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Rheological and surface chemical characterization of alkoxysilane treated, fine aluminum powders showing enhanced flowability and fluidization behavior for delivery applications

Bellamarie Ludwig *, Timothy F. Miller [1]

The Pennsylvania State University, Applied Research Laboratory, North Atherton Street, State College, PA 16801, United States

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ABSTRACT

The effect of surface treatment on the properties of fine aluminum powders was investigated using both chemical and rheological characterization techniques. Four different particle size distributions (PSD) were surface treated with methyltriethoxysilane and subsequently evaluated through classic density measurements and by using an FT4 powder rheometer (Freeman Technologies, UK). The chemical surface properties were analyzed using diffuse reflectance infrared spectroscopy (DRIFTs) and X-ray photoelectron spectroscopy (XPS) which confirmed retention of the silane and production of a siloxane-like layer on all PSD samples. The results of the bulk measurements, both direct and empirical, showed enhanced flowability and easier fluidization, indicating reduction of intrinsic cohesion for all samples. Fluidization testing showed decrease in total energy of the uniformly fluidized bed by ~80–90% in all cases. Shear stress values as a function of applied normal stress were collected to produce Mohr diagrams which generated extrapolated cohesion and unconfined yield strength values using the Mohr–Coulomb criteria. Cohesion and unconfined yield strength were reduced in all surface treated powders which indicated easier flowability and an increase in the flow function at 6 kPa. The compressibility of the treated powders at 8 kPa was decreased by >60% in all cases, indicating significant reduction in entrained air and improvement in packing density. Classical density measurements showed small improvements in the Hausner Ratio and little to no improvement in the Carr index, whereas directly measured properties using powder rheology showed substantial changes in the flow and fluidization properties. Overall, fluidization behavior and flowability properties were enhanced in all PSDs and showed the increased potential for the use of fine aluminum powders after surface treatment in delivery applications.

1. Introduction

The need for efficient delivery of powders spans multiple industries, but especially affects powdered fuel applications. Many fine powders tend to be cohesive, which makes their subsequent transfer in feeder and flow applications difficult and unreliable. Common methods used to mitigate this problem are the deposition of surface treatments [1] or addition of flow additives [2]. Surface treatments can be deposited using a wide variety of methods that enable coating thicknesses from 1 nm thickness using atomic layer deposition to >1 mm using uncontrolled, solution phase techniques [3]. Surface treatments generally leave the particle material intact but provide a slippery coating to enhance flowability.

Enhancing the flowability of powdered metals without consuming the core metallic content is crucial for use in fuel type applications such as missile and rocket propulsion. Spherical aluminum powder, ranging from nanometer to millimeter in average particle size, is commonly used as a propellant and has been advocated as a fuel for water [4–7] and carbon dioxide [8] breathing propulsion applications. In these applications, its timely and controllable delivery is critical to the energy expending processes. Direct feed of these powders into rocket combustion chambers has been demonstrated [3,6,9,10]. Inter-particulate cohesion reduces flowability and impairs the operation of these feed systems. The main objective of this work is to characterize the chemical and bulk properties of alkoxysilane treated aluminum powders to aid in identification of powders capable of reliable and steady flow.

The major inter-particulate forces contributing to the cohesive properties of powders can be classified as surface charge interactions (electrostatic), dipole–dipole (van der Waals) and chemical (hydrogen bonding) in nature [11]. These forces dominate the effect of gravity or inertia in smaller particles as a result of increased surface area and contacts between particles. Surface composition and intrinsic hygroscopity can also increase susceptibility to electrostatic interactions, van der Waals forces and specifically hydrogen bonding. Aluminum powder is subject to multiple types of inter-particulate interactions. The

* Corresponding author. Tel.: +1 814 865 8047.
E-mail addresses: bxb234@psu.edu (B. Ludwig), nfn@psu.edu (T.F. Miller).
[1] Tel.: +1 814 865 1092.

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Table 1
Aluminum powder designations and particle size distributions as given by Valimet and measured in-house (shown in parentheses).

Label	D_{10} (μm)	D_{50} (μm)	D_{90} (μm)
H-5	4.0	8.0	15.0
H-10	6.0, (5.3)	12.0, (11.7)	22.0, (21.5)
H-12	7.5, (7.5)	15.0, (15.3)	28.0, (25.9)
H-15	9.0, (9.8)	20.0, (19.6)	40.0, (37.2)

surface of metallic aluminum is not thermodynamically stable in air; exposure to oxygen forms an amorphous native oxide surface layer [12]. Further sorption of molecular water forms surface hydroxyls, which cause hydrogen bonding between particles and mechanical capillary bridges also form from physisorbed molecular water. Moisture exposure is a difficult parameter to control, as most facilities do not have the ability to hermetically isolate hundreds of pounds of aluminum powder. These forces directly contribute to the flowability and fluidization properties of powders, necessitating the multi-faceted characterization presented here.

