Journal of the European Ceramic Society 23 (2003) 263–271

www.elsevier.com/locate/jeurceramsoc

Influence of slurry characteristics on the morphology of spray-dried alumina powders

G. Bertrand[a,*], C. Filiatre[b], H. Mahdjoub[a], A. Foissy[b], C. Coddet[a]

[a]*LERMPS-UTBM, Site de Sévenans, 90010 Belfort cedex, France*
[b]*LCMI-UFC, 16 route de Gray, 25030 Besançon cedex, France*

Received 28 December 2001; received in revised form 28 May 2002; accepted 1 June 2002

Abstract

Among all the parameters that must be managed to produce plasma sprayed coatings with controlled properties, the powder feedstock is a crucial point. The shape, density, morphology, composition and size distribution are the major characteristics of the powders that influence the coating properties and depend on the way of production. In the present work we focused on the spray drying which is a convenient process for producing sprayable ceramic powders. A systematic study has been performed to determine how the alumina slurry formulation (e.g. dispersant level, pH, binder addition) affects the granule characteristics. Aqueous slurries consisting of 30 vol.% of alumina particles, 0–1.2 wt.% ammonium polyacrylate as a dispersant and 15 wt.% styrene–ester acrylic copolymer as a binder were investigated using settling experiments and rheological analyses. Correlations appeared between sediment volume, zeta potential, yield stress and, viscosity of the slurries. At pH 4 and for 0.08 wt.% added PAA, the maximum flocculated suspension (without binder) is achieved as shown by the highest values of the sediment height (ratio of 0.85), yield stress and viscosity and the lowest zeta potential value. In contrast, at pH 9 and with the same dispersant concentration, the slurry, which is characterised by the lowest sediment ratio (0.45) and viscosity as well as no yield stress, is considered fully dispersed. Several spray dryer operating conditions were also investigated. Granules prepared from pH 4 slurry (flocculated) have solid, spherical shapes while the ones obtained from pH 9 slurry (dispersed) are hollow. It appears clearly that a close link exists between the floc structure and the granules morphology.

Keywords: Al_2O_3; Particle morphology; Rheological behaviour; Spray drying; Suspension

1. Introduction

Plasma spraying has gained in the last two decades an ever increasing importance in the engineering field of surface technology due to the continuously increasing costs of materials as well as greater material requirements.[1] The principle behind plasma spray is to melt material feedstock (commonly powder) and to accelerate the molten particles until impact on a substrate where rapid solidification and deposit buildup occur. The microstructure and the properties of plasma spray coatings depend not only on various process parameters, but are also markedly influenced by the characteristics of the used powder. While the spray parameters have been intensively investigated until recently, research currently focuses on the effects of the powder on the coating properties.[2–5] Up to now, the characteristics of the precursor powder that influence the plasma coating microstructure have been identified as size distribution, flow ability, morphology, density and chemical composition which depend on their means of production.

Among the industrial methods of powder manufacturing, the probably most versatile powder processing method is spray-drying.[6,7] Spray drying is the process by which a water or organic-based suspension (slurry) is transformed into a dry powder by spraying the fluid feed material into a hot drying medium. This process is a widely used method of producing granulated feed material for compaction processes. Indeed, spray drying enables the fabrication of composite powder by aggregation of any kind of small particles using an appropriate organic binder. Atomising and drying lead to a large variety of powder shapes; from uniform solid spheres which are regarded as ideal granules for

* Corresponding author. Tel.: +33-3-84-58-3240; fax: +33-3-84-58-3286.

E-mail address: ghislaine.bertrand@utbm.fr (G. Bertrand).

0955-2219/02/$ - see front matter © 2002 Published by Elsevier Science Ltd.
PII: S0955-2219(02)00171-1

most spraying systems to elongated, pancake, donut-shaped, needlelike or hollow granules.[8] Previous studies paid a great attention to the effects of feed characteristics and dryer operational conditions on the size distribution of the atomised droplets. But, very few authors have discussed on the importance of the slurry formulation on the characteristics of the ceramic granules and on the drying process while noticing that it is a non-negligible factor. Recently, Takahashi et al.[9] have found that decreasing the pH value of aqueous silicon nitride slurries dispersed with nitrilotriethanol deflocculant causes slurry flocculation and produces granules with reduced density. Walker et al.[10] have pointed correlations between aqueous alumina slurry formulation (binder type, solids concentration and PAA deflocculant level), slurry yield stress and granule characteristics. They also have found that high deflocculant level which corresponds to low slurry yield stress results in hollow granules. The work performed by Cao et al.[11] on ZrO_2–Al_2O_3 ceramics confirmed that the suspension preparation is a controlling factor of the properties of spray-dried powders.

The first step in gaining a better understanding of how the characteristics of granules influence the coating properties was to make granules with different shapes and densities. This was done by establishing relationships between the slurry formulation and the resulting spray-dried powders. For that, a study of the slurry behaviour (e.g. settling, rheological properties) as a function of pH, dispersant and binder amounts was conducted. Then, two specific slurries were selected according to their dispersion behaviour and as a last step the corresponding agglomerated powder were fabricated and analysed while using similar atomising conditions.

2. Experimental procedures

2.1. Materials and preparation of slurries

An α-alumina (P152SB, Aluminium Pechiney, France) with a specific surface area of 2.4 $m^2\ g^{-1}$ (standard B.E.T. N_2 method), an average particle size of 1.4 μm and a distribution ranging from 0.3 to 5 μm was used in the present study. In order to achieve self-standing ceramic powders by spray drying, the suspension must contain high solids concentration and be stable during the process. Consequently, experiments were conducted with slurries containing 30 vol.% alumina particles (Table 1). A commercial dispersant, ammonium polyacrylate (PAA-NH_4) with a molecular weight of 7000–8000 (P90, Coatex S.A., France) was used. The slurry pH values were adjusted with standard analytical grade HCl or NaOH solutions. Once the suspensions containing the alumina particles and the dispersant with adjusted pH were homogeneously stirred, the binder, a copolymer of styrene and acrylic ester (Rhodopas, Rhodia, France) was added.

