Aggregate Morphology Evolution by Sintering: Number and Diameter of Primary Particles

D. Kadau\textsuperscript{1}, M.L. Eggersdorfer\textsuperscript{2}, H.J. Herrmann\textsuperscript{3} and S.E. Pratsinis\textsuperscript{2}

\textsuperscript{1}CH-8046 Zürich, Switzerland (private contribution), employed at Wärtsilä Switzerland Ltd, PO Box 414, Zürcherstrasse 12, CH-8401 Winterthur, Switzerland.
\textsuperscript{2}Particle Technology Laboratory, Institute of Process Engineering, Department of Mechanical and Process Engineering, ETH Zurich, Sonneggstrasse 3, CH-8092 Zürich, Switzerland.
\textsuperscript{3}Computational Physics of Engineering Materials, Institute of Building Materials, Department of Civil, Environmental and Geomatic Engineering, ETH Zurich, Schafmattstrasse 6, CH-8093 Zürich, Switzerland.

The structure of fractal-like agglomerates (physically-bonded) and aggregates (chemically- or sinter-bonded) is important in aerosol synthesis of nanoparticles, and in monitoring combustion emissions and atmospheric particles. Agglomerate and aggregate morphology and primary particle size strongly affect aerosol behavior and properties. The aerosol mobility in the free molecular and transition regime depends on structure, number and diameter of constituent primary particles. Besides particle transport, also energy (heat) transfer is determined by primary particle size and agglomerate/aggregate morphology.\textsuperscript{1} The light scattering and absorption of open-structured aerosol agglomerates (D\textsubscript{f} < 2) is a function of structure and primary particle size.\textsuperscript{2} Furthermore the mechanical stability of nanoparticle layers, electron transport and sensitivity of gas sensors and electrical conductivity are significantly influenced by constituent primary particle and aggregate size and degree of sintering.

Recently a new modeling technique for multiparticle sintering dynamics has been developed.\textsuperscript{3} Here the evolution of particle coalescence by viscous flow sintering (e.g. SiO\textsubscript{2}, polymers) and grain boundary diffusion (e.g. TiO\textsubscript{2}, metals) of agglomerates consisting of 16 – 512 primary particles is monitored in detail: from fractal-like agglomerates to aggregates to eventually
compact spheres. The focus is on projected aggregate surface area, mobility diameter, radius of gyration and aggregate morphology ($D_f$, $D_{fm}$) in the free molecular and transition regime where nanoparticle sintering typically takes place at high process temperatures. A scaling between number of primary particles and projected area is combined with the relation between projected area and mobility diameter to calculate the average number and diameter of primary particles in aggregates (Fig. 1). That way the evolution of $D_f$ (radius of gyration-based) and $D_{fm}$ (mobility diameter-based, Fig. 2) and prefactors are investigated during sintering as they are used to characterize fractal-like particles by light scattering and mass-mobility measurements. This method is applied to sintering of silver aggregates to estimate their degree of sintering as they have been characterized by mass-mobility measurements.

**Figure 1:** Evolution of average diameter of primary particles in aggregates, $d_{va}$, as a function of mobility diameter, $d_m$, for the sintering of initial agglomerates of 16 – 512 primary
particles compared to experimental results by Kim et al. For agglomerates of monodisperse spherical primary particles, \( d_{va} = d_p \) independent of mobility size (agglomerate or collision line). \( d_m \) decreases during sintering while \( d_{va} \) increases until \( D_f = 3 \) (coalescence line).

**Figure 2:** At the beginning of sintering the initial agglomerates of 16 – 512 primary particles have a mass-mobility exponent \( D_{fm} = 2.15 \) and prefactor \( k_{fm} = 1.11 \). During the evolution of sintering their mass \( m \) is conserved but their mobility diameter \( d_m \) decreases resulting in a change in scaling until a fully sintered or coalesced sphere with \( D_{fm} = 3 \) and \( k_{fm} = 1 \) is reached.

Aggregate Morphology Evolution by Sintering: Number and Diameter of Primary Particles

D. Kadau¹, M.L. Eggersdorfer², H.J. Herrmann³ and S.E. Pratsinis²
¹CH-8046 Zürich, Switzerland (private contribution), employed at Wärtsilä Switzerland Ltd, CH-8401 Winterthur, Switzerland
²Particle Technology Laboratory, ETH Zürich, CH-8092 Zürich, Switzerland
³Computational Physics of Engineering Materials, ETH Zürich, CH-8093 Zürich, Switzerland

Motivation/Objective

The structure of fractal-like agglomerates (physically-bonded) and aggregates (chemically- or sinter-bonded) is important in aerosol synthesis of nanoparticles, and in monitoring combustion emissions and atmospheric particles. Agglomerate and aggregate morphology and primary particle size strongly affect aerosol behavior and properties. Here the evolution of particle coalescence by viscous flow sintering (e.g. SiO₂, polymers) and grain boundary diffusion (e.g. TiO₂, metals) of several agglomerates consisting of 16 – 512 primary particles made by diffusion limited cluster-cluster agglomeration (DLCA) is monitored in detail.

Conclusions

Average Primary Particle Diameter \( d_{va} \)

\[
d_{va} = 6\nu/a = \left( \pi k_m d_{va}^3 / 6\nu \right)^{1/(3\alpha - 3)}
\]

Evolution of \( d_{va} \) as a function of mobility diameter, \( d_m \). For agglomerates of monodisperse spherical primary particles, \( d_{va} = d_m = d_p \) independent of mobility size (agglomerate or collision line). \( d_m \) decreases during sintering while \( d_{va} \) increases until \( D_f = 3 \) (coalescence line).

Effective fractal dimension \( D_f \) vs. mass mobility exponent \( D_{fm} \)

Evolution of \( D_f \) and \( D_{fm} \) during viscous sintering of DLCA agglomerates. The exponents \( (D_f, D_{fm}) \) are obtained by ensemble averaging over 50 agglomerates of each size. Only \( D_f \) exhibits monotonic behavior and thus can be used to characterize the degree or extent of sintering of aggregates.

DMA-APM data of silver nanoparticle aggregates sintered at different temperatures (faster sintering for same sinter time) by Kim et al.⁴ are post-processed here. The \( D_{fm} \) exhibits a monotonic increase consistent with our sintering simulations.

References