Coating Particles with Alumina Nanolayers Utilizing Atomic Layer Deposition in a Fluidized Bed Reactor

by

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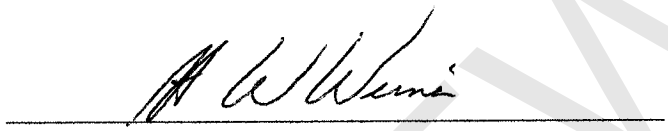

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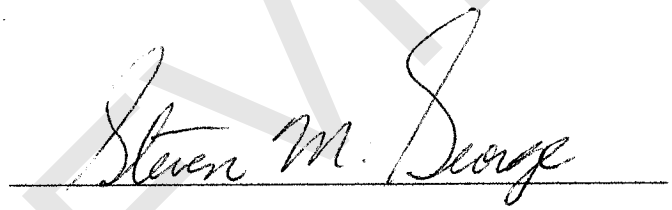

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Abstract

Wank, Jeffrey R. (Ph.D., Chemical Engineering)

Coating Particles with Alumina Nanolayers Utilizing Atomic Layer Deposition in a Fluidized Bed Reactor

Dissertation directed by Alan W. Weimer

There is a current need to provide simple methods to place conformal, pinhole-free, nanoscale-thickness films on fine particles. Such processing can be done using atomic layer deposition (ALD) in a fluidized bed reactor, as will be shown in this thesis. This work is the first application of ALD to coat bulk quantities of fine powders. A fundamental understanding of the fluidization of fine cohesive particles at reduced pressure along with the ALD processing of these particles is the major focus of this thesis. The applications for such nanocoated particles are broad and can be found in many different areas of materials science including microelectronics, defense, biomedical, consumer products, advanced materials, and others.

The minimum fluidization velocity (u_{mf}) of fine cohesive particles at reduced pressure can be calculated using a balance of forces method. Two additional forces are added to a general force balance on a particle with an upward gas flow under vacuum conditions. The final equation is a quadratic in u_{mf}, and can be used to accurately describe u_{mf} for a variety of particle sizes, shapes, and densities. Additionally, as fine particles are coated with an alumina film, the cohesive forces between the particles will change. For the particles of interest in this thesis, the change in the cohesive force is small.

Experiments for alumina deposition on $1.5 \cdot 10^{-4}$ m (150 μm) diameter nickel particles, several different sized boron nitride (BN) particles (from $5 \cdot 10^{-6}$ to $1.5 \cdot 10^{-4}$ m (5 to 150 μm) average diameter), and fine (~$5 \cdot 10^{-6}$m (5 μm)) iron particles were conducted using trimethylaluminum (TMA) and water as dosing reagents at 450 K. Successful deposition of alumina films, with thickness controllable at the angstrom level, was observed based upon TEM imaging, ICP-AES, XPS, particle size distributions, surface area analysis, and WDS imaging. Nickel particles are coated quite easily. For BN platelet particles, a small exposure ($3.25 \cdot 10^{2}$ Pa·s ($2.5 \cdot 10^{6}$ L)) of the reagent gases will coat the edge planes only. A larger dose of $1.3 \cdot 10^{4}$ Pa·s ($1 \cdot 10^{8}$ L) will coat the entire particle. After 10 ALD cycles, the exposure can be lowered back to $1.3 \cdot 10^{2}$ Pa·s ($1 \cdot 10^{6}$ L) as the film is then growing on alumina and not BN. Improved interfacial adhesion between epoxy and the filler material is noted for alumina-coated BN particles. Nanocoated iron particles show improved oxidation resistance relative to uncoated particles, as long as the film is greater than $2.5 \cdot 10^{-9}$ m (25 Å) thick.

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Chapter 1. Introduction

There is a current need to provide simple methods to place conformal, pinhole-free, nanoscale-thickness films on fine particles. Such processing can be done using atomic layer deposition (ALD) in a fluidized bed reactor, as will be shown in this thesis. This work is the first application of ALD to coat bulk quantities of fine powders. A fundamental understanding of the fluidization of fine cohesive particles at reduced pressure along with the ALD processing of these particles is the major focus of this thesis. The applications for such nanocoated particles are broad and can be found in many different areas of materials science including microelectronics, defense, biomedical, consumer products, advanced materials, and others.

Fluidized Bed Reactors

The use of fluidized beds to coat particles began in the 1960's to coat nuclear fuels [1]. In a fluidized bed, intimate contacting between a gas and all particles in the bed is obtained due to constant mixing of the particles by the gas. This leads to excellent heat and mass transfer characteristics within the bed of particles. Additionally, fluidized beds are typically scaleable with some simple and effective scaling equations [2].

There are many different sizes and shapes of powder particles. The fluidization characteristics of different types of powders have been defined, in loose terms, according to their size and density with the definition of Geldart A, B, C or D types [3]. Group C powders are difficult to fluidize due to their cohesive nature.

Fine powders, those considered Geldart C powders, self-aggregate into larger particles when exposed to gas flows in a fluidized bed apparatus, even under vacuum conditions [4-6]. These light aggregates are formed by Van Der Waals forces [7], and the size of the aggregates may depend on several factors such as individual particle type, size, shape, and density, gas flowrate, and vibration applied to the bed.

In the late 1970's, some work was done in the field by researchers studying fluidization at pressures that were sub-atmospheric. The first such papers described a classical model used to calculate the minimum fluidization velocity for pressures less than ~4000 Pa (30 Torr) but greater than ~500 Pa (4 Torr) [8]. In this paper, the authors were using large glass beads as their powder. Geldart and colleagues then described fluidization of Group A powders under a vacuum [9], albeit only down to $2 \cdot 10^4$ Pa (150 Torr).

Low pressure fluidization does not follow normal flow patterns. This is due to the fact that as the pressure is reduced, the fluidizing gas is no longer in a laminar flow regime. Rather, the gas is in a condition known as "slip flow" where the viscous forces acting upwards on the particles are reduced due to an increase in the gas molecular mean free path [10]. Because of this, the usual equations to calculate the minimum fluidization velocity, u_{mf}, may no longer be valid [2].

Experimental results show that the process of fluidizing fine particles usually involves plugging, channeling, disrupting, and agglomerating [4, 5]. When fluidized, the entities fluidized generally consist of particle aggregates varying in size from the largest at the bottom of the bed (some even defluidized) to the smallest at the top (some even unassociated to discrete particles). Easiest to fluidize are the aggregates