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.

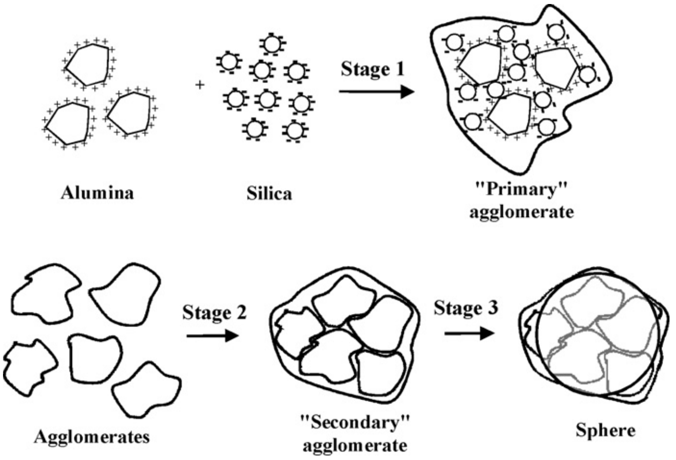
Based on diluted suspensions, a new process of powder granulation was recently proposed to elaborate ceramic spheres directly in suspension. Powder agglomeration takes place via the electrostatic interactions occurring between the particles. For instance, a formulation based on a mixture of alumina ($d_{50} = 400\,\text{nm}$) and of silica ($d_{50} = 25\,\text{nm}$) 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.

With the data of the Mastersizer, fractal approach was also used. A plot of the logarithm of the scattered light intensity (I) versus the logarithm of magnitude of the scattered wave vector (q) provides information on the compactness of agglomerates. When $1/R \ll q \ll 1/r_0$ (R is the radius of "primary agglomerates" and r_0 the radius of the primary particles), the slope of the plot of $\log(I(q))$ versus $f(\log q)$ is related to the fractal dimension (d_F) of the system. The difficulty is to select the data range for the d_F calculation. In particular, the existence of an upper limit introduces a cutoff function. In the literature, a variety of cutoff functions have been proposed, opening a discussion.[10] It was chosen here to analyse the range of $\log(q)$ such as $10/R \leq q \leq 1/10r_0$.[11]

The agglomeration of the mixed system SiO_2/Al_2O_3 was studied by carrying out sedimentation experiments according to the experimental conditions of deagglomeration. Immediately after preparation, the samples were allowed to settle in closed tubes for a total of 7 days. In such conditions, a clear supernatant is observed and the height of cake was measured accurately.

SEM observations of the spheres were conducted with a stereoscan 260 (Cambridge Instrument, UK).

To control the homogeneity in the bulk of the studied spheres, microhardness was measured with a three-sided diamond Berkovich indenter tip using a XP Nano Indenter (MTS Nano Instruments, USA). An XP Basic Tip Calibration method was employed. Hardness was deduced from the load–displacement curves by the calculation of the ratio between the maximum applied load and the overall contact area created by the tip. All measurements were carried out with the same identical load (500 mN) and an indentation depth close to 1.5 μm. The samples were first embedded in resin and polished down to 1 μm to reduce the roughness of the investigated surface. A pure fine-grained and quasi-fully dense alumina (AL23, Degussa) was also characterized as a reference material.

Compression experimental tests ($0.5\,\mathrm{mm\,min^{-1}}$) were carried out using a Lloyd mechanical testing machine with a specific support constituted of fully dense alumina pistons to avoid prints when spheres are crushed. The load causing failure (P_r) was measured between the two diametrically loaded sphere points (25 spheres). The tensile strength σ was determined using the approximate equation:[12]

$$\sigma = 2.8\frac{P_r}{\pi D^2}$$

where 2.8 is a parameter depending on sample size, geometry and elastic properties and D corresponds to the equivalent sample diameter.

3. Results and discussion

3.1. Formation of primary agglomerates

The influence of the homogeneisation method on the "primary agglomerates" compacity was studied with size distribution measurements (Fig. 1) and sedimentation tests (Fig. 2). A pure alumina suspension was added as a reference. Without silica addition, the average size of alumina agglomerates is close to 1.8 μm. The distribution is relatively broad, grains with a size lower than 1 μm are observed. With only the application of ultrasonic treatment (method 1), silica addition increases the median diameter of the agglomerates up to 3.6 μm and the distribution remains a broad one. The shear application used after ultrasonic treatment (method 2) prevents the agglomerates coalescence, but also decreases their average size to 3 μm and reduces the distribution, which becomes narrower.