Table 1
Slurry formulation

Components	Quantity
Solid particles:Al_2O_3	30 vol.%
Dispersant:PAA-NH_4	0–1.2 (dwb[a]%)
Binder:styrene-acrylic ester copolymer	0–15 (dwb%)

[a] dwb: weight amount of product on a dry weight basis of Al_2O_3.

2.2. Slurry characterisation

For such concentrated suspensions, settling experiments and rheological studies have been found appropriate to evaluate their behaviour. After mixing, the 30 vol.% suspensions were poured into test tubes and after 60 h the sediment heights were measured and the relative sedimentation value RSH (sediment cake height over suspension height) was determined. Then, the supernatants were removed and analysed. The amounts of polymer adsorbed onto the surface of the powder were calculated from the difference between the initial concentration and the remaining concentration in the supernatant. The polymer concentration in the supernatant was determined by measuring the carbon content using a Shimadzu 5050 total organic carbon analyser.

After centrifugation of alumina slurries, an aliquot of the suspensions was diluted in the supernatant and used to determine the electrophoretic mobility of alumina particles in a Rank Brothers II apparatus equipped with a rectangular microelectrophoresis cell. The zeta potential (ξ) was calculated using the Smoluchowski's equation.

The rheological measurements of the slurries were conducted using a controlled stress rheometer with a cone-plate geometry from Rheo (Carrimed CSL50). Fresh samples were ultrasonicated for 5 min then left standing for an additional 20 s before measurement. Flow curves were automatically recorded according to the following input conditions: the shear stress increased continuously from 0 to 30 Pa over a period of 2 min and then reversed from 30 to 0 Pa in 2 min. All the experiments were performed at a temperature of 20 °C.

2.3. Powder processing and characterisation

The laboratory spray drying apparatus schematically consists of a peristaltic pump that feeds the slurry into a counter-current stream of hot gas (about 200 °C) allowing a rapid evaporation of the liquid fraction and leaving agglomerated particles. The solid aggregates are collected at the bottom of the chamber and are separated from the gas in cyclone collectors. A schematic view of the spray dryer apparatus designed and realised in the laboratory can be found in a previous paper.[12] The main controlled spray drying parameters are the air temperature at the entry (220 °C), at the exit (143 °C) and inside the chamber (180 °C), the atomising nozzle design and the air and slurry flow rates. The powder morphology was observed by SEM (JSM 5800LV from JEOL) and its size distribution was checked by laser light diffusion (LS 130 from Beckman Coulter). Specific surface area measurements (standard B.E.T. N_2 adsorption) on spray dried granules were provided by Beckman Coulter France S.A.. A flow ability assessment procedure inspired from ASTM B213-90 standard was used to characterise this powder property.[13] The apparent and tap densities were also measured according to the ASTM B329-95 standard.[14] Finally, porosity was evaluated from measurements performed by mercury porosimetry (these experiments were performed graciously by Micromeritics, France).

3. Results and discussion

3.1. Alumina suspension behaviour: influence of pH and dispersant concentration

Without additive, the stability of a pH controlled aqueous suspension of fine Al_2O_3 particles is controlled by the electrostatic forces due to the ionised sites at the oxide surface. The variations of the zeta potential with pH (Fig. 1) indicate that the Iso Electric Point (IEP), pH value for which the zeta potential is null, of this alumina is reached at approximately pH 8.7. This value is in very close agreement with that of Cesarano et al.[15] or Pagnoux et al.[16] Meanwhile a higher value of about pH 9.2 has been reported for very high purity alumina sample.[17] The ionisation of the hydroxyl groups leads to, respectively, a large number of highly positive sites below pH 8.7 and negative sites above pH 8.7. If the alumina surface charges induce a sufficient repulsive potential between the particles, the suspension remains dispersed. At the pH of the IEP, attractive interaction between particles is not countered and the suspension achieves its highest flocculated state. This is confirmed in Fig. 2 where the relative sedimentation height (RSH) values are reported as a function of the alumina suspension pH.

In order to control the aggregation of the fine alumina particles in the slurry, an anionic dispersant (PAA-NH_4) whose functional groups are carboxylic acid groups was added. It is well established that the fraction of dissociated functional groups for a PAA chain varies with the solvent conditions (pH and ionic strength). Potentiometric titrations have shown that above pH 8.5 PAA is entirely negative whereas near and below pH 4 the fraction of dissociated carboxylic groups is almost equal to zero, and the polyelectrolyte is neutral.[18] At basic pH, the polymer is relatively stretched because of the electrostatic repulsion between the negative sites (COO^-), while in acidic solution the neutral polyelectrolyte is in the form of small coils.

