Available online at www.sciencedirect.com
ScienceDirect
Journal of the European Ceramic Society 29 (2009) 1379–1385
www.elsevier.com/locate/jeurceramsoc

Influence of the suspension flocculated state on the microstructure of alumina spheres elaborated by colloidal granulation

Cécile Pagnoux [a,*], Nicolas Tessier-Doyen [b], Antoine Pringuet [a], Manuella Cerbelaud [a], Pascual Garcia-Perez [a]

[a] *SPCTS, CNRS, ENSCI, 47/73 Avenue Albert Thomas, 87065 Limoges, France*
[b] *Groupe d'Etudes des Matériaux Hétérogènes (GEMH, EA 3178), Ecole Nationale Supérieure de Céramique Industrielle, 47/73 Avenue Albert Thomas, 87065 Limoges, France*

Received 23 June 2008; received in revised form 11 September 2008; accepted 13 September 2008
Available online 25 October 2008

Abstract

A process of granulation by a colloidal method based on ceramic powder agglomeration makes it possible to produce millimetric spheres with a very homogeneous distribution in terms of shape and size. The starting suspension consists of a mixture of alumina submicrometer particles and silica nanoparticles such as $mSiO_2/mAl_2O_3 = 1.1\%$. Heterocoagulation between the two oxides occurs forming a flocculated network the structure of which can be modified by a shear application. The outer appearance of the spheres is nearly perfect whereas the inner structure exhibits some defects (cracks and porosity). It has been shown that the green spheres are more porous as well as the grains of the starting suspension are less flocculated. During the drying step, the high mobility of these agglomerates increases the overall density on the surface and leads to the formation of a spherical empty cavity in the sphere centre.

Keywords: Suspension; Microstructure-final; Alumina; Agglomeration; Granulation

1. Introduction

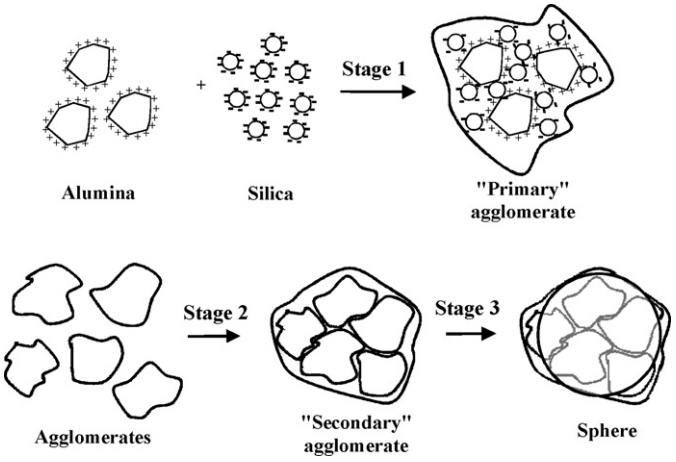
Powder granulation is a widely used process in many industries such as mineral processing, the pharmaceutical industry, foodstuffs, etc... The main interests of this shaping technique are to limit dust emission, to improve powder flowability and bulk density of pressed green parts. Two kinds of industrial processes, wet granulation and spray drying routinely leading to spherical final products can be considered. Wet granulation uses capillary and viscous forces of a binder sprayed on the powder bed to agglomerate the particles in a mixer. The liquid binds the particles together until more permanent bonds are established leading to the granules formation. Research works based on the influence of both formulation and granulation technique investigated on the granules behaviour, make it possible to achieve substantial progress in understanding and in quantifying the mechanisms that control granules attributes.[1–3] For mineral materials, spray drying has sometimes replaced "wet granulation". This process requires the preparation of an aqueous suspension (dispersant and binders) which is nebulized into flowing hot air. The organic binders in the starting suspension confer well-suited cohesive strength and free flowing properties to the sprayed granules. Research works[4–7] about suspension formulation and binder migration to the granule surface describe the ability to obtain solid or hollow granules and to improve the strength of the pressed parts.

Based on diluted suspensions, a new process of powder granulation was recently proposed to elaborate ceramic spheres directly in suspension. Powder agglomeration takes place via the electrostatic interactions occurring between the particles. For instance, a formulation based on a mixture of alumina ($d_{50} = 400$ nm) and of silica ($d_{50} = 25$ nm) powders has been the subject of a recent investigation.[8] There is a common pH range for which the zeta potential of the two powders is of opposite polarity (positive for alumina and negative for silica). For a mass ratio such as $mSiO_2/mAl_2O_3 = 1.1\%$, the nanometric silica adsorbs on the submicronic alumina surface that makes the zeta potential of alumina near zero, causing particles agglomeration and suspension flocculation. Formation of "primary agglomerates" with a size close to 2–3 μm constitutes

* Corresponding author. Tel.: +33 5 55 45 22 22; fax: +33 5 55 79 09 98.
E-mail address: cecile.pagnoux@unilim.fr (C. Pagnoux).