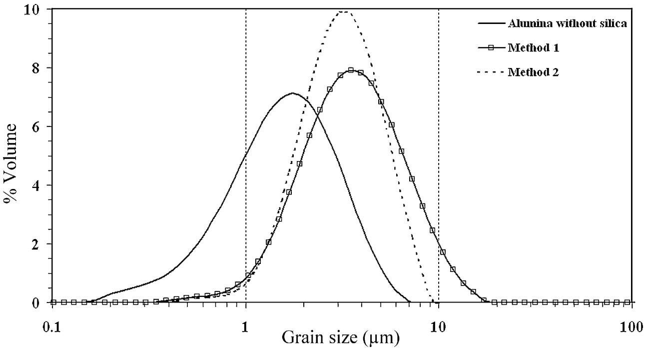


Fig. 1. Grain size distribution of alumina suspension prepared without silica and with silica ($mSiO_2/mAl_2O_3 = 1.1\%$).

The sediment with the higher density was obtained with a pure alumina suspension; a very low height (18 mm) of cake was measured. With a ratio $mSiO_2/mAl_2O_3 = 1.1\%$, the suspension is strongly destabilised and the height of the sediment increases, but its final height depends on the method of homogeneisation. A value of 80 and of 54 mm is measured for, respectively, methods 1 and 2. The application of a shear makes the sediment more compact. Silica adsorption on the alumina surface neutralizes the alumina surface charge, reduces the zeta potential so that it induces agglomeration. But as shown by sedimentation experiments and grains size distribution, the compactness of the "primary agglomerates" network is enhanced with an additional

Fig. 2. Picture of 3 vol.% alumina suspensions with (a) no silica and with silica ($mSiO_2/mAl_2O_3 = 1.1\%$) according to the deagglomeration method (b) method 1, (c) method 2.

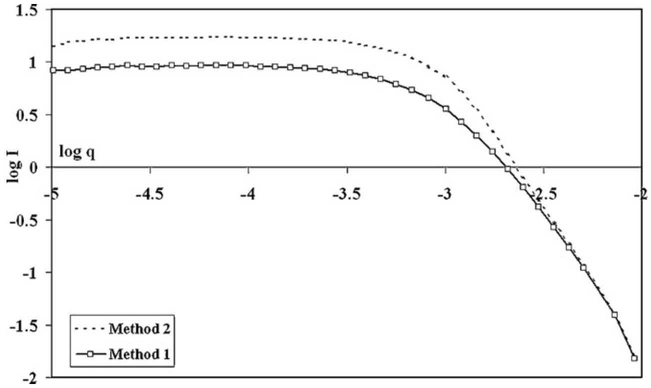


Fig. 3. A plot of log(*I*(*q*)) versus log(*q*) for the size distribution obtained with the mixed system Al_2O_3/SiO_2 according to the deagglomeration method.

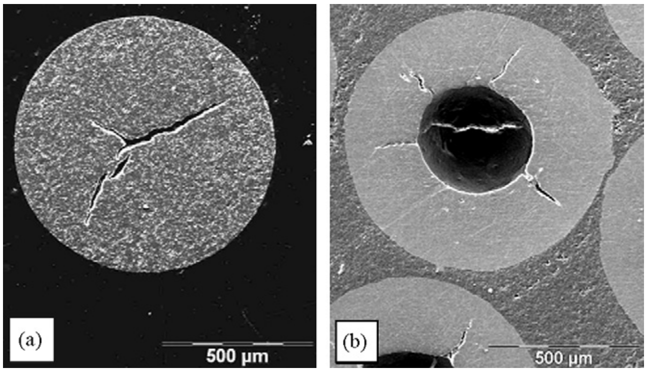


Fig. 4. SEM picture of the inner structure of a sphere elaborated by colloidal granulation according to (a) method 1, (b) method 2 of powder deagglomeration.

stirring step (method 2) because the agglomerates size is lower than that obtained with method 1.