Fig. 3 shows the adsorption isotherms of PAA on alumina particles at various pH values, plotted as Γ (mg of adsorbed PAA per m^2 of alumina particle) versus the initial amount of added PAA. The diagonal dot-line corresponds to 100% of adsorbed PAA. For pH 9, the polyelectrolyte is negatively charged whereas the zeta potential of the alumina particles is close to zero. In this case, either binding with some $M–OH_2^+$ groups or hydrogen interaction with M–OH sites can explain the adsorption of the PAA on the particle surface.[19] The polyelectrolyte chains adsorb in a relatively flat conformation, covering a large surface of the particle with some tails still extended into solution, leading to an electrosteric stabilisation of the suspension.[20] So, the saturation plateau is achieved for a value of Γ_{max} of 0.5 mg m^{-2}. In contrast, for pH < pH_{IEP} (pH 6 and 4), the surface charge of the particles is positive leading to an electrostatic interaction with the negatively charged groups of the polyelectrolyte chains. Due to the diminishing polyelectrolyte charge with the increase of the pH, the polymer chains achieve a loop configuration and cover a relatively small particle surface area leading

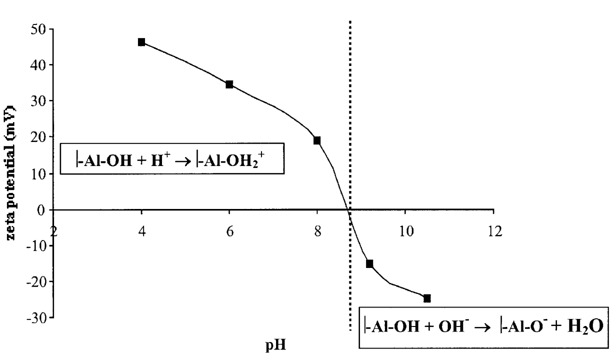

Fig. 1. Zeta potentials of alumina aqueous slurries without organic additives as a function of pH.

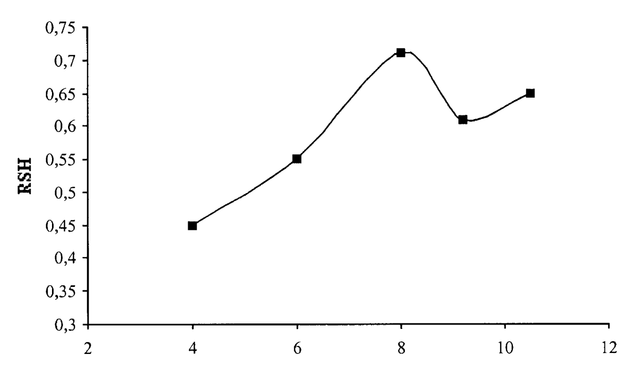

Fig. 2. Relative Sedimentation Height (sediment cake height over suspension height, RSH) versus pH for alumina suspensions in water (without organic additives).

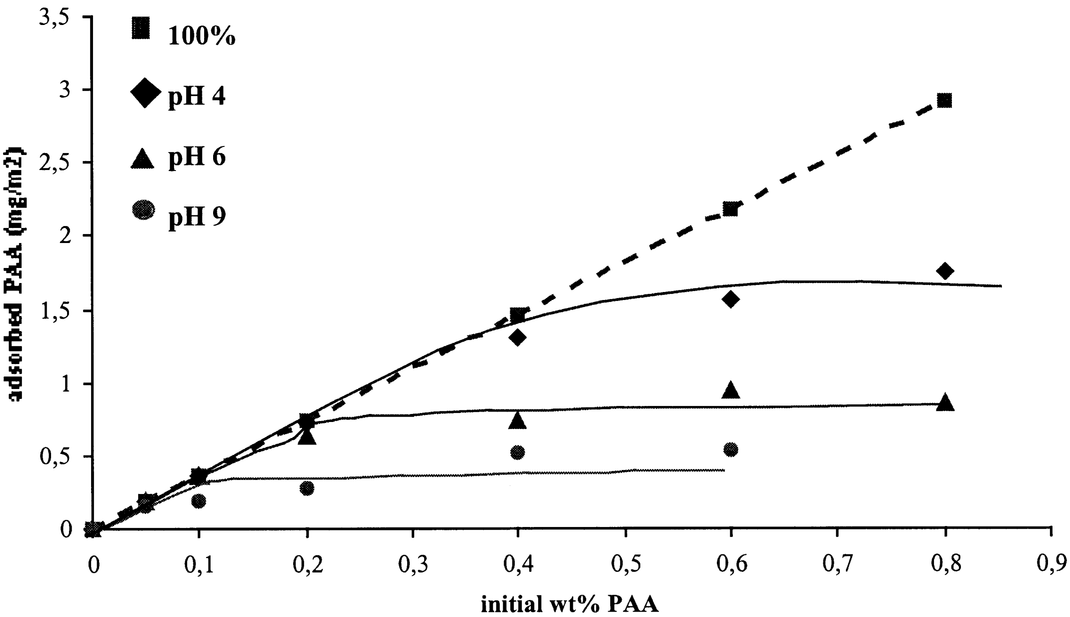

Fig. 3. Adsorption isotherms of PAA on Al_2O_3 as a function of pH.

to a greater amount of dispersant (at pH 4 $\Gamma_{max} = 1.5$ mg.m^{-2}) needed to reach the saturation level.

The influence of the PAA dispersant on sedimentation behaviour is reported on Fig. 4 for slurries at different pH. It can be noticed, for pH 4 and 6, that the sedimentation curves show a maximum of the settled volume, which corresponds to a flocculated slurry. This behaviour can be correlated with the zeta potential values reported on Fig. 5. Indeed, the maximum of the sedimentation curves occurs at the PAA concentration where the zeta potential is close to zero. Same correlation has also previously been suggested by different authors.[21,22]

At these pH values, small additions of PAA progressively neutralise the particle charge and lead to subsequent flocculation. This behaviour is evidenced by the

