Hierarchically Ordered Particle Mixtures by Thermally-Triggered Granulation†

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Abstract

A method was developed to granulate ceramic particles using metallo-organic soap as a binder. A high shear mechanical mixer (i.e., mechanofusion) was used to coat the soap over the ceramic particle surfaces. Agglomeration of the coated particles was triggered by increasing the mixing temperature to the softening point of the soap and transforming the soap from a crystalline to an amorphous phase. The crystalline soap acted as a solid lubricant and the amorphous phase was a cohesive binder. Granule growth was correlated to the thermomechanical properties of the soap, which depended on temperature, applied pressure and compaction history. The resultant spherical granules were densely packed assemblages of coated particles (i.e., multicore microcapsules). Sequential cladding of layers onto pre-formed core granules resulted in microstructures with hierarchical compositional ordering.

1. Introduction

Mechanofusion is a high energy powder mixing process used to mechanically bond coatings to core particles. Typically, at least one of the components in the powder mixture must be subject to plastic deformation, and mechanical bonding occurs either by embedding a hard coating particle into a softer core or by shearing a soft coating material over the surface of a harder core. Mechanofusion has been used to form single core coated particles (i.e., single-core microcapsules) using substantially spherical core particles.1−3 The authors previously expanded on this approach to include granulation by coalescence of coated particles (i.e., multicore microcapsules).4 The current work further expands this to include compositional ordering on a granular scale by layering additional components onto a granular structure. Single-core, multicore and hierarchical structures are illustrated as a function of their forming mechanisms (Fig. 1).5, 6

In the current work, mechanofusion is used to mix relatively soft powders (i.e., metallo-organic soaps) with harder core particles (i.e., ceramic oxides). During initial mixing, the soap coats the ceramic particle surfaces and acts as a dry lubricant. This improves the flowability of the fine powders and reduces adhesion of fine powders to the mixer. As the mixing temperature increases to a critical softening point, the soap becomes cohesive and is transformed into a binder. The transition of the soap from a lubricant to a binder is critical to the granulation process.

A noteworthy feature of the current process is dry-state mixing of solid phase precursor materials (i.e., no solvent removal is required). In addition, the process may be used with irregularly shaped precursor particles with little restriction on particle size distribution or the particle size ratio of core and coating components. The process results in dense spherical granules with high tap density and narrow size distribution. The sequential addition of precursors results in agglomerate structures that are compositionally ordered on both particle and granular scales.

2. Experimental

The process was run in a laboratory-scale batch mixer (Mechanofusion Model AM-15F, Micron Powder Systems, Summit, NJ, USA). The powder was loaded batch-wise into the mixing chamber (Fig. 2). Approximately 100−200 g of powder was processed per batch. During processing, the internal fixed piece and scraper assemblies remain stationary while the chamber rotates. For the experiments described in this work, the spacing of the fixed piece...
relative to the chamber wall was held constant at ~1.2 mm, and the scraper edge was adjusted as close to the chamber wall as possible without making physical contact. A convective heater was used to heat the air surrounding the mixing chamber; the heated air temperature was monitored by an external thermocouple. The temperature inside the mixing chamber was monitored by an internal thermocouple, which was located inside the fixed piece. The end of the internal thermocouple and the outside surface of the fixed piece was separated by ~2 mm of stainless steel. A calibration experiment showed only a slight lag in the temperature of the internal thermocouple (<5°C) for heating rates used in the process.

The compositions used in this work were based on the molar ratios required to form compounds in the system lead-zinc-magnesium-niobate, Pb$_3$(Mg$_{1-x}$Zn$_x$Nb$_2$)O$_9$, where 0 ≤ x ≤ 0.5. Precursors included lead oxide (PbO, Fisher Scientific, Fairlawn, NJ, USA), magnesium oxide (MgO, Fisher Scientific), zinc oxide (ZnO, Fisher Scientific), niobium pentoxide (Nb$_2$O$_5$, Alfa Products, Johnson Matthey, Danvers, MA, USA), magnesium stearate (Mg(C$_{17}$H$_{35}$COO)$_2$, Witco Corp., New York, NY, USA) and zinc stearate (Zn(C$_{17}$H$_{35}$COO)$_2$, Witco Corp.). The mean particle sizes of the ceramic particles were finer than 10 μm; the stearate particles were finer than 100 μm. The melting points of stearate soaps, Mg(C$_{17}$H$_{35}$COO)$_2$ and Zn(C$_{17}$H$_{35}$COO)$_2$, were ~145°C and ~125°C, respectively.