The log–log plot of scattered intensity (I) versus wave number (q) is reported on Fig. 3 for the two mixed systems. Provided the size of the agglomerates (3.0–3.6 µm) is at least an order of magnitude greater than the primary particle size (0.4 µm), the agglomerate obeys a power law scattering. In the [−2/−2.5] range of log(q), the scattered light intensity is the same, whatever the considered deagglomeration method. But the curve corresponding to the agglomerates obtained with "method 2" exhibits a power law on a larger range of log(q) than that obtained with "method 1". The slope determined in the [−3.0/−2.2] log(q) range is of −2.40 and −2.76 ± 0.05, respectively, for methods 1 and 2. Formation of "primary agglomerates" occurs according to a fractal model and they are denser with "method 2", which confirms the sedimentation results.

For this oxides ratio, silica is totally adsorbed and is distributed among the alumina surface.[9] The coverage of the alumina surface by silica is in a stationary state. No exchange with the solvent occurs as for a soluble molecule. Then silica covered alumina particles are under a rather short range effective attraction and the agglomeration process starts. For "method 1", the formation of chain like agglomerates could explain such an open structure in the final cake. The application of a high shear (method 2) must break the chain that gives smaller agglomerates which can rearrange themselves and build a sediment with a high compacity. Similar observations were made by Kim and Berg[11] with a system based on negatively or positively charged silica nanoparticles. Under a high shear, reorganisation of the particles network occurs by break up, reagglomeration processes and internal rearrangement.

The modification of the agglomerates network structure does not prevent their coalescence when the mixture is stirred under a rotational movement at a low speed. Spheres are formed but with a slowing down of the kinetic formation.

3.2. *Internal structure of the spheres*

Whatever the homogeneisation method, the spheres obtained after the granulation step exhibit a very homogeneous distribution in terms of shape and size. Table 1 summarizes diameters and density values of green and sintered spheres. Spheres exhibit similar diameters whatever the deagglomeration method, but the density of spheres obtained with method 1 is about 10% higher, in particular after the sintering step. Fig. 4 shows the internal structures of the sintered spheres. With "method 1", solid spheres are obtained; some cracks appear, starting from the sphere centre and are propagating toward the surface. The microstructure exhibits porosity homogeneously distributed inside all the sphere. For the second method, a spherical cavity appears located in the sphere centre; its diameter represents 47% of the total one. A few small cracks start from the cavity toward the surface. The microstructure of the external shell (0.23 ± 0.02 mm in thickness) seems very much denser compared with that of the solid sphere.

To determine the formation mechanism of the spherical cavity, spheres prepared with "method 2" were cut to optically analyse their internal structure during the drying and sintering steps (Fig. 5). The first image (Fig. 5a) represents the structure of a sphere which was voluntary frozen just after its removal from the suspension liquid. The sample exhibits a porous structure free of cavity. The second image (Fig. 5b) corresponding to a dried sphere shows that a cavity has already formed and its diameter increases after the sintering step (Fig. 5c).

For both systems, the granulation process occurs in the same way, the only difference concerns the kinetics of the sphere for-

Table 1
Characteristics of green and sintered spheres.

	Green spheres		Sintered spheres		
	Diameter (±0.02 mm)	Density (±0.03 g cm^{-3})	Diameter (±0.02 mm)	Density (±0.02 g cm^{-3})	σ_f (MPa)
Method 1	1.03	2.29	0.87	3.80	200 ± 30
Method 2	1.03	2.00	0.87	3.38	28 ± 5

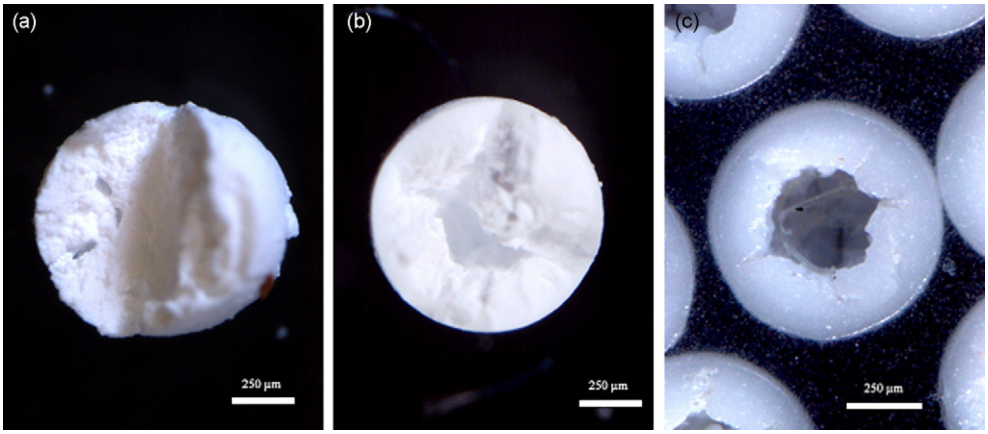


Fig. 5. (a) Picture of a sphere frozen without be dried, (b) picture of a dried sphere and (c) picture of a sintered sphere.

