In Situ SAXS Studies of Continuous Nanoparticle Synthesis

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Introduction

In the last few years, there has been an increased interest in the synthesis of ever-smaller materials. The research has focused mainly on developing micron-sized and nano-sized materials and on controlling their morphology and size distribution. The goal is to manufacture materials that have much better properties than those of conventional metals and ceramics of macroscopic dimension. Such monodispersed, nanoscale, spherical ceramic particles can aggregate into larger micron-sized structures of various shapes and sizes, yet they will still possess the various structural properties, such as a high specific surface area, that are normally associated with nano-sized particles. The properties of these micron-sized particles depend on their size, size distribution, state of aggregation and agglomeration, and history (thermal), and all of these depend closely on the processing conditions. One of the most popular methods for synthesizing such particles is the flame aerosol process, which involves the combustion of ceramic precursors. Continuous nanoparticle-producing flames have been studied for some time and have been evaluated for producing the different characteristics mentioned above [1, 2].

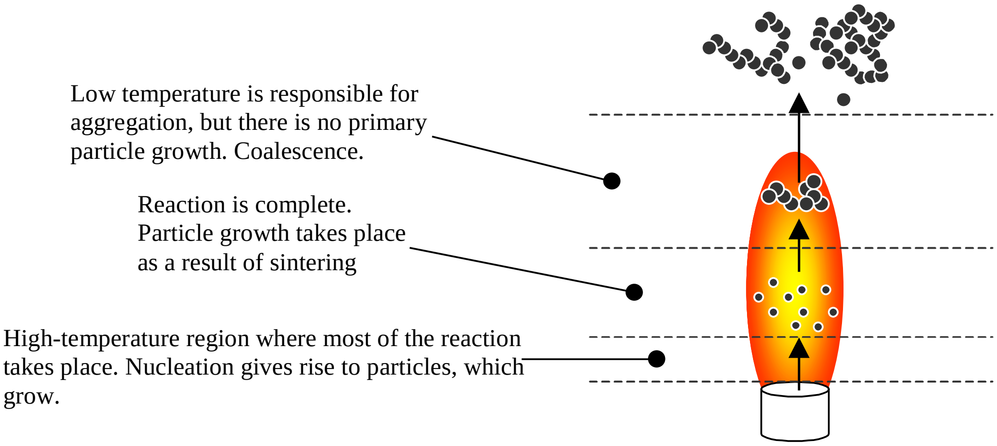
Particle size and phase composition are important features controlled by the flame temperature, precursor concentration, fuel-to-oxidizer ratio, and residence time of the particles in the flame. Monitoring the chemical changes in the flame is extremely difficult, because of the extremely fast nature of the reaction. The process of the formation of primary particles and aggregates is understood only in general forms. The reaction reaches completion in the hottest region of the flame (just outside the burner), and all the particle growth takes place entirely in the hot flame. Particles stop growing outside the flame, but they aggregate to form structures that are an order or two larger in scale than the primary particle sizes.

Methods and Material

A premixed flame that produces silica from hexamethyldisiloxane (HMDSO) was studied. The silica-nanoparticle-producing flames were stabilized with a honeycomb premixed burner (25 mm inner diameter) [3]. The HMDSO (Sigma-Aldrich, 99%) was saturated in a heated, bubbling flask. With nitrogen used as the carrier gas, the HMDSO was then mixed with the oxidizer (oxygen), the fuel (methane), and more nitrogen (all 99.99% AGA) before entering the burner. For ultrasmall-angle x-ray scattering (USAXS) background measurements in the absence of particles, a premixed flame with less nitrogen diluent was used to achieve flame shapes (flat) similar to those of the particle-laden flames.

Results and Discussion

Two different flames, A and B, were studied. Flame A was "colder" than flame B. The highest temperature of flame A was around 2350K at a height of about 5 mm and the highest temperature of flame B was 2490K at a height of about 10 mm. The axial temperatures decreased almost



Low temperature is responsible for aggregation, but there is no primary particle growth. Coalescence.

Reaction is complete. Particle growth takes place as a result of sintering

High-temperature region where most of the reaction takes place. Nucleation gives rise to particles, which grow.

FIG. 1. Different regions in the flame showing particle growth.

uniformly with increasing height [4]. All the USAXS plots were fit by the unified fit [5, 6].

Figure 2 shows an example of the increase in the primary particle size for the premixed flame A. As can be clearly seen, along the flame axis, the particles in the flame increase in size (~10 mm high), after which they remain constant at about 10 nm. The particles laterally outside the flame experience a lower temperature and hence are smaller than 10 nm in size. This can also be seen clearly in the figure, which shows the variation in primary particle size and the number of particles with respect to the height above the burner. There is a general trend of increasing primary particle size for both flames. Since flame A has a lower silica production rate, the silica concentration above a height of 40 mm is very low and does not allow for a good USAXS measurement. Flame B, meanwhile, is a high-production-rate flame; thus, measurements up to 100 mm yield estimates for particle sizes. The number concentration for silica increases steeply around 4-5 mm, which is an indication of the nucleation event. This can explain the dip in the average primary particle size. The nucleation event is followed by an increase in particle size due to sintering and coalescence. A secondary nucleation may occur at a height of about 40 mm, as indicated by the small increase in the number concentration, and it is also accompanied by a drop in particle size. There is also an indication that some particles are present even beyond the burner wall. The particle size decreases, laterally outside the flame, as expected, because the temperature outside the flame is considerably lower than the flame temperature.

