

The effect of the slurry formulation upon the morphology of spray-dried yttria stabilised zirconia particles

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Abstract

A study has been performed to determine how the characteristics of spray-dried granules prepared from aqueous yttria doped zirconia slurries can be affected by the spray-drying process parameters: dispersant amount, pH and binder type. First, the colloidal stability of aqueous zirconia suspensions as a function of polyacrylic acid content, pH and binder nature has been investigated in order to establish a stability map. The concentration of dispersant required to stabilise the zirconia suspensions decreases with increasing pH (for instance $\Gamma_{\max} = 0.93 \text{ mg m}^{-2}$ at pH 4 and 0.1 mg m^{-2} at pH 10). The addition of a binder may modify the state of dispersion. The stability map makes it possible to define regions of stable (dispersed) and unstable (floculated) suspensions. Then, dried granules have been produced by means of a single droplet drying method. Granules prepared from a dispersed slurry (low Ratio Sediment Height—RSH < 53%) result in hollow shapes that contain a single large open pore. Changing the nature of the binder from latex to an hydrosoluble compound (polyvinyl alcohol) has an effect on the wall thickness of the hollow granules. Conversely, granules obtained from a floculated slurry (high RSH > 62%) result in full granules. The sedimentation volume, which represents the state of dispersion of the suspension, is the major factor controlling the droplet drying mechanism.

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1. Introduction

Plasma-sprayed thermal barrier coatings (TBC) are widely used in gas turbine engines by the aeronautical industries.¹ A TBC consists of a thermally insulating ceramic top layer—most generally, yttria partially stabilised zirconia (PSZ)—and an intermediate oxidation resistant metallic bond-coat layer. The main purpose of this dual layer system is to provide thermal insulation of the superalloy components, thus improving performance or lifetime.² The life and thermal properties of the plasma-sprayed TBC are closely related to the microstructure of the ceramic top coating, which has been described as a build-up of flattened lenticular grains with microcracks and laminar pores of various sizes and lengths.³ It is now assumed that the thermal conductivity of this ceramic coating is governed by the

void microstructures (coarse and fine pores and fine cracks) which are in turn determined by both the spraying conditions and the feedstock material.^{4,5} The first step in enhancing the thermal behaviour of the plasma-sprayed TBC coatings is to control and then optimise the powder feedstock, which are, for YSZ-TBC, mainly originated from the spray-drying process.

When making ceramics, spray drying is the process by which a water-based suspension (slurry) is transformed into a dry agglomerated powder by spraying the fluid feed material into a stream of heated air. Spray drying enables the fabrication of composite powder by aggregation of different small particles using an appropriate organic binder. The rapid heat and mass transfer which occurs during drying combined with the presence of various slurry compounds result in dried granules having a large variety of shapes; from uniform solid spheres which are regarded as ideal granules for most ceramic systems to elongated, pancake, donut-shaped, needlelike or hollow granules.^{6,7} Both factors—slurry properties

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and drying conditions—which affect the spray granulation mechanism, are receiving increasing attention. The object of this study is to assess the effect of the state of dispersion and sedimentation stability of the slurry on the drying of a single droplet.

Indeed to determine the effect of the process variables upon the morphology of the spray-dried particles, several approaches can be used in experimental studies. The most common involves the analysis of dried powders collected after the granulation.⁸ Although this provides information concerning the powder morphology, it gives no information about the granulation mechanism. On the other hand, the direct observation of particle formation in situ is very difficult. Consequently, the single droplet drying method seems to be appropriate to catch information concerning the formation of the particle.⁹ This allows real-time analysis—with simultaneous measurements of surface area, weights, . . .—of the drying pendant droplet under controlled conditions of air temperature, velocity and humidity. But up to now, few works deal with the influence of the preparation of the slurry on the drop drying as the formulation of the slurry is usually not considered as part of the drying operation.

The slurry preparation and the control of the state of dispersion and sedimentation stability of colloidal suspensions were considered here as key factors in determining the formation mechanism of the different dried particles shapes. It is noteworthy that ceramic particles in solution are naturally positively or negatively charged depending on the pH conditions. But, in high solid content suspensions, it is difficult to obtain homogeneity and stabilisation without adding a dispersant.¹⁰ Polymers, among which anionic polyelectrolytes, are widely used to manage the state of dispersion of aqueous suspension. Depending on the nature of the ceramic particles, particle size distribution, surface impurities as well as pH and ionic strength, the amount of dispersant must be optimised to achieve the saturation adsorption coverage of the solid particles in the suspension. Besides, to provide self-standing compact agglomerated granules, a binder—PVA, latex, . . .—is added in the suspension.^{11,12} Thus, the suspension is a complex system in which all additives can interact between themselves and with solid particles.¹³

The present investigation is an attempt to understand better the relationships between the slurry formulation and the granule characteristics. First, various amounts of PAANH₄ (ammonium salt of poly(acrylic acid)) acting as a dispersant were added to a suspension based on yttria partially stabilised zirconia particles (ZrO₂–8 wt.% Y₂O₃) and the slurry behaviour was investigated as a function of pH in order to find out the suitable stabilisation conditions. The effect of the addition of two different binders, which are the compounds that allow to achieve agglomerated granules, on the dispersion state of

the slurry was also studied. Once the stability map was established for the slurries containing all the additives, a single droplet drying test was performed. The objectives are to identify the factors of the slurry that affect the drying result and how they modify the shape of the relevant granule.