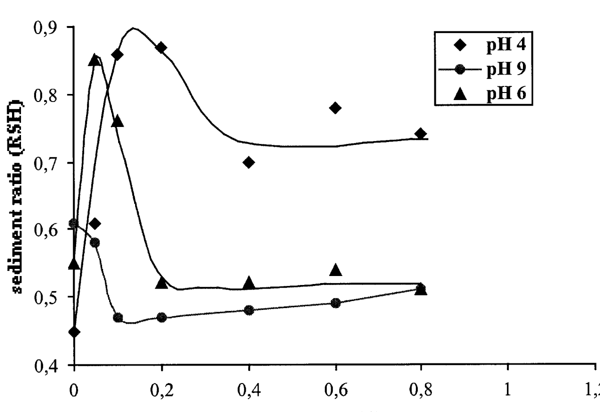

Fig. 4. Relative Sedimentation Height (RSH) versus amount of added PAA for 30 vol.% alumina slurries as a function of pH.

decrease to zero of the alumina particle zeta potential (Fig. 5). Fig. 4 also shows that beyond the maximum RSH value, increasing the PAA concentration decreases the RSH to a constant value of 0.5 at pH 6 and 0.7 at pH 4. These constant RSH values are reached when PAA concentrations equal respectively 0.4 wt.% at pH 4 and 0.2 wt.% at pH 6, which coincides with the onset of constant particle zeta potential around −40 mV. At pH 6 the suspension is dispersed (RSH = 0.5) whereas at pH 4 the suspension is still unstable (RSH = 0.7). This phenomenon could be attributed to the presence of ions provided, at such an acidic pH, by the dissolution of alumina (or surface impurities due to the fabrication process) as suggested by Jacquet.[23] Indeed, the work of this author showed that alumina powder (the same as the one used in this work) could release Al^{3+} but also Na^{+} and Ca^{2+} ions into the solution.

For pH 9, when the particles and the PAA are both negatively charged, the RSH value decreases from 0.6 to 0.45 with the increase in the PAA concentration and then stays constant for a PAA concentration higher than 0.08 wt.% (Fig. 4). In the same manner, the zeta potential decreases from −10 to −60 mV and then remains constant for the same PAA concentration (Fig. 5). For pH 6 and 9, the quality of the dispersion is correlated to the zeta potential.

Rheological measurements also provide information about the interactions between particles. An example of shear stress evolution versus shear rate flow curves as a function of PAA concentration is presented in Fig. 6. The slurries have a plastic behaviour. The yield stress values were determined from the experimental curves and the viscosity was obtained from the slope of the

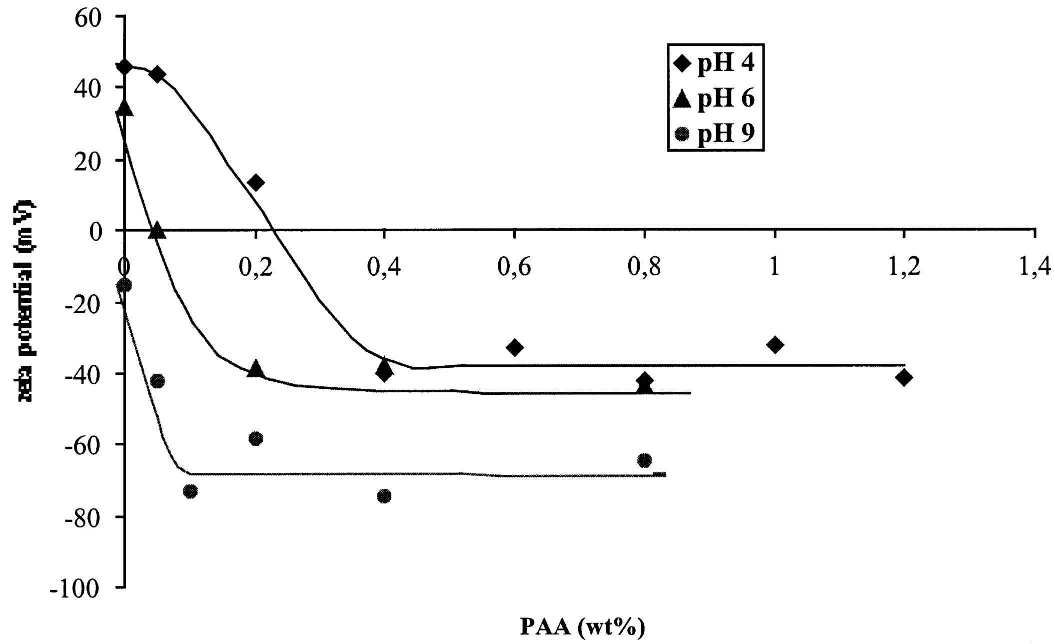

Fig. 5. Zeta potentials versus amount of added PAA for 30 vol.% alumina slurries as a function of pH.

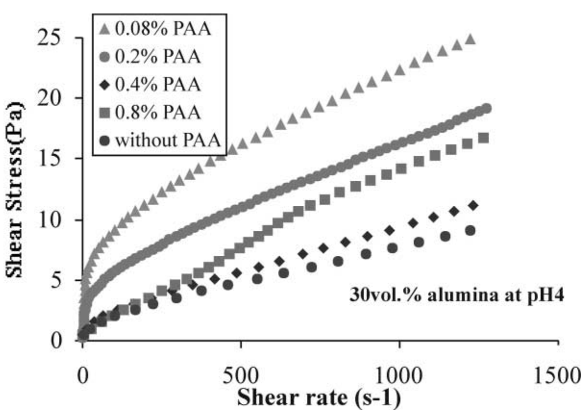

Fig. 6. Flow curves for 30 vol.% alumina slurries as a function of PAA concentration (fitting with the Casson model).