Processing of powder mixtures in the mixer was done according to 1-step and 2-step procedures. Process variables included external heating, rotation speed of the mixer and processing time. In the 1-step method the full powder mixture was processed in a single batch operation, resulting in the coalescence of fine coated particles to form granules (Fig 1b). The 2-step method used the results of the first step as seed granules, to which a second mixture of fine...
powders was added and processed to form an agglomerate layer onto the seed granules (Fig 1c).

Process conditions were documented using a 2-step mixing process (Fig. 3) with a net composition of Pb₂(Mg₀.₉Zn₀.₁Nb₂)O₉. The first step in the process used a mixture of 3 PbO + 0.375Nb₂O₅ + 0.375 Mg(C₁₇H₃₅COO)₂ with no granule seeds; the volume fractions of components were 26% PbO, 7% Nb₂O₅, and 67% Mg(C₁₇H₃₅COO)₂. The external heater was required to heat the mixture to ~85°C; above this point, frictional forces were sufficient to continue up the temperature ramp (Fig. 3, flags c-e). Granulation of the mixture occurred at ~120 to 130°C (Fig. 3, coalescence), which is ~20°C below the melting point of the Mg(C₁₇H₃₅COO)₂ binder. These granules were the seeds for the second process step, to which a mixture of 0.625 Nb₂O₅ + 0.525 MgO + 0.1 Zn(C₁₇H₃₅COO)₂ was added. The volume fractions of the added powders were 35% Nb₂O₅, 7% MgO, and 58% Zn(C₁₇H₃₅COO)₂. The cladding of the added powders onto the seed granules occurred at a substantially lower temperature (Fig. 3, layering), ~35°C below the melting point of the Zn(C₁₇H₃₅COO)₂ binder.

To avoid runaway situations, it was important to turn off the external heater well enough in advance of granulation (Fig. 3, flag c) to allow for a reversal in the thermal gradient across the mixing chamber wall. In addition, it was important to gradually reduce the rotation speed near the onset of granulation (Fig. 3, flag d) to prevent the generation of excess frictional heat during granulation.

The sequence of granulation was investigated by extracting samples intermittently during the process, prior to and after the onset of granulation. To measure to progression of agglomerate size growth, the extracted powder samples were dispensed in isopropanol and sized using laser light diffraction (Microtrac FRA, Leeds and Northrup, Willow Grove, PA, USA). Particle and granule morphology was observed using light microscopy. Structural transformation of the soap binder was examined by X-ray diffraction (XRD, Siemens AG, Karlsruhe, FRG), using Cu Kα radiation at 40 keV 30 mA. Powder tap density of the samples was also measured.

The sequence of particle coating was investigated by extracting samples prior to the granulation onset. The extent of particle surface coating was measured using X-ray photoelectron spectroscopy (XPS, Model XSAM-800, Kratos, Ramsay, NJ, USA) with Mg Kα radiation at 15 keV and 15 mA. XPS is sensitive only to elements found on the near-surface layer (i.e., <10 nm) of the sample. As such, it can be used to measure the obscuration of a core particle element (e.g., Pb) by the soap coating, which produces a measurable signal for carbon. The atomic concentration of lead (Cₚb) with respect to

![Fig. 3 Process schedule: a) load powder for first step, mix at 800 rpm, heater on low; b) 1200 rpm, heater on medium; c) heater off; d) gradually reduce rotation speed; e) 500 rpm; f) stop, end of first step; g) add powder for second step, mix at 800 rpm; h) 900 rpm; i) gradually reduce rotation speed; j) 500 rpm; k) stop, end of second step.](https://www.kona.or.jp/kona-bjournal/KONA No.12 (1994) 113)
Carbon and oxygen was calculated according to eq. 1, where $I_i$ is integrated signal intensity and $S_i$ is a known scaling factor for each element. The peaks used for evaluation were Pb 4f, C 1s and O 1s.