mation which is lower for "method 2". Finally, spheres exhibit the same dimensions but their density and microstructure depend on the deagglomeration method. The volume of the spherical empty cavity represents 10% of the total sphere volume, this value corresponding to the difference in the sintered density. The crack formation from the centre of the sphere should be due to the evolution of the structure during the drying step. The liquid removal starts from the sphere surface that induces a moisture gradient into the sphere. The grains should be compacted on the sphere surface and form a rigid crown. Moreover during the water evaporation, as the green structure is porous, the grains probably migrate from the centre to the surface, which enhances the compacity of the sphere surface. The "free of solid" volumes coalesce in the sphere centre and initiate the cracks or the cavity for, respectively, low and high porosity. The shrinkage also induces circomferential compressive strength which emphasizes radial cracks.

The structure rearranges itself during the drying step. The mechanism could be compared to what occurs during the formation of spray-dried granules.[13–16] Several authors showed that a dispersed suspension leads to hollow granules, whereas a flocculated one leads to solid granules. In this present study, similar observations are made. Even if the two starting suspensions, based on a mixed system of alumina and silica are flocculated, the one obtained with "method 2" is less flocculated (see sedimentation experiments) and leads to hollow spheres. When agglomerates are cohesive, grains are immobilized and do not rearrange themselves a lot under the drag force of water evaporation. No shell appears and solid spheres form. The sintering step does not reduce the porosity of the agglomerates network. With a less flocculated slurry, agglomerates become mobile. They migrate to the sphere surface along with the capillary induced moisture flow and are able to pack densely at the sphere surface as water evaporates. This rearrangement leads to the formation of a microporous solid layer acting as a rigid shell which contributes to maintain a constant external sphere diameter. Then, there is no shrinkage of the sphere and a cavity is formed.

The average values of hardness measured by nanoindentation technique across the diameter of three alumina semi-spheres prepared with method 2 are reported on Fig. 6. Because of the non-homogeneity of the cracks profile inside the spheres resulting from method 1, hardness measurements do not give consistent results. Zero value on the distance axis corresponds to the sphere centre; indents are spaced 50 µm from each other. For AL23 alumina characterized as a reference, the average value measured with 25 indents is close to 26 ± 2 GPa which is in agreement with typical values included generally in the 25–30 GPa range.[17] Spheres elaborated by colloidal way exhibit a hardness gradient from the centre to the surface, and values similar to AL23 alumina reference are obtained. But the tensile strength (Table 1) of these spheres are very low compared with fully dense alumina spheres supplied by Brace (ref. GmbhB_500, 840 MPa ± 80). These results highlight the heterogeneity of samples characterized by SEM observations as well as the presence of critical defects in the sphere centre.

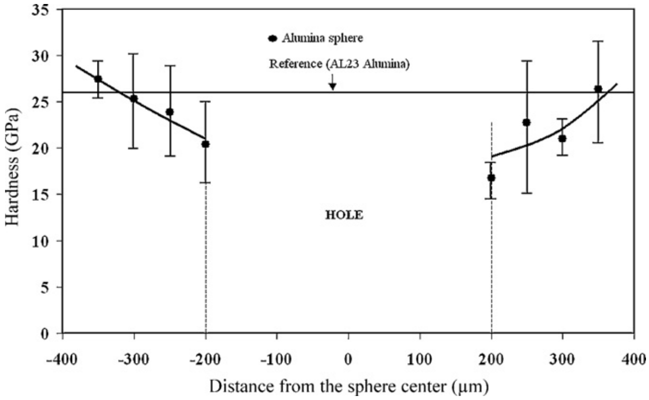


Fig. 6. Hardness profile of sintered alumina spheres elaborated with "method 2".

