

Ceramic Microsphere Production Systems

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Introduction:

The Ceramic Industry is consistently moving towards increasingly higher quality ceramic materials for a variety of high tech applications. Materials such as partially stabilized Zirconia, Hafnia, Ceria, and other metal oxides may be formed into high-density spheres or spheres with tailored pore size and surface area with a uniform spherical geometry and a narrow grain size distribution.

Brace GmbH of Germany has developed and patented an innovative process for the high volume production of spherical ceramic materials with a uniform particle size distribution. This process was developed over 15 years ago for the nuclear industry and has been utilized for a wide variety of Ceramic applications throughout Europe.

Harper International, Lancaster, NY, has brought this patented technology to North America and has added a dedicated laboratory at its Technology Center for the development and manufacture of microspheres from a variety of Ceramic materials. Harper is the exclusive supplier in North America.

The Brace Microsphere system consists of vibrating nozzles whereupon exiting fluid streams break up into uniform droplets. The droplets are molded into perfect spheres due to their surface tension. Gelation of the spheres is induced during a short period of free fall. Solidification can be induced in a gaseous and/or liquid medium through cooling, drying, or chemical reaction. There are no constraints on the type of liquid used; molten materials, solutions, dispersions, sols, or suspensions can be used to manufacture perfectly spherical Microspheres.

Uniform microspheres may be formed within a wide range of diameters with an exchange of nozzles. Spheres can be formed from 50 microns in diameter up to 6000 microns in diameter with the Brace technology. Advantages of the patented Brace microsphere systems are scale-up to 1000 liters per hour, small footprint of the equipment, quiet operation, automatic control systems, and low energy consumption, along with narrow particle size distribution.

Applications:

Dry metal oxide Microspheres produced on the basis of a sol (Al₂O₃, ZrO₂, HfO₂, TiO₂, CeO₂, SiO₂ and mixed oxides) can be used as highly sinter active press-feed for the production of high tech ceramics. Through calcining, the pore size and surface area of the Microspheres can be tailored to exacting specifications. These Microspheres make excellent catalyst carriers, homogeneous catalysts, or filtering material. Unusually effective and abrasion resistant Microspheres for grinding other materials are made from sintered Al, Zr, and Hf-oxides.

Sol-Gel Production Process:

A number of metals can form hydroxide sols and can be used as starting material for the production of microspheres. Sols with low viscosity, such as Zirconium or Hafnium hydroxide stabilized with organic compounds like poly-alcohols or with pore formers like urea, can easily be pressed through a nozzle system. Gelation in the gaseous phase is obtained by the reaction with ammonia. Dropping the spheres into an aqueous solution of ammonia continues the solidification process. This solidification can be tailored to the desired properties of the microspheres by varying the reaction time and the concentration of ammonia in the precipitation bath. Aqueous solutions of nitrates or carbonates are also excellent starting materials for the production of microspheres. The pre-neutralized solutions formed into spheres are also gelled in a gaseous reaction with ammonia. They are ultimately precipitated in an aqueous solution of ammonia. Even without chemical pre-solidification in the gaseous phase, the solidification is possible provided that the precipitation solution shows a low surface tension to avoid deformation of the spheres.

Subsequent treatment of the microspheres allows for different compositions and structures of the spheres. The spheres may be processed for high density, various degrees of porosity, hard, soft, coated, or embedded, with precise control or just free flowing, activated, or doped with additives.

Precursors of Zirconia and Hafnia:

Aqueous solutions of Zr, Hf in nitric acid pre-neutralized with ammonia are the precursors in the formation of high purity microspheres. Precipitation as a gel is obtained even when the molar nitrate/zirconium ratio exceeds 1.1:1. Hafnium and or Zirconium salts such as carbonates, nitrates, or chlorides with stoichiometric composition, for example HfOCl₂ or ZrO(NO₃)₂ can also be used. Additives like Magnesia or Yttria for crystal stabilization must be used if sintered products are desired. Organic-derived precursors can facilitate the preparation. The use of partially alkoxide derived precursors and completely organic derived precursors can be used. The preparation of mixed oxides, e.g. ZrHfO₄ may be obtained with mixtures of alkoxides:



Sols can also be prepared from nitrates (e.g. Zirconium, Uranium). The solution may be changed from a solution, to a sol, to a gel depending on the pH of the solution.

Subsequent Treatment of Microspheres:

The chemical reaction between metal salt solutions and ammonia produces ammonia salts. These salts must be washed out before the particles are processed further, otherwise the particles would be destroyed during heat treatment as these salts decompose. Washing of the microspheres is completed in only a few minutes since the exchange rate, diffusion, between particles and the surrounding liquid is extremely fast.

After washing, the particles are dried at 100-180°C in air, evaporating the washing fluid. The dried gel particles are then calcined in air at 600-900°C in order to decompose the organic polymer. Depending on the composition of the precursor solution, residual carbon contents ranging from 10-50 ppm, BET surface areas ranging from 10-200 square meter per gram, and crushing strengths >20 –50 Newton/particle can be specifically achieved, with particle sizes between 0.2mm and 0.6 mm final diameter of particles containing at least 80wt.% ZrO₂ or HfO₂.

Sintering under hydrogen at 1700°C can produce microspheres of very high density (95% to 98% of theoretical density) without cracking (see Fig. 1). Sintering at 1500°C in air leads to high-density spheres as shown in (Fig. 2).

The Harper Technology Center develops formulations and performs pilot scale processing of a variety of ceramic microspheres. Post processing of microspheres is independent of the encapsulation process. As required for specific applications, microspheres may be dried, calcined, sintered, coated and sorted with a variety of technologies available from Harper International and Brace GmbH. These include drum dryers, fluidized bed, rotary calciners, and specially designed precision sorting tables.

For additional information on the processing of ceramic microspheres, please contact Harper International at www.info@harperintl or call 716-684-7400 and visit our web site at www.harperintl.com