2. Materials and experimental procedures

2.1. Materials

A zirconia powder, containing 8 wt.% yttria with a specific surface area of 6.7 m² g⁻¹ (N₂ BET method) and an average particle size of 0.6 μm was used in the present study (supplied by Saint-Gobain Ceramic Materials). To achieve well-stabilised and dispersed zirconia slurries, a commercial polyelectrolyte—an anionic dispersant—the ammonium salt of polyacrylic acid (PAANH₄), with an average molecular weight of 7000–8000 (Coatex S.A., France) was added.

A very strict mixing procedure was carried out. A specific amount of dispersant was first added to distilled water and stirred for 5 min. Then the zirconia powder is gradually added and the suspension was stirred again for an additional 15 min. At that time the pH was adjusted with diluted solutions of HCl (1N) or NaOH (1N). Until equilibrium was reached, the suspension was continuously stirred (about 30 min).

Finally a binder, either latex based on a copolymer of styrene and acrylic ester (Rhodia, France) or an hydro-soluble polyvinyl alcohol—PVA (Rhodia, France) was added.

2.2. Slurry characterization

In order to achieve spray dried ceramic powders, the slurry must contain high solids loading and be stable during the process. For such concentrated suspensions, settling studies have been found appropriate to evaluate the suspensions behaviour. After mixing, the suspensions were poured into test tubes and after about 90 h the sediment heights were visually 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 zirconia slurries, an aliquot (50 μl) was diluted in the supernatant and used to determine the electrophoretic mobility of zirconia particles in a Rank Brothers II apparatus equipped with a

rectangular microelectrophoresis cell. The zeta potential (ζ) was calculated using Smoluchowski's equation.

2.3. Drying studies of suspended single droplets

A single droplet drying technique was used to investigate the drying behavior of droplets containing suspended solids in order to evaluate the effect of the slurry on the dried powder. Fig. 1 shows a schematic view of the experimental device developed in the laboratory.

Individual droplets were suspended using a hypodermic syringe in a stream of heated air provided by a regulated hotplate equipped with an insulation device. The drying air temperature was measured near the droplet surface using a thermocouple, and kept constant at about 150 °C. The relative humidity of the air, measured using an hygrometer, was about 25%. Once in place, the droplet shape was registered during the drying stage by a CCD camera installed in front of the pendant drop and coupled with an image acquisition system.

Images of the droplet were recorded every 40 s at the beginning of the drying period and every minute beyond 5 min. To obtain information about the drop features, the input images were first converted to binary images using an image analysing software (Scion). The conversion was done by manual thresholding. Then, the droplet surface was defined and its projected surface area was calculated and reported versus the drying time. Finally, A/A_0 , which is the ratio of the projected surface area at the end of drying, over the initial projected surface area measured at the beginning, was calculated. To ensure a good accuracy of the results and to control the reproducibility, three drying tests were realised with each slurry.

At the end of the drying period, the dried granules were collected, embedded in a fluid epoxy resin under low pressure, carefully polished with a 3 μm diamond suspension on a cloth and then observed to determine their basic morphologies.

3. Results and discussion

3.1. Yttria-doped zirconia suspension: influence of pH, solid loading and dispersant concentration

Metal oxides hydrolyse in the presence of water and at every pH the hydroxide layers containing MOH groups ($\text{M} = \text{Zr}^{4+}, \text{Y}^{3+}$) react with protons or hydroxyl ions. The ionisation of the hydroxyl groups leads to changes in the surface charge. The isoelectric point (IEP) of the powder corresponds to the pH value at which the electrokinetic surface charge of the particle is zero. The variations of the zeta potential with pH show that the IEP of the used zirconia is situated at approximately pH 5.8 (Fig. 2). This value is in good agreement with that of Agrafiotis et al.¹⁴ Values lying between pH 6 and 9 have been reported depending on the yttria content.¹⁵ Indeed reported values for the IEP of pure yttria show more basic values than values for the IEP of zirconia. The net surface charge of the zirconia particles is positive at $\text{pH} < \text{IEP}$ and negative at $\text{pH} > \text{IEP}$. It is noteworthy that the suspension stability is related to high zeta potentials. As a consequence in a pH zone far from the IEP value it can be expected that the zirconia surface charges are sufficient to induce a repulsive force between the particles leading the suspension to remain dispersed. But, on top of the pH which affects the zeta

