Design, Fabrication, and Testing of a Ceramic Microreactor for Nanoparticle Synthesis

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ABSTRACT

Nanoscale ceramic powders offer attractive prospects as building blocks for microscale and mesoscale 3-D sintered structures for various high performance applications due to their excellent mechanical, thermal, dielectric and corrosion properties. Despite the availability of a plethora of nanoparticle synthesis processes the difficulties in controlling the shape, size, and obtaining highly pure and stable nanoparticles in large quantities in a safe and cost-effective manner, have been the factors adversely limiting the applications of ceramic nanoparticles. Recent experiments have shown that to study the process of growth and formation of nanoparticles, a reactor having much smaller dimensions, namely a microreactor is more appropriate. Prior work has shown that the shape, size, and yield of nanoparticles are strongly influenced by the mean residence time required to produce the nanoparticles. A microreactor provides control over the mean residence time and hence over the nanoparticle size and shape. This paper deals with the design, fabrication, and testing issues related to a high temperature, ceramic microreactor and investigate the use of reactive gas streams in arrays of microchannel reactors to overcome the barriers associated with synthesis of ceramic nanoparticles in large quantities.

Keywords: Nanoscale ceramic powder, nanoparticle synthesis, silicon nitride, high temperature microreactors, ceramic microfabrication

1 INTRODUCTION

Nanotechnology is receiving increasing attention as its potential of revolutionizing science and technology becomes more apparent. It involves the design, fabrication, characterization, and utilization of materials, structures, and devices which are less than 100 nm in atleast one dimension [1]. One area of development in the field of nanotechnology involves nano building blocks such as nanoparticles. Nanoparticles can either directly, or with further functionalization, offer novel structural, electronic, light emission and absorption, sensing, or magnetic properties. Nanoparticles can help in miniaturization and find applications in various fields such as cosmetics, pigments for paints, cellular antennas, filters and sensors.

Among the different categories of nanoparticles, nanoscale ceramic powders offer attractive prospects as building blocks for microscale and mesoscale 3-D sintered structures. They find use in various high performance applications such as, non-carbon nanoabrasives, electroplated coatings, bioactive carriers, nanofilters, oral dentifrices, semiconductors, and floppy disks etc., due to their excellent mechanical, thermal, dielectric and corrosion properties [2]. The performance of these nanoscale ceramic powders is strongly affected by particle properties like particle size, size distribution, and shape. Therefore, to keep up with the trend of industrial production of nanoparticles, it is necessary to control the particle properties precisely.

Conventionally large-scale batch reactors were used for the synthesis of nanoparticles [3]. However, the particle size and the distribution of particle size synthesized in the conventional manner do not satisfy the requirements of the nanoparticles. Prior work has shown that the shape, size, and yield of nanoparticles are strongly influenced by the mean residence time and temperature required to produce the nanoparticles. A microreactor provides control over the mean residence time, mixing and temperature due to its several features such as, high temperature gradient, short and controllable residence time, portability, and high heat transfer rates and hence over the nanoparticle size and shape. Also, due to its portability the capital costs and the time required to build a microreactor will be much lower than for a traditional pilot plant.

This paper deals with the design and fabrication issues related to a microreactor with multiple microchannels and investigate the use of reactive gas streams of SiO and ammonia in arrays of microreactor to overcome the barriers associated with synthesis of silicon nitride nanoparticles in large quantities.

