This observation fully agrees with results reported for different experiments in the literature.

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Figure 4 Contour plots of the temperature distribution in the reaction chamber for (a) radial injection and (b) axial injection; inlet gas flow rate of 30 lpm, T=2000K and injection cold mixture of Ar/NH₃ of 20/3 lpm, respectively.

Figure 5 Contour plots of the nucleation rate (J) of particles in the reaction chamber for (a) radial injection and (b) axial injection; inlet gas flow rate of 30 lpm, T=2000K and injection cold mixture of Ar/NH₃ of 20/3 lpm, respectively.

Figure 6 Contour plots of the particles specific surface area mean diameter in the reaction chamber for (a) radial injection and (b) axial injection; inlet gas flow rate of 30 lpm, T=2000K and injection cold mixture of Ar/NH₃ of 20/3 lpm, respectively.

Figure 7 Contour plots of the number density of particles in the reaction chamber for (a) radial injection and (b) axial injection; inlet gas flow rate of 30 lpm, T=2000K and injection cold mixture of Ar/NH₃ of 20/3 lpm, respectively.
NOMENCLATURE

%AlN = percentage of AlN in a particle (%)
B = birth term in the moment conservation equation
$C_p$ = specific heat (J/kg.K)
D = mass diffusivity (m$^2$/s)
D = death term in the moment conservation equation
G = surface growth rate (m$^3$/s)
$\lambda G_r$ = free energy change related to the heterogeneous nitridation reaction (J/kg)
h = enthalpy (J/kg)
i = chemical species index (Ar, NH$_3$, N$_2$, H$_2$, or Al)
J = nucleation rate (1/m$^3$.s)
k = thermal conductivity (W/m.K)
$M_k$ = $k^{th}$-moment of particle size distribution (k = 0, 1 or 2)
n = particle number density (1/m$^3$)
p = pressure (N/m$^2$)
t = time (s)
T = temperature (K)
r = radius (m)

$S_b$ = energy conservation equation source term
$S_i$ = chemical species conservation equation source term
SSA = specific surface area (g/m$^2$)
u = velocity (m/s)
$u_{th}$ = thermofores velocity de termofores (m/s)
$v_1$ = equivalent monomer size (m)
w = mass fraction
$x_{AI}$ = molar fraction of aluminum vapor
$X_c$ = mole fraction of free Al in a particle
$z$ = longitudinal distance (m)
$v_c$ = critical particle volume (m$^3$)
$v_g$ = geometric average particle volume (m$^3$)

Greek letters

$\beta^*$ = equivalent impinging rate
$\nu$ = viscosity (kg/m.s)
$\rho$ = gas density (kg/m$^3$)
$\sigma$ = geometric standard deviation
$\theta$ = dimensionless average surface energy

References