4. Discussion

Through a convenient colloidal process which requires few and no costly equipment, an innovative method of liquid/solid separation is proposed in order to elaborate the objects directly in suspension. The suspension consolidation is based on the attractive interactions between the powder surfaces inducing the coalescence of the "primary agglomerates". These phenomena take place when the alumina surface carries both positive charges due to the ionisation of the hydroxyl surface groups

($Al–OH_2^+$) and negative charges ($Si–O^-$) due to the silica nanoparticles adsorption. It can be explained on a simple basis involving surface chemistry. But if the spheres exhibit a perfect outer appearance (size, shape, smooth surface), the inner structure includes some defects such as cracks and porosity. The microstructure of the spheres results from the coalescence of an agglomerates network with a very open structure. In the case of "method 1" of deagglomeration, the network of crosslinked chains delimits large volumes free of solid. Sedimentation experiments show how a small amount of added silica increases the filled out volume occupied by alumina particles into the suspension. Under the continuous rotational movement, the chains should coil up to form millimetric objects with a porous structure. These chains should be broken by the applied shear (method 2) and with fragments, the inner structure of the sphere becomes more porous because the length of the starting entities to coil up is reduced.

During the drying step, the cohesion between the agglomerates is not high enough to prevent crack formation due to green porosity and to grains migration toward the sphere surface. Cohesion is due to the interactions between alumina and silica surfaces and in particular to the bonds between hydroxyl surface groups. Silica nanoparticles act as "a binder" for alumina. It is not possible to add to the suspension formulation an organic binder or a salt which could improve cohesion inside the spheres because these additives would modify the oxides surface properties and it would poison the coalescence of the agglomerates. The study of parameters such as solid loading of the suspensions or $mSiO_2/mAl_2O_3$ ratio did not allow to improve the agglomerates cohesion into the spheres.[8]

The mechanical properties show that spheres produced by this granulation process cannot be used for grinding, attrition or surface treatment, because even though the sphere surface should withstand the abrasion, the compression strength of the overall sphere is too low. The formulation conditions are too restrictive to make it possible to produce dense spheres with similar mechanical properties at a lower cost than the processes of electrofusion or "oil drop". For the granulation process using a colloidal route, the drawback is that ionic strength would have to be very low to allow electrostatic interactions between surface sites.

Spheres are considered as "hollow" if the ratio between the wall thickness and the total diameter is lower than 0.1;[18] that is not the case of the spheres elaborated with the selected system (ratio = 0.23/0.87 = 0.26). To reduce wall thickness, spheres with a very high porosity must be elaborated. The use of silica particles with a size similar to alumina ones could be beneficial. Yates and al.[19] determined the optimum particle dose to produce clear supernatant of alumina suspension through silica particles addition as a function of the $dSiO_2/dAl_2O_3$ size ratio. The quantity of silica particles required to achieve optimum agglomeration decreases as the particle size ratio increases. Thus larger particles are more efficient in terms of number in promoting heteroagglomeration. Authors observed that as the size ratio decreases, the coverage of the alumina surface by silica particles also decreases whereas the distance between alumina particles in the heteroagglomerates increases. Then, it would be possible to obtain a very porous network of agglomerates from a mixed suspension of alumina and silica particles with similar sizes but with an amount of silica higher than the ratio used in the present study ($mSiO_2/mAl_2O_3 = 1.1\%$).

Finally, this process of granulation by a colloidal method would be applied for powders with high specific areas for catalysis or filtration applications or for mixed systems of organic and mineral powders to elaborate spheres with a controlled porosity.[20,21]

5. Conclusion

The microstructure of millimetric spheres elaborated by colloidal granulation of agglomerates was investigated as a function of the flocculation state of the starting suspension. The addition of a very small amount of silica nanoparticles in a suspension of submicronic alumina particles leads to a very porous heteroagglomerates network which can, under high shear, rearrange itself to become more compact. The size and the structure of the heteroagglomerates influence the compacity of the green sphere and drying occurs in a way similar to that of spray-dried granules. Agglomeration of less flocculated particles forms a more porous green body and their relative mobility under the drag force of liquid evaporation during the drying step leads to spheres with a centred cavity.

It would be of a great interest to study accurately the link between the structure of heteroagglomerates and the microstructure of the spheres with mixed systems of alumina and silica as a function of the size and mass ratio between the two oxides.