The classification of powder flowability has been described historically through density, resulting in calculation of the Hausner ratio [13] and Carr index [14]. The Hausner ratio describes material packing capacity through the ratio of tapped to apparent density. The ability of a powder to pack well can suggest better flow properties. The Carr index uses the apparent and tapped densities to describe flowability as related to the powder's compressibility which is greatly affected by properties such as inter-particulate forces and the resulting spatial arrangement of the particles. These properties also affect a powder's ability to flow and, as a consequence, this index is commonly used as a flowability indicator. A problem with these classification methods is that they are not properties intrinsic to the powder; the results depend greatly on the methodology and technique used to obtain the density values.

In an attempt to incorporate the role of particle size and density on the ability to gas fluidize a powder, Geldart produced his seminal classification chart based on experimental data collected using cracking catalysts and plastic molding powder [15]. This classification relates average particle size to the density difference between the powder and fluidizing gas to predict flow properties and contains four different categories: cohesive (C), aeratable (A), sand-like (B), and spoutable (D). In general, granular materials (D_{50} > 100 μm) with low density are considered to be aeratable (Group A). The materials considered here are fine powders (D_{50} ≥ 20 μm) and fall in the cohesive category (Group C), based on size and the density difference using argon as the fluidizing gas. Geldart's classification procedure was drawn from the idea that smaller particles contain increased surface area, which increases the amount of inter-particulate forces [16]. When the inter-particulate forces favor the formation of aggregates and are stronger than the forces exerted by the fluidizing gas, this decreases the fluidizability due to the change in hydrodynamic forces required to fluidize the powder mass. This also causes the fluidizing gas to escape via channels, rather than being uniformly dispersed in the powder void space. In this paper, we demonstrate that surface treated aluminum powders can become aeratable in gas-fluidizing environments, even at small particle size (D_{50} ~ 8 μm) after surface treatment. This concept has been demonstrated previously using printer toner powders with flow additives and various other surface treatments [17].

Due to the empirical nature of the Hausner ratio and Carr index, compression and flow tests were developed to directly measure

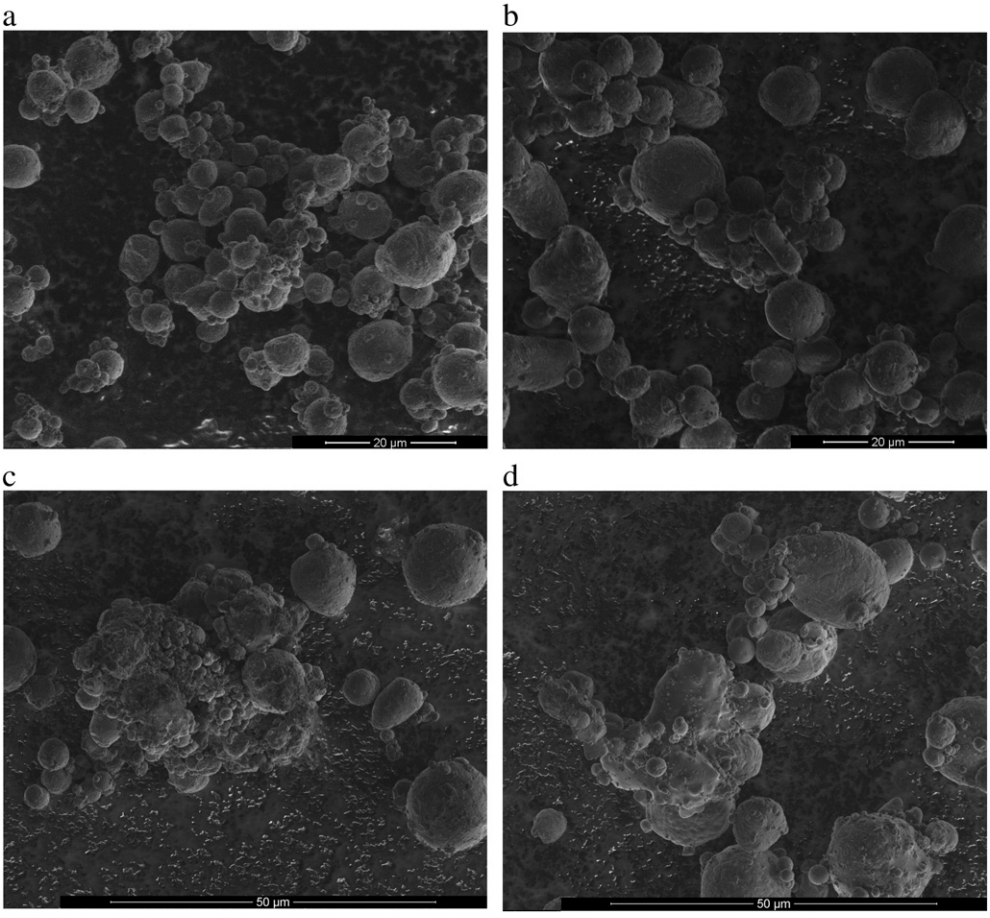

Fig. 1. Scanning electron micrographs of aggregate particles found in raw powders: H-5 (a), H-10 (b), H-12 (c), and H-15 (d).