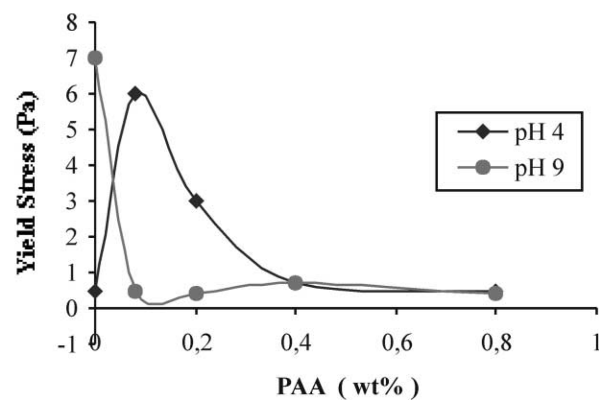

Fig. 7. Variation of the Casson yield value, τ_C, with PAA concentration for 30 vol% alumina slurries at pH 4 and pH 9.

linear part of the curve for shear rates ranging from 500 to 1200 s^{-1}.

Figs. 7 and 8 show respectively the evolution of the yield stress and the viscosity values as a function of the PAA concentration for pH 4 and 9 slurries. At pH 9, both the yield stress and the viscosity reach maximum values—respectively 7 Pa and 12 mPa s—when there is no additive in the suspension. In this case as the pH is close to the IEP (see Fig. 1), the inter-particle attraction is maximum, and so the particles form a network throughout the slurry. Adding the PAA dispersant decreases both the yield stress and the viscosity. A minimum in the viscosity value is observed at a PAA concentration of 0.08 wt.%. It corresponds to a minimum in the sediment height (Fig. 4) and to the highest absolute value of the zeta potential (Fig. 5). It seems that the suspension is better stabilised at this PAA concentration for pH 9. However the saturation limit of adsorbed polyelectrolyte is not reached. Guo et al.[24] showed that a saturated adsorption state was not necessary to obtain stabilisation of an aqueous alumina-ammonium polyacrylate suspension in the case of a non-high affinity adsorption and that over an optimum polyelectrolyte coverage the free polymer has a negative effect on the stability of these suspensions. Same trends are observed for pH 4. The yield stress (6 Pa) and the viscosity (12 mPa s) are maximum at the IEP for a PAA concentration close to 0.2 dwb%. The minimum of yield stress and viscosity that appear at a PAA concentration of 0.4 dwb% correspond to a minimum of the sediment ratio (RSH of 0.7) on Fig. 3 and also to the highest absolute zeta potential value (−40 mV). Between 0.4 and 0.8 wt.% PAA concentration, both an increase of viscosity and of the sedimentation ratios were observed.

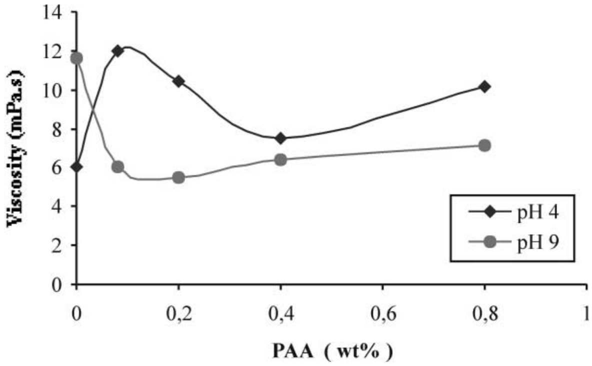

Fig. 8. Variation of the viscosity, η, with PAA concentration for 30 vol.% alumina slurries at pH 4 and 9.

3.2. Effect of the addition of a binder to the alumina suspension

Before spray drying, a binder (in the present study a copolymer of styrene and acrylic ester) must be added in the slurry in order to ensure sufficient mechanical strength of the produced agglomerated powders. 15 wt.% were found to be an adequate value for the latex binder used in this work to achieve round, cohesive and sprayable powders.

The effect of the binder addition was checked on two kinds of alumina slurries selected from the previous study: those elaborated at pH 4 and 9. Adding 15 dwb% binder to an alumina suspension (30 vol.% Al_2O_3 in water without dispersant) leads to RSH values respectively of 0.65 and 0.45 at pH 4 and 9. It also has to be noticed that the binder changes the pH of the acidic suspension which tends to pH 7.5. As observed previously, the alumina slurry at pH 9 without dispersant has a plastic behaviour whereas the slurry at pH 4 tends to have a Newtonian one (Fig. 9). Adding 0.08 dwb% PAA leads to the opposite behaviour for both slurries; a yield stress appears on the pH 4 curve while it strongly decreases at pH 9. Correlatively, the addition of 0.08 dwb% dispersant increases the RSH values from 0.45 to 0.85 in the case of an acidic slurry whereas it decreases from 0.6 to 0.45 for a slurry at pH9. Finally when 15 dwb% binder is added, the curves do not show a yield stress and no viscosity variations are noticeable whatever the pH (7.5 or 9) (Fig. 9) and the PAA concentration (Table 2). So in the studied conditions the binder seems to govern the rheological properties of the slurries. However, drops of slurries observed with an optical microscope showed the presence of particles aggregates in a slurry at pH 4 (pH value adjusted before or after the addition of the binder) whereas for the slurry at pH9 the particles are isolated and very mobile.