References

1. Iveson, S. M., Litster, J. D., Hapgood, K. and Ennis, B. J., Nucleation, growth and breakage phenomena in agitated wet granulation processes: a review. *Powder Technol.*, 2001, **117**, 3–39.
2. Hoornaert, F., Wauters, P. A. L., Meesters, G. M. H., Pratsinis, S. E. and Scarlett, B., Agglomeration behaviour of powders in a Lödige mixer granulator. *Powder Technol.*, 1998, **96**, 116–128.
3. Cameron, I. T., Wang, F. Y., Immanuel, C. D. and Stepanek, F., Process systems modelling and applications in granulation: a review. *Chem. Eng. Sci.*, 2005, **60**, 3723–3750.
4. Tanaka, S., Chia-Pin, C., Kato, Z. and Uematsu, K., Effect of internal binder on microstructure in compacts made from granules. *J. Eur. Ceram. Soc.*, 2007, **27**, 873–877.
5. Zhang, Y., Tang, X. X., Uchida, N. and Uematsu, K., Binder surface segregation during spray drying of ceramic slurry. *J. Mater. Res.*, 1998, **17**, 1881–1887.
6. Ben Romdhane, M. R., Chartier, T., Baklouti, S., Bouaziz, J., Pagnoux, C. and Baumard, J. F., A new processing aid for dry-pressing: a copolymer acting as dispersant and binder. *J. Eur. Ceram. Soc.*, 2007, **27**, 2687–2695.
7. Kim, J., Wilhelm, O. and Pratsinis, S. E., Packaging of sol–gel made porous nanostructured titania particles by spray drying. *J. Am. Ceram. Soc.*, 2001, **84**(12), 2802–2808.
8. Garcia-Perez, P., Pagnoux, C., Pringuet, A., Videcoq, A. and Baumard, J. F., Agglomeration of alumina submicronparticles by silica nanoparticles: application to processing spheres by colloidal route. *J. Colloid Interf. Sci.*, 2007, **313**(2), 527–536.
9. Garcia-Perez, P., Pagnoux, C., Rossignol, F. and Baumard, J. F., Heterocoagulation between SiO_2 nanoparticles and Al_2O_3 submicronparticles; influence of the background electrolyte. *Colloids Surf. A*, 2006, **281**(1–3), 58–66.

10. Bushell, G. C., Yan, Y. D., Woodfield, D. and Raper, D., On techniques for the measurement of the mass fractal dimension of aggregates. *J. Adv. Colloid Interf. Sci.*, 2001, **95**, 1–50.
11. Kim, A. Y. and Berg, J. C., Fractal heteroaggregation of oppositely charged colloids. *J. Colloid Interf. Sci.*, 2000, **229**(2), 607–614.
12. Hiramatsu, Y. and Oka, Y., Determination of the tensile strength of rock by a compression test of an irregular test piece. *Int. J. Rock Mech. Min. Sci.*, 1996, **3**, 89–99.
13. Walker Jr., W. J. and Reed, J. S., Influence of slurry parameters on the characteristics of spray-dried granules. *J. Am. Ceram. Soc.*, 1999, **82**(7), 1711–1719.
14. Bertrand, G., Roy, P., Filiatre, C. and Coddet, C., Spray-dried ceramic powders: a quantitative correlation between slurry characteristics and shapes of the granules. *Chem. Eng. Sci.*, 2005, **60**, 95–102.
15. Mahdjoub, H., Roy, P., Filiatre, C., Bertrand, G. and Coddet, C., The effect of the slurry formulation upon the morphology of spray-dried yttria stabilised zirconia particles. *J. Eur. Ceram. Soc.*, 2003, **23**, 1637–1648.
16. Fair, G. E. and Lange, F. F., Effect of interparticle potential on forming solid, spherical agglomerates during drying. *J. Am. Ceram. Soc.*, 2004, **87**(1), 4–9.
17. Krell, A. and Schädlich, S., Nanoindentation hardness of submicrometer alumina ceramics. *Mater. Sci. Eng. A*, 2001, **307**, 172–181.
18. Bertling, J., Blömer, J. and Kümmel, R., Hollow microspheres. *Chem. Eng. Technol.*, 2004, **27**, 829–837.
19. Yates, P. D., Franks, G. V., Biggs, S. and Jameson, G. J., Heteroaggregation with nanoparticles: effect of particle size ratio on optimum particle dose. *Colloids Surf. A*, 2005, **255**, 85–90.
20. Ismagilov, Z. R., Shkrabina, R. A. and Koryabkina, N. A., New technology for production of spherical alumina supports for fluidised bed combustion. *Catal. Today*, 1999, **47**, 51–71.
21. Dilsiz, N. and Akovali, G., Study of sol–gel processing for fabrication of low density alumina microspheres. *Mater. Sci. Eng. A*, 2002, **332**, 91–96.