$$C_{PB} = \frac{I_{PB}}{I_{PB} + I_O(S_{PB}/S_O) + I_C(S_{PB}/S_C)}$$

A coating efficiency parameter ($E_{coat}$) was developed in order to normalize for ubiquitous surface carbon and the number fraction of lead atoms in the bulk mixture (eq. 2).

$$E_{coat} = 1 - \frac{N_{PB,0}}{N_{PB}} \cdot \frac{C_{PB,0}}{C_{PB}}$$

Coating efficiency was calculated by comparing the lead concentration at the surface of the as-received PbO powder $C_{PB,0}$ to the lead concentration detected at the surface of the coated particles ($C_{PB}$). This was done in order to account for carbon that is routinely present on the surface of commercial powders (i.e., surface carbon due to washing and/or adsorbed $CO_2$). The coating efficiency was also normalized to the calculated number fraction of lead atoms in the bulk mixture ($N_{PB}$) relative to the number fraction in the pure PbO powder $N_{PB,0}$. Normalization to the bulk number fraction of lead atoms in each mixture was done to account for the change in the bulk ratio of carbon, oxygen and lead atoms for each level of soap addition. A coating efficiency of 100% indicates a uniform coating thick enough to completely attenuate the Pb 4f photoelectrons (i.e., coating thickness >10 nm).

The thermo-mechanical properties of the stearate soap binders were evaluated using thermo-mechanical analysis (TMA-7, Perkin-Elmer, Plainfield, NJ, USA). Samples for TMA experiments were made by pressing the soap powders into pellets (diameter = 9.5 mm; thickness = 2.5 mm). Pre-compaction of the Mg(C$_{17}$H$_{35}$COO)$_2$ soap powder was investigated by making a series of pellet samples pressed to 6, 23, 90 and 340 MPa. The sample pellets were individually loaded into the TMA and a penetration probe was centered on the flat pellet surface. Samples were heated at a constant rate of 6°C/min using a probe tip force of 100 mN (0.13 MPa). The penetration rate was calculated as the time derivative of tip position. A penetration rate of -0.2 μm/s was selected as the criterion for the onset of softening (i.e., initial softening point). A penetration rate of -2.0 μm/s was the criterion for the point of rapid deformation (i.e., viscous flow).

The compositional distribution of components within the granule structure was examined by scanning electron microscopy with energy dispersive x-ray spectroscopy (SEM/EDS, Model 1400, AMRAY, Inc., Bedford, MA, USA). Cross sections were prepared by mounting the granules in a low-viscosity epoxy and polishing on a wet cloth with an alumina polishing compound. The polished samples were carbon coated and examined using an accelerating voltage of 20 keV. EDS mapping was done using Pb $M\alpha$, Na $L\alpha$, and Mg $Ka$ transition energies.

3. Results and Discussion

Particle coating occurred during the initial stages of mixing, well in advance of agglomerate growth. Fine ceramic oxide particles were coated by stearate soap as a result of high shear mixing without a substantial increase in mixing temperature. This is shown by the increase in coating efficiency with time (Table 1). Thus, the surfaces of the ceramic oxide particles were already modified by a stearate soap coating prior to the onset of granulation. Tap density also increased steadily during the initial stages of mixing (Fig. 4) indicating that powder flow and packing was improved by the stearate soap coating.