0955-2219/$ – see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jeurceramsoc.2008.09.007

the first step of the process. When such "primary agglomerates" are mixed under a continuous rotational movement, they form a powder bed immersed into water, in which they are in permanent contact. As the alumina surface is not entirely covered by silica nanoparticles, opposite charges exist locally, which induce mutual attraction between agglomerates and ensure their combination provided that collisions occur during the rotational movement. This second step leads to "secondary agglomerates" which exhibit a typical size of 1 mm very close to that of the final sphere. The mutual friction of the objects and in contact with the bottle wall makes them round and smoothens the surface while keeping the agglomerates cohesion. This process can be considered as a "wet granulation by colloidal method" using a diluted suspension. The three main steps can be illustrated by the following diagram:



To properly control the formation of the "primary agglomerates" and their coalescence, it is previously necessary to study the surface properties of the two raw materials in water and the adsorption properties of the silica nanoparticles on alumina.[9] The formulations for granulation were then selected according to the following parameters: ratio of the two oxides, solid loading of the suspension, pH and ionic strength. It should be noted that any molecule or ion adsorbed onto the oxides surface poisons the agglomerates coalescence (stage 2). Spheres exhibit a nearly perfect spherical shape and a smooth surface state. The main feature is their homogeneous distribution in terms of shape and size. This article concerns the characterization of the primary agglomerates and the microstructure of the spheres after drying and sintering steps according to the procedure used for the suspension deagglomeration. This parameter influences the network structure of heterocoagulated particles as well as the structure of spheres obtained after the agglomerates coalescence. Sedimentation experiments, size distribution measurements, microstructure observations and mechanical properties provide useful tools to characterize each system.

2. Experimental section

2.1. Raw materials

A high purity (99.9%) alumina powder (AKP30, Sumitomo, Japan) was used ($d_{50} = 400$ nm, 7 $m^2\,g^{-1}$). An aqueous suspension of this powder exhibits a natural pH of 6.5 and a positive zeta potential with a high amplitude (+50 mV). Silica nanoparticles (Ludox TM50, Grace Davison USA, $d_{50} = 25$ nm, 140 $m^2\,g^{-1}$) were dispersed in an alkaline medium which reacts on the surface to produce a negative charge and a zeta potential of −35 mV. The natural pH is 9. This silica is an amorphous compound, but to facilitate the notation, SiO_2 will be used throughout this text. SEM images of these two raw materials were shown in a previous article.[8]

2.2. Elaboration of spheres

The mixed suspensions used to produce spheres were prepared with a solid loading of 3 vol.% and a mass ratio $mSiO_2/mAl_2O_3 = 1.1\%$. No additive was added. Two methods of homogeneisation were used. The first one consists in applying a powerful ultrasonic treatment ($P = 450$ W) during 60 s to the suspension. For the second one, in addition to the ultrasonic treatment, there is a second step which consists in stirring vigorously with rollers the bottle containing the suspension during 24 h at a very high speed (0.420 m s^{-1}). These methods will be referred to, respectively, as "method 1" and "method 2".

To induce the growth of agglomerates and the formation of spheres, the mixture (50 cm^3) was stirred under a controlled speed (0.056 m s^{-1}) to obtain complete agglomeration. The cylindrical vessel ($h = 60$ mm, $d = 30$ mm), put horizontally, is submitted to a continuous movement using a stirrer called "rollers rock'n roll" (Bioblock, France), which creates a sinusoidal wave. The rotation of the vessel due to the rollers is coupled with a pendulum motion perpendicular to the vessel axis, at the same speed (0.056 m s^{-1}). The maximum duration of stirring was 7 days.

2.3. Spheres drying and sintering

As the spheres cohesion is sufficiently high, they can be easily transferred from the vessel to a large dish. The liquid was removed and the spheres were dried in a controlled oven in terms of temperature (T) and moisture (RH). The experimental conditions were as follows: $T = 293$ K and RH = 95% during 36 h and during the following 24 h, the temperature was gradually increased to 363 K and RH decreased to 10%. After the total evaporation of the liquid, the spheres were sintered at 1600 °C (3.3 °C min^{-1}, 3 h).

2.4. Methods of characterization

The grain or agglomerate size distribution of alumina in the suspensions was determined by laser granulometry with a Mastersizer 2000 (Malvern Instruments, Worcestershire, UK). The Mastersizer monitors simultaneously the intensity of light scattered at a number of angles from 0° to 46°. These data are subsequently used to calculate the particle or aggregate sizes. The software of the equipment considers any scattering object as a solid sphere and not as a porous object. Anyway, one expects the observed trends in the change of particle size versus the method of homogeneisation to be still valid.