Table 2
Viscosity values of 30 vol.% Al_2O_3 slurries with 15 dwb% binder at various PAA concentrations for pH 4 and 9

PAA concentration (dwb.%)	0.08	0.2	0.4	0.8
pH 4	8.2	6.7	8	7.4
pH 9	7.1	7.8	8	8.8

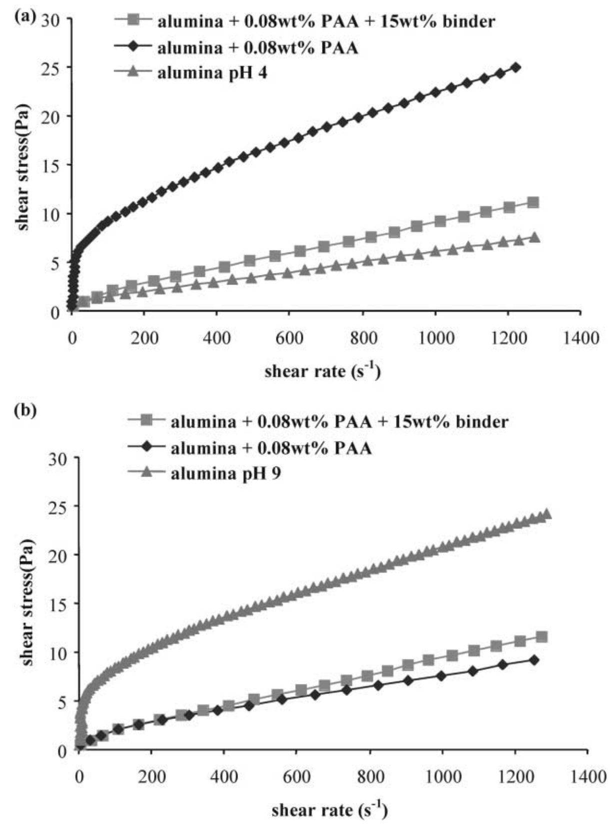

Fig. 9. Effect of dispersant and binder additions on flow properties of 30 vol.% alumina suspensions at (a) pH 4 and (b) pH 9.

3.3. Correlation between the granule characteristics and the slurry behaviour

According to the previously described results on the slurry behaviour, two specific compositions were selected to produce spray-dried powders: 30 vol.% Al_2O_3, 0.08 dwb% PAA-NH_4, 15 dwb% binder at an acidic pH (pH 4) and a basic pH (pH 9). The drying step was kept unchanged for all experiments: drying temperature of 180 °C and flow rate of heated air of 15 m^3/h. While the atomising nozzle design was fixed, the influence of the feeding rate and the atomising air flow rate on the particle size were investigated.

The relationships between the granule size, the tapped density, the flow ability and the drying operating conditions are reported in Table 3. It is clearly shown that atomising air flow rate and to a less extent feeding rate have the most effective influence on particles size whereas tapped density and flow ability highly depend on slurry flocculation. It is noteworthy that the factors which influence flow ability of the powder include particles size, particles size distribution, particles

Table 3
Influence of operating conditions of the spray-dryer on the characteristics of alumina powders (granule size range from 36 to 63 μm)

Sample	pH	Feeding rate (l/min)	Air flow rate (m^3/h)	ϕ50[a]	d[a]	Flow ability (g/min)
AL01	9	1.25	15	33	1.02	520
AL02	9	1.25	12	46	1.00	610
AL03	9	1.5	15	38	1.02	535
AL04	9	1.5	12	–	–	–
AL05	4	1.25	15	35	1.32	–
AL06	4	1.25	12	45	1.35	3570

[a] ϕ50 and d are respectively the mean particles size and tapped density of the dried powders.

morphology and moisture content. Our results evidenced the fact that solid spherical powders (AL05) with few surface defaults are freeflowing powders whereas powders with irregular hollow shapes such as AL01 are only semi-freeflowing ones.

Fig. 10 shows typical granule shapes. Most granules are roughly spherical, but some are elongated or twined. A common feature of spray-dried ceramic materials is the formation of particles with a large crater as shown in Fig. 10b. The aggregates formed from basic slurries contain more granules with crater than those made from acidic slurries. In fact, it seems that the morphology of the powder depends highly on the formulation of the slurry and more precisely on the state of dispersion or flocculation of the solids particles. Fig. 11 shows polished cross-sections of the granules from acidic (AL05) and basic (AL01) slurries. The granules described as 'aggregates with crater' are in fact hollow powders. The crater corresponds to a large single open pore. Porosity measurements confirm these observations as an

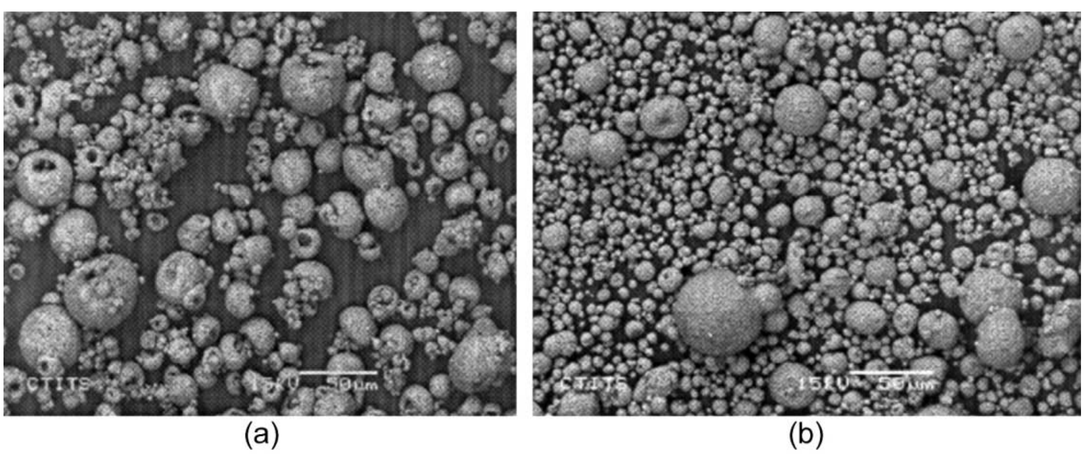

Fig. 10. Typical granules: (a) AL01 0.08% deflocculant, 15% binder, pH 9 and (b) AL05 0.08% deflocculant, 15% binder, pH 4.