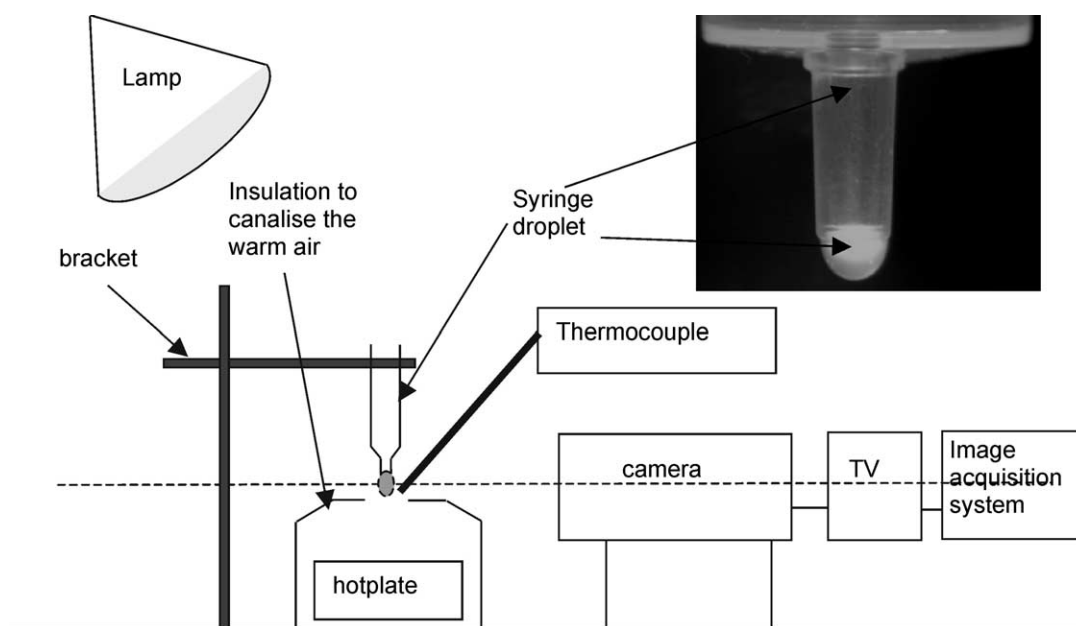


Fig. 1. Single droplet drying apparatus.

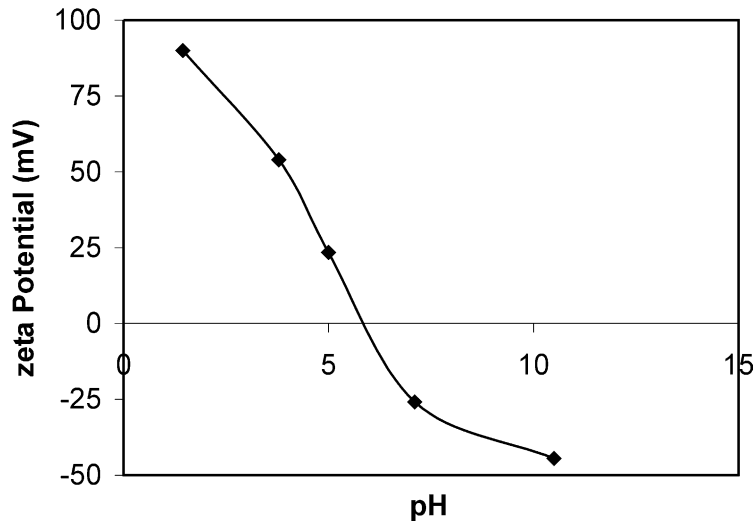


Fig. 2. Zeta potential of yttria-doped zirconia aqueous slurries as a function of pH. Solid loading: 50 wt.%.

potential, the solid loading may also have an influence on the particle behaviour.

Fig. 3 shows the results of the sedimentation experiments for zirconia suspensions at various pH and solid loadings. A 10 wt.% solid loading suspension shows similar sedimentation heights whatever the pH. In that case, the suspension is sufficiently diluted to consider that the particles behave as isolated particles. For more concentrated slurries (>20 wt.%), interactions between particles can appear and induce a pH dependence of the sedimentation behaviour. In fact, two domains can be defined where the sedimentation phenomenon is different:

(a) $5 < \text{pH} < 8$: the sedimentation phenomenon is fast and total. The sediment/liquid interface is clearly defined.

(b) $8 < \text{pH} < 5$: the sedimentation rate is slower and the sediment/liquid interface is not clearly defined due to the turbidity of the supernatant.

For concentrated suspensions (20 and 35 wt.%), the sedimentation heights between pH 5 and 8 are nearly twice those over pH 8 and below pH 5. As expected, in the pH range lying between 5 and 8, which includes the IEP, the attractive interactions between particles are dominant and the suspension achieves its most flocculated state. On the contrary when the zeta potential is over 25 mV, well-dispersed slurries seem to be obtained below pH 5 and between pH 8 and 10. In highly basic solutions ($\text{pH} > 10$), RSH values increase. To achieve the basic condition, more NaOH is needed to adjust the pH, the ionic strength is increased, reducing the thickness of the electric layer. The particles come close to

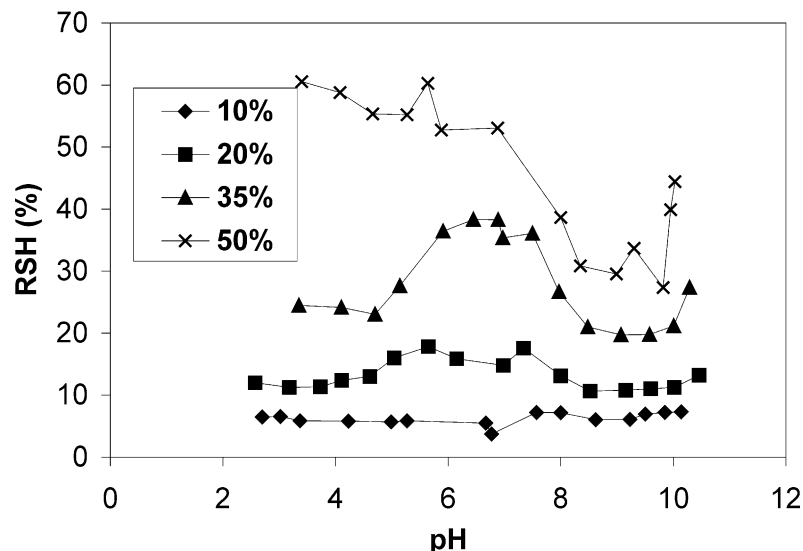


Fig. 3. Sedimentation height as a function of pH and solid loading (10, 20, 35 and 50 wt.%).

each other, risking attraction due to Van der Waals forces; the stability of suspensions may thus be strongly affected giving the higher sedimentation heights measured.