The coalescence of fine powders to form granules occurred abruptly upon reaching an agglomeration onset temperature (Fig. 4). Particle size analysis showed very little change in the particle size distribution of powders mixed below the agglomeration onset temperature. The non-granulated powders exhibited similar size distributions to the volume sum of the precursor particles (i.e., <100 μm). The sample processed above the agglomeration onset temperature had a narrow size distribution with a mean size of ~200 μm and only a small remnant of the initial fine powder distribution. Granules formed by this process were very uniform in size and spherical in shape (Fig. 5). Typically, sieving resulted

| Table 1. Coating efficiency ($E_{coat}$) as a function of the amount of zinc stearate coating phase and processing conditions for a PbO + Zn(C$_{17}$H$_{35}$COO)$_2$ mixture. Samples were extracted before the onset of granulation |
|---|---|---|
| amount of coating phase (vol%) | 350 rpm, 5 min. | 1200 rpm, 20 min. |
| 28.6% | 50.1% | 95.3% |
| 44.4% | 65.3% | 96.5% |
in >80 product wt% in the cut between 125 and 250 μm.

The granulation onset was accompanied by a transition in the phase structure of the stearate soap binder. XRD results show peaks for crystalline magnesium stearate at points prior to granulation while the pattern for the granulated sample is amorphous (Fig. 6). Thus, the combination of heat and high shear mixing energy acted to transform the stearate soap binder from a crystalline to an amorphous state. It should be noted that there was no evidence of bulk melting during this transition. It is hypothesized that substantial softening of the binder was localized to the high shear region of the mixer between the chamber wall and the fixed piece (Fig. 2), where high frictional interactions were sufficient to transform the crystalline soap to a more cohesive amorphous phase.

The softening properties of the stearate soap correlated empirically to granulation behavior. Coalescence was empirically correlated to the rapid deformation temperature of the stearate binder (i.e., penetration rate = −2.0 μm/s). In contrast, layering of additional fines onto pre-formed seed granules occurred at a substantially lower temperature, correlating to the initial softening point of the second step binder (i.e., penetration rate = −0.2 μm/s).

Process stability appeared to be related to the thermo-mechanical properties of the binder. In terms of process stability, coalescence was much more sensitive to small process variations (i.e., temperature, time, speed) than layering. If process conditions were...
Not carefully controlled during coalescence, the binder became too soft, causing over agglomeration and/or make-up in the mixer. During granule formation and growth, the binder was substantially compressed by the high shear and compressive forces in the mixer. Increased compression resulted in a reduction in the temperature of rapid deformation (Fig. 7), further softening the binder phase and promoting more agglomeration. On the other hand, increased compression had the opposite effect on the initial softening point; therefore, the layering mechanism was not as susceptible to overgrowth.

The internal microstructure of the granules consisted of densely packed ceramic particles in a matrix of the metallo-organic soap (Fig. 8). The particles were well dispersed in the matrix and there was no evidence of internal porosity. The microstructure represents an ordered mixture of core particles coated by a matrix component. For the 2-step pro-

![Fig. 7 Thermo-mechanical properties of magnesium stearate as a function of sample compaction pressure. Initial softening point (penetration rate = 0.2 μm/s) correlated to layering; rapid deformation (penetration rate = 2.0 μm/s) correlated to coalescence](image)

![Fig. 8 Cross sectional SEM micrograph (450x) of granule produced in 2-step process. Box shows area of detail for Fig. 9](image)

![Fig. 9 Element map of detail area shown in Fig. 8: a) Pb, b) Mg, c) Nb. Darker areas correspond to higher elemental concentrations](image)

cess, an additional level of compositional ordering was evident on a granular scale. The central granular core was comprised of components processed in the first step (i.e., predominantly PbO, (Fig. 9a)). A sharply defined layer, rich in components added in the second step (niobium and magnesium), appeared at the outer surface of the granular core.
Beyond this layer, however, there was a distribution of elements from both seed and cladding compositions. Thus, it appeared that significant attrition of seed granules occurred in the second processing step, and the attrited material was incorporated into the outer cladding layer.

4. Conclusion

A dry-mixing technique was developed to form granules with a multicore microcapsule morphology. Additional agglomerate cladding layers could be added to granular cores to form hierarchical structures with compositional ordering on both particle and granular scales. The technique used a thermally activated binder that formed a matrix around primary particles. For the initial coalescence of fine particles, the agglomeration onset temperature corresponded to the rapid deformation (i.e., viscous flow) of the binder phase. For subsequent layering, the agglomeration onset occurred at a lower temperature, corresponding to the initial softening point of the binder.

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