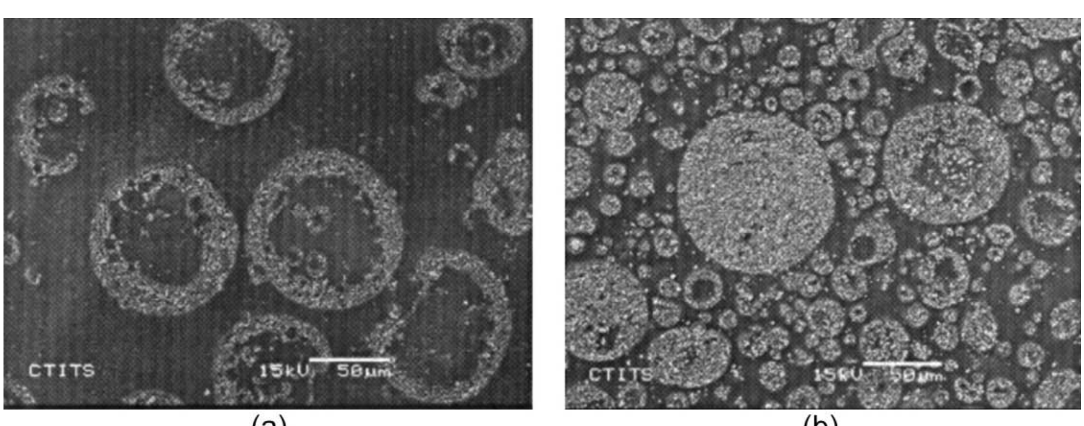

Fig. 11. Polished cross sections of granules AL01 (a) and AL05 (b).

average pore size of about 15 μm was observed for AL01 sample (Table 4). In contrast, granules AL05 are solid aggregates with an average porosity size around 5 μm in diameter.

From these observations, it is possible to propose an explanation for the formation of solid or hollow granules in the case of ceramic slurries based on a model proposed by Walker et al.[10] As the slurry is atomised, its fluidity is sufficient ($\eta_\infty < 15$ Pa s) to form spheres in most cases. Indeed, very few irregular shapes were observed during granule morphology analyses. During the drying process, the water migrates outside the granule and evaporates at the surface. As the binder is a water-soluble compound, it is able to migrate with the water. When particles are fully dispersed in the slurry with no interaction between each other, which is the case of the basic suspension, they are very mobile and can pack densely. Consequently, particles and binder move to form a dense shell leaving behind an internal void. Because of the difference of pressure between the internal void and the ambient atmosphere, one part of the granule collapses generating a hollow powder. In contrast, when the slurry is flocculated (acid slurry), the particles can be considered as immobile; the shell does not appear and solid granules are formed. In this case, the binder can also migrate with water toward the outside of the granule but a diffusion process in the opposite way may occur because of the development of a concentration gradient as proposed by Baklouti et al.[25] The shell formation and binder segregation, which are enhanced in hollow granule, can be correlated with specific area measurements. As the specific area was evaluated on the same granules size distribution for AL01, AL05 and AL05-sintered, the reported evolution could be closely linked with the binder presence and segregation (Table 4). Indeed, the low specific surface area measured for hollow granules seems to indicate that the shell composed of alumina particles embedded in a binder matrix is impermeable. When the binder is burnt during the 'debinding stage' for AL05-sintered solid particles, the initial specific surface area is recovered which confirms the binder segregation phenomenon.

These results are in accordance with observations performed by Ishimori et al.[26] in the case of a silica spray-dried powder, Cao et al.[11] in the case of a YSZ spray-dried powder and more generally concerning ceramic powders by Lukasiewicz.[27] All these works concluded that the major factor controlling the density of the granules is the slurry preparation. We shown here more precisely that the floc structure (probably its strength, size and shape) is the key parameter to control the final granule density and shape. Consequently, it seems to appear that the spray-dryer operating conditions did not influence whether the granules are hollow or solid but control the granule size distribution. However the effects of the slurry on the characteristics of the granules have to be studied together with the drying step.

Table 4
Evolution of the specific surface area (BET) and porosity (Hg intrusion) as a function of spray-dried powder morphology (granule size range from 36 to 63 μm)

Sample	Specific surface area (m^2/g)	Porosity (μm) intragranular–intergranular
Al_2O_3 initial	2.4	0.4
AL01	0.6	0.3–15
AL05	1.7	0.4–5
AL05-sintered	2.4	

4. Conclusion

The present work has established unequivocally that the spray-dried granule characteristics are very sensitive to the nature and strength of the inter-particle interactions. Rheological measurements (e.g. viscosity and yield stress) and sedimentation tests seem to be appropriate means of probing these inter-particle agglomerates in concentrated alumina slurries. Thus, it was shown that:

1. Strong correlation exists between sediment volume, zeta potential, yield stress and viscosity. A low sediment height ratio corresponding to low yield stress and viscosity leads to a dispersed slurry as it was the case for the pH 9 alumina suspension with 0.08 dwb% PAA. Adsorption of the dispersant PAA on the solid particles was explained in the light of surface charge density leading to the conclusion that the stabilisation was mainly electrosteric.
2. Adding 15 dwb% binder to the suspension leads all the slurries to have the same rheological behaviour (with no pH post-adjustment) dictated by the binder rheology. Meanwhile, the interaction between the dispersant and the binder is not yet clearly understood.
3. A flocculated slurry leads to solid granules whereas a dispersed suspension leads to hollow granules. An explanation was proposed based on the mobility of solids particles during the drying step correlated to their mobility in the suspension.