Contrary to the zeta potential measurements ($\zeta \gg 25$ mV at pH < 5), higher sedimentation heights have been observed for the more concentrated suspensions (50 wt.%) in the acidic range below pH 5. The mismatch between the zeta potential and the RSH in the acidic pH zone may possibly be attributed to an yttria dissolution. Indeed, it has been shown that yttria is highly basic and prone to dissolve in acidic solutions.^{15–18} The amount of yttrium ions Y^{3+} leached out in the media can become important after several hours leading to compression of the diffuse layer. The stability of the suspension may thus be strongly affected as observed in sedimentation experiments that lasted for several days and where the solid loading was high (50 wt.%). This phenomenon did not appear during electrophoretic mobility measurements because the particles were exposed to acidic media for a short time.

In a zirconia/water suspension, particles may possibly become dispersed in a repulsive manner by electrostatic forces developed on their surface depending on the solvent conditions (pH and ions). But, it is difficult to obtain homogeneous, well stabilized and dispersed high zirconia content suspensions without the use of a dispersant.

To control the zirconia slurry stability against sedimentation, an anionic dispersant PAANH₄ with carboxylic acid groups was added. Potentiometric titrations indicated that ionisation of PAANH₄ with increased pH led to a configurational transformation from a compact random coil at low pH to a fully expanded molecule at high pH. The number of COO⁻ dissociated groups increases with pH and above pH 8.5 PAA is entirely negative whereas near and below pH 4 the fraction of dissociated groups is almost equal to zero.¹⁹ At a given pH, the adsorption saturation limit of the polyelectrolyte depends on the available sites for adsorption of the dissociated groups on the particle surface, on the charge density and on the configuration of the polyelectrolyte.

Thus, the adsorption isotherms of PAANH₄ on ZrO₂ particles, as a function of pH are presented in Fig. 4. These plots show Γ (mg of adsorbed polyelectrolyte per m²) versus the initial amount of PAA added to the suspension. The dashed line represents the adsorption behaviour that would occur if 100% of the PAANH₄ added were adsorbed. For all pH values investigated, the adsorption curves show a characteristic plateau, which corresponds to the amount of PAANH₄ required for full coverage. The Γ_{\max} values for which the saturation plateau is achieved are reported in Table 1. A decrease in the amount of the adsorbed polymer is observed with the increase of the pH. For pH 4, nearly all the polymer was adsorbed until the adsorption plateau was reached. Therefore, for acidic pH values, the

adsorption behaviour is of high-affinity type due to the diminishing polyelectrolyte charge; the polymer chains achieve a loop configuration and cover a relatively small particle surface area leading to more dispersant to reach the saturation level. For the other isotherms the adsorption behaviour is of low affinity, with most of the polymer remaining free in the solution. The polyelectrolyte chains adsorb in a relatively flat conformation covering a large surface of the particle. The polymer and the particles are both negatively charged, which is an unfavourable situation for polymer adsorption. But a special phenomenon seems to appear on this curve: the presence of a plateau before reaching the saturation level showing a very low amount of PAA adsorbed.

Fig. 5 shows the effect of the dispersant on the sedimentation behavior of slurries at pH 4, 7, and 10. At pH 4, between 0 and 0.5 wt.% PAA added to the slurry, the sedimentation curve shows a maximum of the settled volume, which suggests flocculated slurries. This result can be correlated to the zeta potential values shown in Fig. 6. Indeed, these elevated sedimentation heights occur near the PAA concentration where the zeta potential is almost equal to zero. At pH 4, the few negatively charged carboxyl groups from the slightly dissociated PAA are very easily adsorbed on the positive charged zirconia surface. Consequently the powder is progressively covered by the polyelectrolyte which neutralises the particle charge and leads to the formation of flocs. Shojai et al.²⁰ observed an increase in viscosity at pH 4 with 3Y-TZP particles for low amount of polyelectrolyte and assumed that the polymeric chains adsorb on more than one particle and generate, in this way, bridges between particles. In our zirconia slurries, it should be difficult for the polymeric chains to adsorb on more than one particle due to the loop configuration of the PAA. Tang et al.²¹ showed that in the case of high-affinity adsorption, observed for 3Y-ZrO₂ slurries in acidic conditions, a heterogeneous distribution of the polyelectrolyte at low amount of added dispersant occurs which destabilizes the slurry and leads to agglomeration. For over 0.5 wt.% dispersant added, the sedimentation height is constant and coincides with a constant zeta potential around -28 mV. But the RSH value, which is about 60%, is quite high and seems to indicate that the suspension is still unstable. This result may possibly be linked to a high amount of Y^{3+} ions leached out in the media leading to an increase in ionic strength and a decrease in the range of the double layer repulsion.¹⁵

At pH 7 and 10, the particles and the PAA are both negatively charged and the sedimentation heights decrease when increasing the PAA amount. At pH 7, particles are slightly negative and the adsorption saturation limit is around 0.17 wt.%. At this pH, increasing the amount of polyelectrolyte tends to decrease the zeta potential and the sedimentation