2 BASIS OF THE WORK

Silicon nitride (Si_3N_4) has been chosen for this work for several reasons. It has tremendous technological significance in high temperature structural applications as a result of its unique thermal, mechanical, dielectric, and

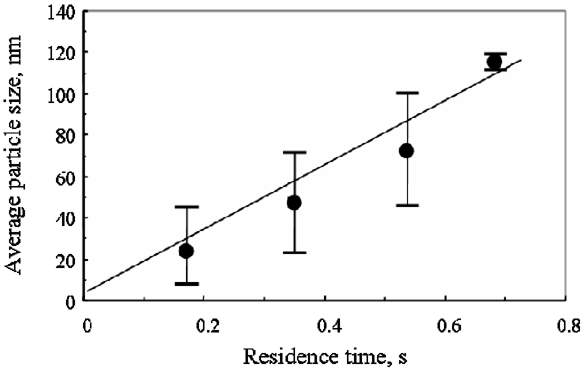

Figure 1: Growth of average Si_3N_4 particle size with the residence time of reactant gas mixture.

corrosion properties like high temperature capability (1000°C), high hardness (14-16 GPa), good thermal conductivity (29-30 W/m.K), low thermal expansion coefficient (3.3 x 10^{-6}/°C), and good oxidation and thermal shock resistance. It finds use in a number of industrial applications, such as reciprocating engine and wear components, bearings and cutting tools, hot metal handling, and semiconductors. Nanosized silicon nitride powder also increases additive free sinterability and plasticity, thus permitting large plastic deformation at low temperatures, and improving strength and toughness of sintered parts [4].

Prior work in a tubular flow reactor has identified that nanoscale particle formation is limited by diffusion between reactant and gas streams [5]. The effects of mean residence time as well as the reaction temperature on the growth of nano-sized particles were investigated. Figure 1 shows that the average particle size is roughly proportional to the mean residence time of reactants in the reaction zone. Based on the thermodynamic conditions, the critical radius for a silicon nitride nucleus to be stable and grow is 0.3-0.6 nm. Figure 1 show that the minimum residence time to produce particles of critical size turned out to be about 6 ms. This indicates that the mean residence time achieved in the tubular flow reactor [5] is much larger than the residence time needed for the formation of stable clusters. So, to study the process of nanoparticle formation and growth, a reactor having smaller dimensions namely, a microreactor is more appropriate. When a microreactor is used, the mean residence time can be easily controlled upwards of 0.1 ms, and the average particle size is reduced to those close to critical size. The yield of nano-sized silicon nitride powder in the tubular reactor was found to be at most 43% because of the formation of whiskers and crystals [6]. However, the use of microreactor is expected to increase and control the residence times and yield scalable throughputs of highly pure ceramic nanoparticles. In addition to requiring small quantities of reagent, the microreactor having sub-millimeter reaction channels will allow for the precise control of reaction variables, such as reagent mixing, flow rates, reaction time, and heat and mass transfer which is ideal for integration into post processing system.

3 MATERIAL SELECTION

Ceramics have the potential to add beneficial properties to microreactors for applications involving high temperature reactions due to their key properties such as high thermal and chemical resistance, high temperature stability, good corrosion and wear resistance, and superb heat conductivity [7]. Based on the design considerations and the material requirements, the microreactor was fabricated using ceramic alumina (Al_2O_3). Alumina possesses strong ionic inter-atomic bonding giving rise to its desirable material properties such as high hardness (11-14 GPa), good thermal conductivity (27 W/m°C), high temperature stability (1750°C), and low thermal expansion coefficient (8.4 x 10-6/°C), thus making it a suitable material for high temperature applications of microreactors.

4 FABRICATION

Conventionally, ceramic microreactor were not employed due to the costs associated with their design and development and because methods for the production of larger series were not fully established [7]. During product development, high costs were incurred for the fabrication of models and prototypes for design optimization. However, to speed up this process and to reduce the costs involved, different patterning techniques such as laser machining, micro-punching, extrusion, etching, photolithography, electro discharge machining (EDM), are nowadays increasingly used for fabricating ceramic microreactors [7]. Fabrication of microreactors involves two different steps-design, and patterning and bonding.