Aggregation can be characterized by the mass fractal dimension (d_f) and by the degree of aggregation (*DOA*) which is simply the number of primary particles in an aggregate. Figure 3 shows the variation in the d_f and *DOA*. Arrows indicate the primary and secondary nucleation mentioned above. In the hotter flame B, aggregates appear at a later stage and have a d_f of 2.5, which decreases slightly with respect to height. The aggregates grow gradually, as indicated by *DOA*, in flame B. In the colder flame A, the particles show a greater affinity to aggregate. The d_f increases from 1.5 initially to 2.5 at a height of 50 mm. The *DOA* value shows a steep increase that corresponds to the nucleation event, and it then steadies to a uniform value. The d_f remains constant between 2 and 2.5 laterally outside the flame, as seen here.

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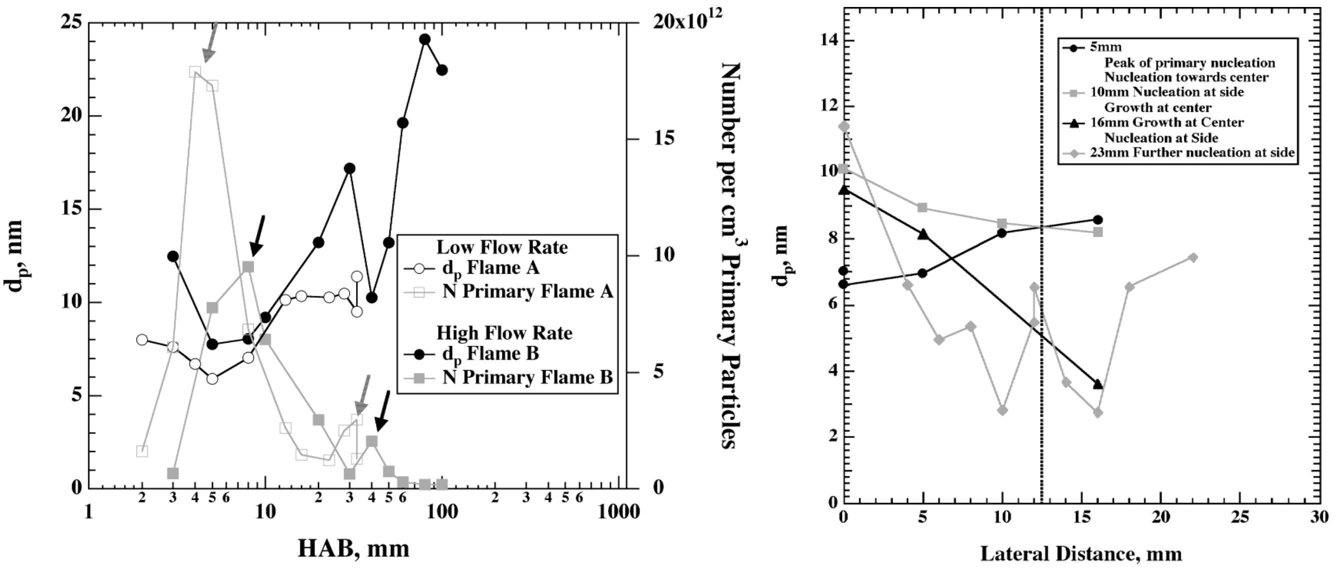

FIG. 2. Variation in the particle size (d_p) and number (N) of particles with the height above the burner (HAB) and lateral distance.

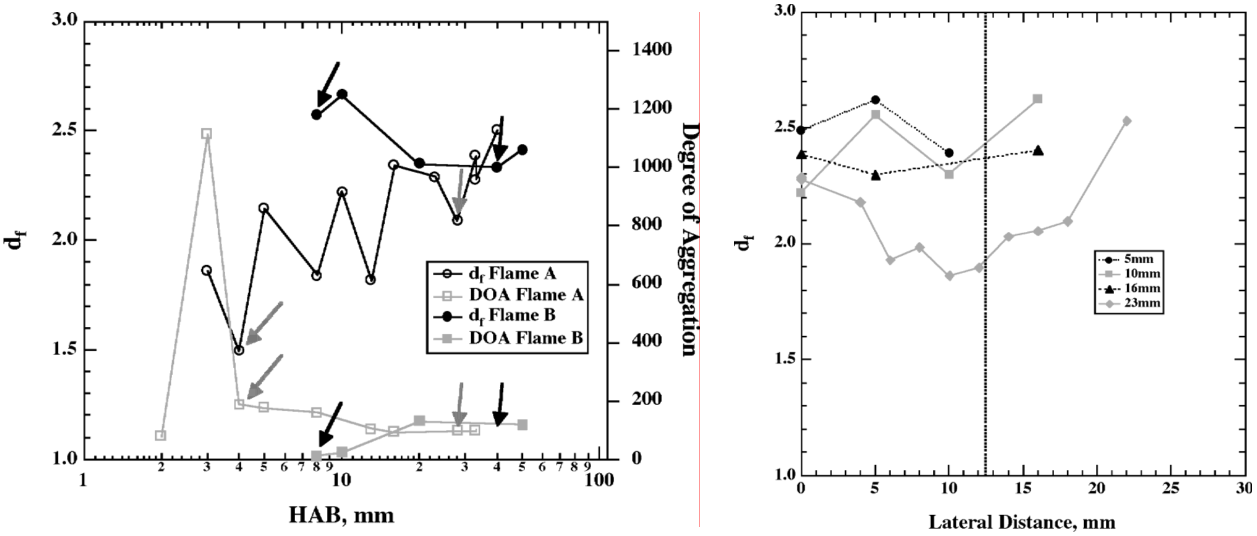

FIG. 3. Variation in the fractal dimension (d_f) and degree of aggregation (DOA) with the height above the burner (HAB) and lateral distance.

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