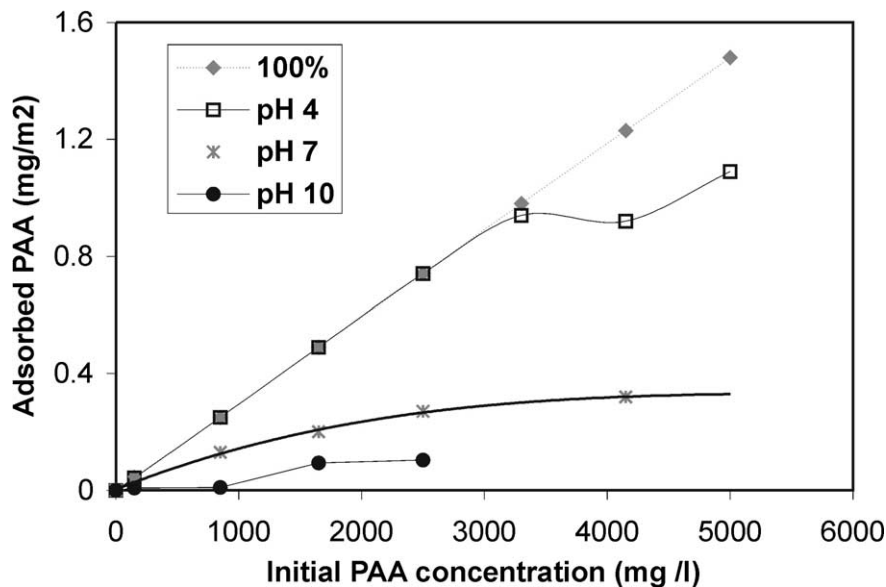


Fig. 4. Adsorption isotherm of PAANH_4 on the ZrO_2 -8% Y_2O_3 surface, as a function of the initial amount of PAANH_4 added in the pH range of 4–10.

Table 1
Monolayer adsorption of PAANH_4 as a function of pH

pH	4	7	10
Adsorption (mg m^{-2})	0.93	0.29	$9 \cdot 10^{-3}$ 0.1

heights tend to increase. At pH 10, particles have a highly negative net charge and the fraction of dissociated PAA is the highest. Thus, the adsorption takes place on the minority of positive sites and the adsorption saturation limit is low. Therefore, the minimum

sedimentation height is achieved with 0.03 wt.% of PAA at pH 10. The lower decrease of RSH value observed at pH 10 coincides with the small increase of the zeta potential. With higher amount of polyelectrolyte the zeta potential becomes constant (as the sedimentation heights) but slightly lower. The increase in ionic strength resulting from the presence of free polymer (conductivity varies at pH 10 from 0.81 mS with 0.03 wt.% PAA up to 3.75 mS with 1 wt.% PAA) could destabilise the suspensions by reducing the electrostatic repulsion between negatively charged side groups of polyelectrolyte.

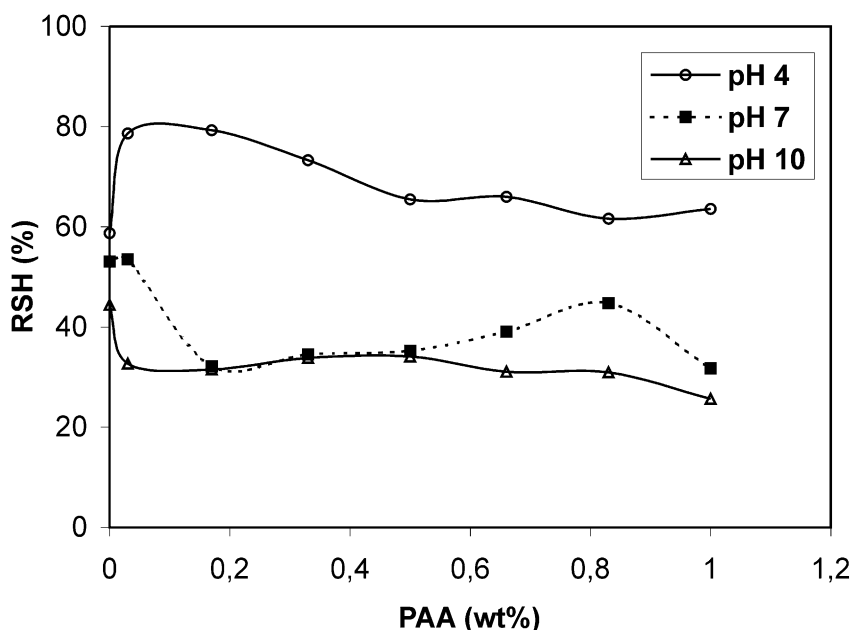


Fig. 5. Sedimentation height as a function of amount of PAA added as a function of pH. Solid loading: 50 wt.%.