Acknowledgements

The authors are grateful to C. Clément from CATION S.A. for the SEM observations. Special thanks go to S. Sigrist from Micromeritics France S.A. for mercury intrusion tests on spray-dried powder samples and to P. Ramseyer from Beckman Coulter France S.A. for BET measurements.

References

1. Pawlowski, L., *The Science and Engineering of Thermal Spray Coatings*. J. Wiley and Sons, New York, 1995.
2. Chuankian, D., Zatorski, R. A., Herman, H. and Ott, D., Oxide powders for plasma spraying. The relationship between powder characteristics and coating properties. *Thin Solid Films*, 1984, **118**, 467–475.
3. Wigren, J., de Vries, J.-F. and Greving, D., Effect of powder morphology, microstructure, and residual stresses on thermal barrier coating thermal shock performance. In *Thermal Spray: Practical Solutions for Engineering Problems*, ed. C. C. Berndt. ASM International, OH, USA, 1996, pp. 855–861.
4. Kollenberg, W. and Decker, J., Influence of powder characteristics on the microstructure of ceramic plasma spray coatings. *Fresenius J. Anal. Chem.*, 1993, **346**, 327–333.
5. Georgiopoulos, E., Tsetsekou, A. and Andreouli, C., The effect of $YBa_2Cu_3O_{7-x}$ powder characteristics on thick coatings prepared by atmospheric plasma spraying. *Supercond. Sci. Technol.*, 2000, **13**, 1539–1548.
6. Thümmler, F. and Oberacker, R., In: *Introduction to Powder Metallurgy*; Ed. I. Jenkins and J. V. Wood. Institute of Materials, London, 1993.
7. Masters, K., *Spray Drying Handbook*, 4th edn. Wiley and Sons, New York, 1985.
8. Walton, D. E. and Mumford, C. J., Spray dried products—characterization of particle morphology. *Trans IchemE*, 1999, **77** (Part A), 21–38.
9. Takahashi, H., Shinohara, N. and Uematsu, K., Influence of spray-dry slurry flocculation on the structure of sintered silicon nitride. *J. Ceram. Soc. Japan*, 1996, **104**(1), 59–62.
10. Walker, W. J. jr, Reed, J. S. and Verma, S. K., Influence of slurry parameters on the characteristics of spray-dried granules. *J. Am. Ceram. Soc.*, 1999, **82**(7), 1711–1719.
11. Cao, X. Q., Vassen, R., Schwartz, S., Jungen, W., Tietz, F. and Stöever, D., Spray-drying of ceramics for plasma-spray coating. *J. Eur. Ceram. Soc.*, 2000, **20**, 2433–2439.
12. Bertrand, G., Meunier, C., Bertrand, P. and Coddet, C., Dried particle plasma spray in-flight synthesis of spinel coatings. *J. Eur. Ceram. Soc.*, 2002, **22**, 891–902.
13. Standard Test Method for Flow Rate of Metal Powders, ASTM B 213–90.
14. Standard Test Method for Apparent Density of Metal Powders and Compounds using the Scott Volumeter, ASTM B 329–95.
15. Cesarano III, J., Aksay, I. A. and Bleier, A., Stability of Aqueous α-l_2O_3 Suspensions with Poly(methacrylic acid) Polyelectrolyte. *J. Am. Ceram. Soc.*, 1988, **71**(4), 250–255.
16. Pagnoux, C., Laucournet, R., Chartier, T. and Baumard, J-F., Dispersion of aqueous Al_2O_3 suspensions with electrolytes; influence of the counter ion. *The Korean Journal of Ceramics*, 2000, **6**(3), 280–285.
17. Palmqvist, L. M., Lange, F. F., Sigmund, W. and Sindel, J., Dispersion and consolidation of alumina using a bis-hydrophilic diblock copolymer. *J. Am. Ceram. Soc.*, 2000, **83**(7), 1585–1591.
18. Pochard I., PhD Thesis, University of Franche-Comté, Besançon, France 1999.
19. Gourmand M., PhD Thesis, University of Paris VI, Paris, France, 1998.
20. Cesarano III, J. and Aksay, I. A., Processing of highly concentrated aqueous α-alumina suspensions stabilized with polyelectrolytes. *J. Am. Ceram. Soc.*, 1988, **71**(12), 1062–1067.
21. Leong, Y. K., Scales, P. J., Healy, T. W., Boger, D. V. and Buscall, R., Rheological evidence of adsorbate-mediated short-range steric forces in concentrated dispersions. *J. Chem. Soc. Faraday Trans.*, 1993, **89**(14), 2473–2478.
22. Petterson, A., Marino, G., Pursiheimo, A. and Rosenholm, J. B., Electrosteric stabilization of Al_2O_3, ZrO_2, and 3Y-ZrO_2 suspensions: effect of dissociation and type of polyelectrolyte. *J. Colloid Interface Sci.*, 2000, **228**, 73–81.
23. Jacquet, A., PhD Thesis, University of Franche-Comté, Besançon, France, 1998.
24. Guo, L-C., Zhang, Y., Uchida, N. and Uematsu, K., Adsorption effects on the rheological properties of aqueous alumina suspensions with polyelectrolyte. *J. Am. Ceram. Soc.*, 1998, **81**(3), 549–556.
25. Baklouti, S., Chartier, T. and Baumard, J. F., Binder distribution in spray-dried alumina agglomerates. *J. Eur. Ceram. Soc.*, 1998, **18**, 2117–2121.
26. Ishimori, T. and Senna, M., Control of microstructure and disintegration properties of silica granules from PVA slurries by spray drying. *J. Materials Science*, 1995, **30**, 488–495.
27. Lukasiewicz, S. J., Spray-drying ceramic powders. *J. Am. Ceram. Soc.*, 1989, **72**(4), 617–624.