Powder Technology 221 (2012) 26–35

Contents lists available at SciVerse ScienceDirect

Powder Technology

journal homepage: www.elsevier.com/locate/powtec

# Atomic layer deposition of solid lubricating coatings on particles

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ARTICLE INFO

Available online 31 January 2012

*Keywords:*
Nanocomposites
Powder flow
Rheology
Atomic layer deposition (ALD)

ABSTRACT

Atomic layer deposition (ALD) has been used to deposit ceramic films on the surfaces of particles to improve the slurry and dry powder rheology of bulk powders. An overview of several studies is presented here, which demonstrates the extent and limitations for this ceramic coating platform technology to improve the tribological and/or flow properties of microfine and ultrafine particles. Direct evidence of the effect of the nanoscale ceramic coatings is shown via a significant improvement in flow properties of dry particles, including dynamic, bulk and shear properties obtained using a FT4 Powder Rheometer, and a marked reduction in slurry viscosity at high solids loadings. Microfine zinc powders, similar to those used in alkaline batteries, have been coated using boron nitride ALD films of sub-nanometer thickness, or about 0.1 wt.%. The low surface energy coatings reduced the cohesion of 1–5 μm particles by 52%. A highly-loaded slurry of the same material in concentrated KOH showed a 10–30% reduction in slurry viscosity over a range of shear rates, with a shear-thinning effect at high shear rates. Boron nitride platelets were coated using $Al_2O_3$ and $SiO_2$ films to change the surface properties from hydrophobic to hydrophilic. The coated and uncoated powders were dispersed into an epoxy to evaluate the solids loading to viscosity ratio. The ALD films improved the particle–resin adhesion and decreased the viscosity of equivalently-loaded slurry of uncoated powder. Coated microfine nickel, aluminum and iron powders were also dispersed into epoxies, and lower viscosities and yield stresses were observed due to ceramic–epoxy interactions being more favorable than metallic–epoxy interactions. The ALD platform can be used to modify surfaces of primary particles in order to change the interparticle and particle–liquid forces, which provides a lubricating effect without detracting from the bulk properties of the core particles themselves.

## 1. Introduction

Surface coatings that provide enhanced lubricity to particles in the dry or slurry state would be desirable in a wide variety of industries [1,2]. Improving the “flowability” of powders can lead to reduced wear on the internal surfaces of industrial equipment, conveying lines and similar, which can reduce product contamination, repair/maintenance downtime and energy consumed during the manufacture of products that incorporate powders [3]. Each of these negatively impacts the operating costs of industrial manufacturing processes. Oftentimes flow additives, including liquid-phase surfactants and emulsifiers or solid-phase inert particles, will be incorporated into slurries or pastes to improve the flowability of the material, though these can be costly and only serve to decrease the content of the useful material that needs to be conveyed [4]. The ALD film thicknesses required to achieve a demonstrable lubricating effect are relatively thin, and as such end up being a very small, oftentimes negligible, weight percentage of the final slurry. The cost of applying the ALD lubricating film can be cheaper than the cost of the flow additives that yield similar performance, even for commodity powders found in cements, paints and other products where consistent dispersion within an end-use product is paramount to product and brand integrity.

Ensuring that these flow additives are well dispersed within a system can be a more tenuous process than ensuring the primary phase continues to flow from point A to point B. The chaotic process of slurry destabilization, which can lead to irreversible segregation, can be a costly problem to diagnose in terms of why, how, where and when, and each may vary even with minute batch-to-batch variations within equipment, processing conditions and the slurries

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doi:10.1016/j.powtec.2011.12.021

themselves. The deposition of chemically-stable solid films onto the surfaces of the primary particles that go into a slurry, guarantees that 100% of the coating material lies at the interface between the solid phase and the dispersion medium, and also holds true for powders in the dry state where interparticle interactions (e.g. cohesive forces) dominate material flowability.

ALD is a vapor-phase deposition technique that is an analog of chemical vapor deposition (CVD) [5]. A binary CVD process comprises the administration of two precursors that react with one another, but not with themselves. In the case of $Al_2O_3$ CVD, one precursor provides the aluminum (e.g. trimethylaluminum or TMA), and the other provides the oxygen (e.g. $H_2O$). CVD processes deposit the desired material onto substrates of varying geometries, including particles, but also form gas-phase nanoparticles via gas-phase side reactions that do not occur on the particle surface. These nanoparticles subsequently become incorporated into the film, either individually or after ripening into larger gas-phase particles, effectively creating highly-porous films with little opportunity for film thickness control, especially on the three-dimensional surfaces of particles. The binary CVD reactions for two insulating materials, $Al_2O_3$ and $SiO_2$, are shown in Eqs. (1) and (2), respectively:

$$2Al(CH_3)_3 + 3H_2O \rightarrow 2Al_2O_3 + 6CH_4 \tag{1}$$

$$SiCl_4 + 2H_2O \rightarrow SiO_2 + 4HCl \tag{2}$$

With ALD, the reactive precursors are separated by crucial inert gas purge steps that exist exclusively to prevent the gas-phase side-reactions and nanoparticulate generation. The ALD process utilizes self-limiting surface reactions that hinge on ligand-exchange chemistry at activated surface sites containing functional groups [5,6]. For instance, Eq. (1) can be split into the following two half-reactions that occur only on a surface, [S]:

$$[S]:(OH)_2* + 2Al(CH_3)_3 \rightarrow [S]:\left(O_2Al(CH_3)_2\right)_2* + 2CH_4 \tag{3}$$

$$[S]:\left(O_2Al(CH_3)_2\right)_2* + 3H_2O \rightarrow [S]:(Al_2O_3)_2:(OH)_2* + 4CH_4 \tag{4}$$

Similarly, Eq. (2) can be split into the following two half-reactions:

$$[S]:(OH)_2* + SiCl_4 \rightarrow [S]:(O_2SiCl_2)* + 2HCl \tag{5}$$

$$[S]:(O_2SiCl_2)* + 2H_2O \rightarrow [S]:(SiO_2):(OH)_2* + 2HCl \tag{6}$$

In order to balance the nomenclature in each of these cases, the formed metal oxide layer becomes incorporated into the substrate, [S], upon completion of the cycle. The successive cycling of Eqs. (3) and (4) deposits $Al_2O_3$ ALD films at a rate of ~0.1 nm/cycle. $SiO_2$ ALD films grow at ~0.05 nm/cycle by the successive repetition of Eqs. (5) and (6). The exact growth rates are heavily dependent on the type of precursors being used as well as the deposition temperature. The similarities and differences between mechanisms of the CVD and ALD techniques for coating particles are depicted in the schematic in Fig. 1. It is important to note the difference in size scales. CVD is generally only appropriate for micron-sized and larger particles, as gas-phase side reactions may agglomerate smaller particles together. ALD processes, which rely on growth at a surface, can be operated such that nanoparticles are not agglomerated together to a significant extent since linear film growth occurs at the atomic scale.

The $Al_2O_3$ and $SiO_2$ coatings are examples of some of the simpler chemistries and materials that can be deposited. In addition to metal oxide ceramics, metal nitrides, metallic, polymeric and hybrid ceramic/polymeric films have all be deposited using sequential vapor-

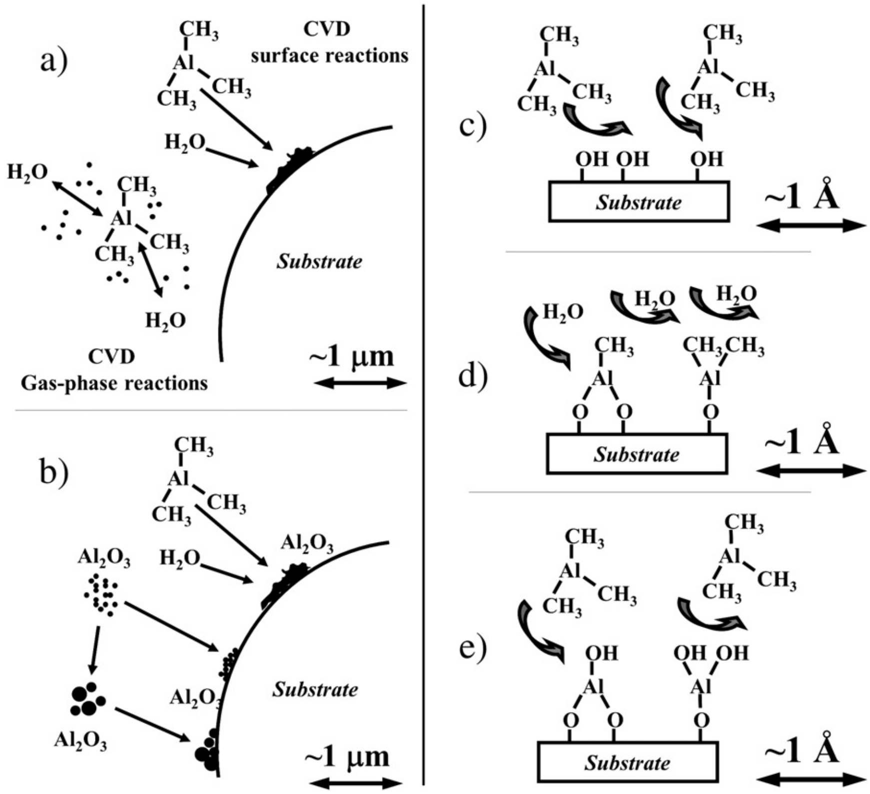

**Fig. 1.** Schematic of the CVD (a–b) and ALD (c–e) reaction pathways for $Al_2O_3$ deposition using TMA and $H_2O$. CVD processes allow gas-phase side reactions that deposit particulate products on the substrate, whereas the dose/purge/dose/purge precursor administration strategy in the ALD process does not. (a–b) Modified from [9].