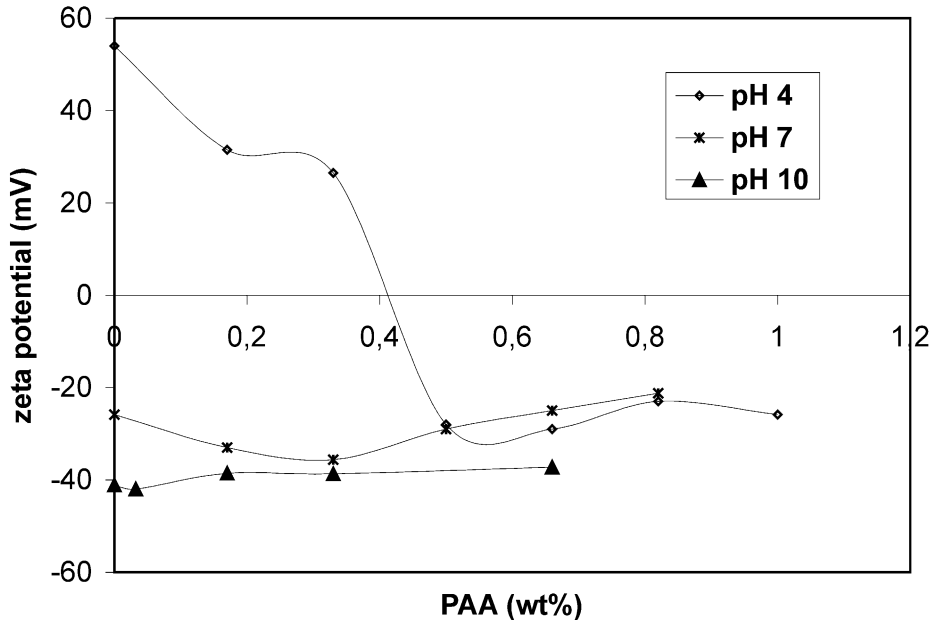


Fig. 6. Zeta potential of slurries containing 50% powder with different amounts of dispersant ranging from 0.03 to 1% as a function a pH.

3.2. Stability map

The effects of PAANH_4 concentration on stabilising aqueous zirconia suspensions at different pH are summarised in a stability map in Fig. 7, deduced from the results on adsorption (Γ_{max}) and sedimentation (RSH). The dashed curve, which represents the transition between stable and unstable areas, shows a decreasing trend of required PAANH_4 amount with increasing pH to obtain stable aqueous zirconia suspensions. Below the curve, the suspensions are unstable and flocculated. Near and slightly above the curve the suspensions are stable. Far away above the curve the increase in ionic

strength resulting from the presence of free polymer could destabilise the suspensions.

Before the spray drying process the addition of a binder is necessary in order to produce solid compact granules. Two organic binders among the most widely used for aqueous tape casting were used in the present study. The first one is a latex and can be described as a stable colloidal dispersion (weight fraction around 0.5) of a copolymer of styrene and acrylic ester in an aqueous medium. The polymer particles, which are spherical with a diameter around 100 nm form a film upon drying when the water phase evaporates. Indeed, the polymeric particles coalesce and lead to a polymeric

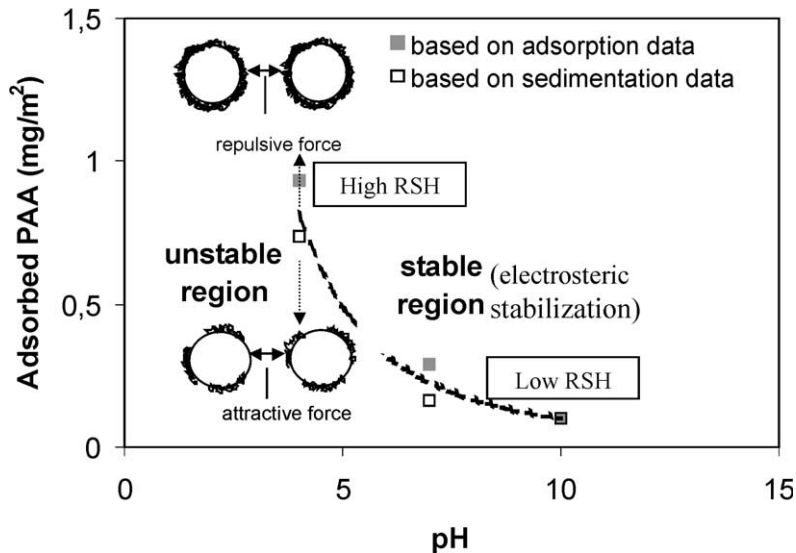


Fig. 7. Stability map of zirconia suspensions as a function of adsorbed PAA and pH.

network. Latexes are quite insensitive to moisture and insoluble after drying. The second binder is a water-soluble polymer, a polyvinyl alcohol obtained from hydrolysis of polyvinyl acetate.

Fig. 8 shows the effect of the two binders on the sedimentation behaviour of slurries at pH 7 (0.17% dispersant) and pH 4 (0.5% dispersant). Before adding a binder, zirconia slurries are situated in the transition region between stable and unstable areas. At pH 4 (the pH was measured before the binder addition), the sedimentation curves show a large decrease of the settled volume when a small amount of binder, whatever its nature, is added (1 wt.%). In the presence of latex, the RSH value is quite low (around 25%) but simultaneously the slurry pH becomes more basic. By adding a latex binder the stability/instability boundary region is crossed: the zirconia suspension becomes more stable. On the contrary, the addition of polyvinyl alcohol does not modify the slurry pH but in this case the RSH value remains quite high (around 50%). With PVA, the zirconia suspension is still near the transition region between stable and unstable areas. At pH 7, whatever the binder, the sedimentation curves show very few differences of the settled volume with increasing binder concentration. The zirconia suspension becomes more stable because the pH of the slurry is slightly increased with the addition of latex or a polyvinyl alcohol. Indeed, it is situated in the stable region after binder addition. Thus, it appears that the RSH value can be drastically modified by adding a binder and consequently the state of dispersion of the suspension (stable or unstable) can be displaced.