4.1 Design

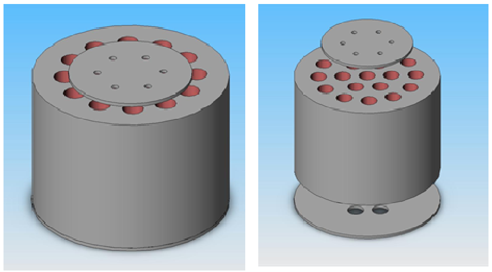

Figure 2: 3D model of the microreactor created using SolidWorks.

A computer model of the microreactor and its parts was created using commercially available 3D CAD software SolidWorks. These computer generated images of the microreactor were then used to produce the microreactor using different microfabrication techniques. Figure 2 shows 3D model of the microreactor, which consists of the top plate and the bottom plate with 17 mm diameter and 0.5 mm length, and the extruded body with 27 mm diameter and 20 mm length.

4.2 Patterning and Bonding

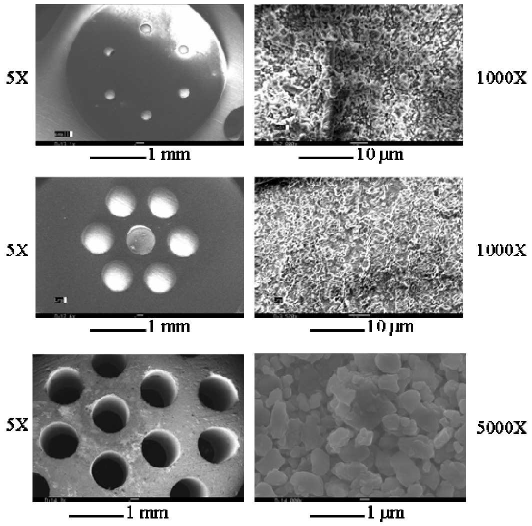

Figure 3: SEM images of the top plate, bottom plate, and extruded body at different magnifications

In the microreactor, the top plate and the bottom plate were fabricated using laser machining green tape alumina at PNNL, Richland WA. The green tape alumina used for these plates was Alcoa A-16 Super Grind with Rohm & Haas Duramax B-1000 aqueous binder. The laser used for fabrication was a CO_2 laser with 35 W as its beam power. One repetition along with 28% beam and 20% speed were the cutting parameters used to fabricate the top and bottom plates. Both these plates were sintered with the following schedule: 0.5 C/min to 400°C/1hr hold and 3.0°C/min to 1600°C/1hr. However, the extruded body was fabricated using highly porous alumina (50-60% porosity) at BHEL, India.

All these parts were then characterized using SEM. Figure 3 shows the SEM images of all the three parts at different magnifications. The reason behind using highly porous alumina for extruded body was because ammonia gas will be diffused in the microreactor through the pores of extruded body. The SEM image of extruded body at 5000X magnification (refer Figure 5) confirms the presence of pores in the extruded body. Followed by patterning, all these parts of the microreactor were then bonded using alumina paste to obtain the final microreactor assembly.

5 TESTING

Recently considerable efforts have been made to obtain particles that are few nanometers in diameter. A number of methods have been proposed to produce nanoparticles, including low-pressure CVD, laser-induced CVD, thermal plasma, etc. But, all of these processes result in high cost and lower quality of product. In principle, gas phase reactions give high purity silicon nitride nanoparticles and are recognized as simple, fast, efficient, and economical method for mass-producing nanoparticles. These processes involve an evaporation phase, where the reactants are vaporized to react, followed by rapid cooling which leads to nucleation and growth of particles. The ammonolysis process has been used to produce non-oxide ceramic powders, such as Si_3N_4 because of the low cost of NH_3. There are two major sources of Si to produce Si_3N_4-chlorinated silicon ($SiCl_4$, SiH_2Cl_4, etc.) and SiO.

$$3SiCl_4 + 16NH_3 \rightarrow Si_3N_4 + 12NH_4Cl \text{, at T > 1000°C}$$

$$3SiH_2Cl_2 + 10NH_3 \rightarrow Si_3N_4 + 6NH_4Cl + 6H_2 \text{, at T > 600°C}$$