3.3. Droplet drying mechanism

To investigate the influence of the slurry formulation on the drying of droplets, a single droplet drying apparatus has been developed involving drying by convection in hot air at 150 °C of single suspended droplets. Experiments have been performed with various formulations—including the dispersant content, the binder nature and the pH value—of the aqueous suspensions containing 50 wt.% of zirconia as reported in Table 2.

As can be seen in Fig. 9, two different kinds of morphologies were identified by observing with binocular cross-sections of granules after drying. The first shape corresponds to spherical full solid granules homogeneously filled with zirconia particles whereas the second one is represented by spherical hollow granules with a central crater and a distinct wall thickness.

In Fig. 10, sedimentation heights have been reported versus the granule morphology. It clearly shows that when the RSH (sedimentation volume) is below 53%, hollow granules are achieved whereas when it is over 62%, the granules are full. A global size reduction of the droplet area is shown in Fig. 11 where a difference appears between full and hollow granules.

At the beginning, when the droplet is placed in the stream of hot air, the water is first evaporated from the surface and the water vapour is transferred from the droplet into the air by diffusion and convection. As long as the liquid interface exists, the water evaporation proceeds and the droplet carries out a uniform drying shrinkage to the whole volume. Indeed, it can be supposed that the liquid interface is maintained by a convective fluid flow inside the droplet as suggested by

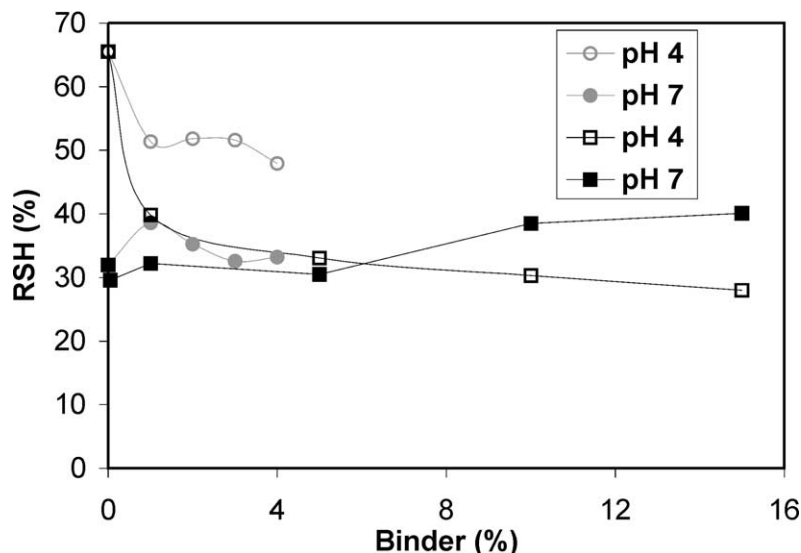


Fig. 8. Sedimentation height as a function of amount of binder added [(circle) PVA and (square) latex] as a function of pH. Solid loading: 50 wt.%.

Table 2
Experimental conditions chosen for single droplet drying experiments

Reference slurry	Without binder				With binder								
	A	B	C	D	15% latex				4% PVA				
					E	F	G	H	I	J	K	L	M
% PAA	0.03	0.17	0.17	0.5	0.03	0.17	0.17	0.5	0.17	0.5	0.03	0.17	0.17
pH	7.6	7.6	4	4	8.6	8.9	4 ^a 7.6 ^b	4 ^a 7.6 ^b	4 ^b	4 ^b	7.5	7.5	4 ^b
RSH	53	32	80	66	35	40	40	28	100	45	8	33	62
comments	F. S.	D. S.	F. S.	F. S.	D. S.	D. S.	D. S.	D. S.	F. S.	F. S.	D. S.	D. S.	F. S.

D.S.: dispersed slurry; ^apH before binder addition.
F.S.: flocculated slurry; ^bpH after binder addition.

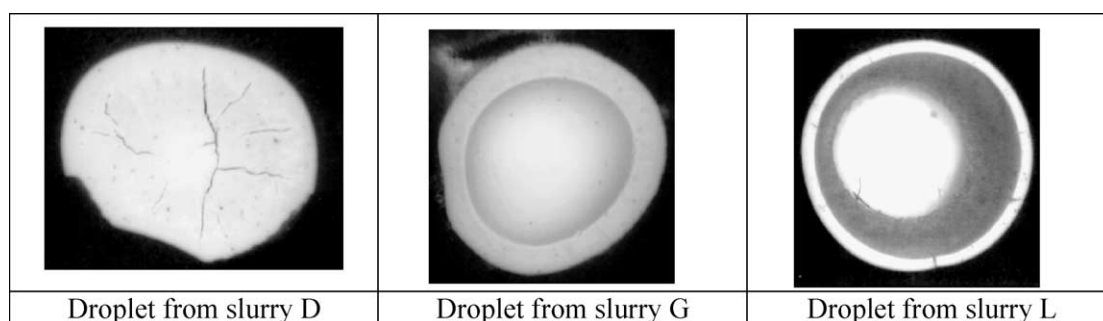


Fig. 9. Droplet cross sections after drying observed by binocular.