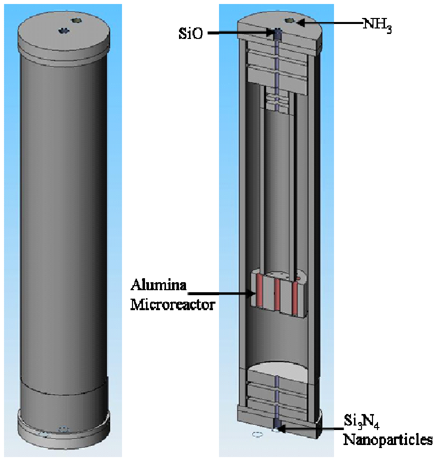

Figure 4: 3D view and the sectional view of the final microreactor assembly

As evidenced by the above reactions, the reaction between chlorinated silicon and ammonia results in a solid byproduct ammonium chloride (NH_4Cl), which can get mixed with the silicon nitride nanoparticles. So, the paper focuses on the ammonolysis of silicon monoxide in microchannel arrays of the reactor to synthesize silicon nitride nanoparticles at elevated temperatures ranging from 1300°C to 1400°C. Figure 4 shows the sketch of the microreactor assembly used to synthesize silicon nitride nanoparticles.

SiO vapor will be generated from a heated mixture of silica and silicon powders, and then carried in the hot reaction zone of the reactor by argon gas from the top plate of the microreactor, whereas the ammonia gas will be diffused through the extruded body of the reactor. The reaction between SiO and ammonia will take place in the extruded body at high temperatures to produce silicon nitride nanoparticles which will then be collected through the outlet.

$$3SiO(g)+4NH_3(g)\rightarrow Si_3N_4(s)+3H_2O(g)+3H_2(g)$$

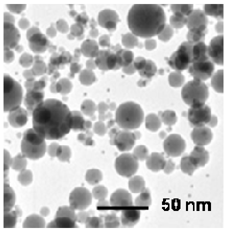

Figure 5: Si_3N_4 nanoparticles obtained using ammonolysis of SiO vapor

The silicon nitride nanoparticles obtained will be characterized using various characterization techniques such as transmission electron microscopy (TEM) and X-ray diffraction (XRD) to determine the amount of product, particle size distribution, and chemical composition The control of key variables such as contact pattern of reactant gas, feed concentration of ammonia and SiO, the residence time of reactant gas mixture in the uniform temperature zone, and the reaction temperature will provide great flexibility over the size and shape of the product as shown in Figure 5. Further ammonolysis of SiO forms no solid and toxic by-products, thus resulting in pure silicon nitride nanoparticles [8].

6 CONCLUSIONS

The discovery of new phenomena, properties, and processes on the nanoscale has led to a wide range of applications and opportunities for these nanosized materials. Thus, the synthesis and properties of nanoparticles have attracted considerable scientific and commercial interest. Silicon nitride nanoparticles in particular, have attracted much attention in various fields due to their unique properties. However, due to difficulties in controlling the reaction parameters and particle morphology and thus obtaining highly pure and stable nanoparticles in bulk using different synthesis processes, the applications and economics of silicon nitride nanoparticles are limited.

This work investigates the use of reactive gas streams in multiple microchannels of the microreactor as a means to overcome the barriers associated with the prior approaches in the synthesis of silicon nitride nanoparticles with controlled size and shape attributes. It will help us to identify, understand, and remove several key barriers in materials, manufacturing and economics of silicon nitride nanoparticles. This work can further be extended to produce non-oxide ceramic nanoparticles such as, TiN, SiC and AlN by varying the above reactant gas streams.

Microreactors also offer tremendous promise as a generalized platform for portable and distributive systems for energy generation, chemical and pharmaceutical production, and environmental remediation. Thus, the proposed work will also provide crucial insights into wide-ranging platforms for delivering nanoscale functionality in microchannel reactors of interest to many commercial areas.

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