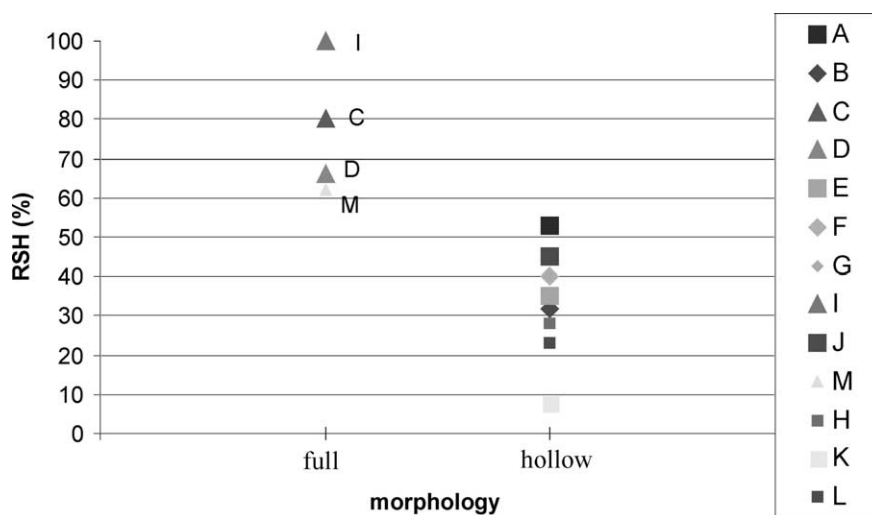


Fig. 10. Granule morphology as a function of sedimentation height after drying.

Walton.²² At that time, two behaviours must be distinguished leading to either a full granule or a hollow one.

In the case of drops originating from a flocculated slurry, the volume shrinkage (around 50%) due to the water evaporation induces a packing behaviour of the particle clusters (flocs) similar to the one observed during the sedimentation experiment. In these conditions, the particle clusters behave as rigid flow units, not very mobile because of the high binding energy between the

particles. This behaviour prevents the flocs from flowing by convection until the clusters achieve the maximum packing, whose density depends on the strength of the flocs. At that stage of the droplet drying, some water still remaining inside the clusters regularly evaporates. This mechanism is in good agreement with the observation of the distribution of the binder in the resulting granules. Indeed, dried granules containing binder were heated in an oven at 250 °C for half an hour. At this temperature binders lead to brown species issued from

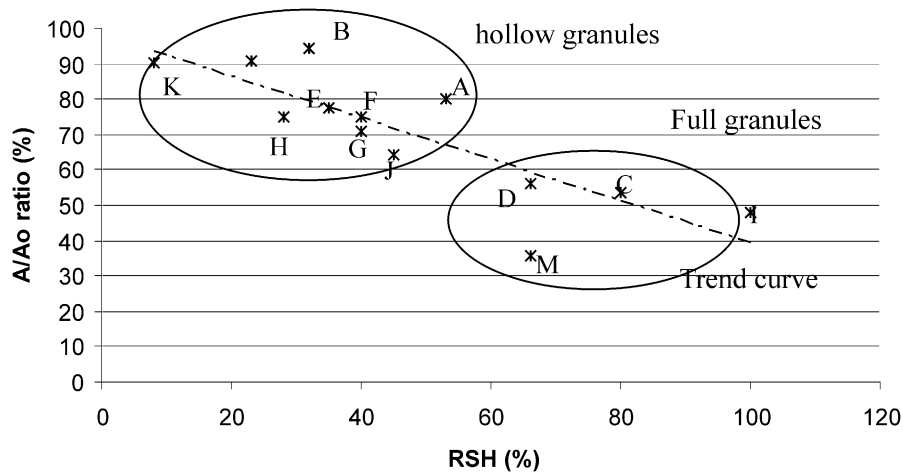


Fig. 11. A/Ao ratio as a function of sedimentation height.

polymer degradation, which help to trace the distribution of binders using an optical microscope. All the heat-treated dried droplets obtained from flocculated slurries ($RSH > 63\%$) were analysed and revealed the presence of the binder on the whole granule. As the PVA is a water-soluble compound it must probably migrate with water. The fact that an homogeneous distribution of the binder was observed clearly implies that water evaporates from inside the flocs leaving behind the PVA. Besides, some interactions between the binder and the solid particles for instance hydrogen bonds may probably happen thus enhancing the regularity of the distribution. When using latex this phenomenon is enhanced because the particles of latex are embedded inside the floc structures as their size is around 100 nm. These explanations corroborate the correlation established between the RSH and the area reduction in Fig. 11. The volume occupied by latex is greater than the one of PVA leading to granules with higher surface area and lower packing.

As shown in Fig. 11, in the case of dispersed slurries, the droplet size is reduced from 10 to 35% depending

mainly on the RSH value. This puts in evidence the fact that this shrinkage is rapidly stopped in contrast with the observation performed for full granules. It has also to be noticed that this phenomenon occurs without and with binder. To the authors knowledge, all the studies dealing with the drying of ceramic slurries have been performed on slurries containing a binder (dissolved or not). In these conditions, as the drying progresses the particles volume fraction and the binder concentration are supposed to become so high near the surface of the droplet that a crust may form. Crosby et al.²³ have already observed the formation of a rigid or semi-rigid structure on the surface during the drying of droplets containing suspended solids. Others argue that a gel-shell of soluble binder (e.g. PVA) that hardly shrinks is formed by the surface segregation.²⁴ This shell or crust must prevent the external shape of the droplet from further decreasing. As observed by optical microscopy on cross sections of hollow heat-treated granules (containing a binder), a brown ring appears at the outer surface. The binder surface segregation is demonstrated and it certainly acts to freeze the drop diameter. But this

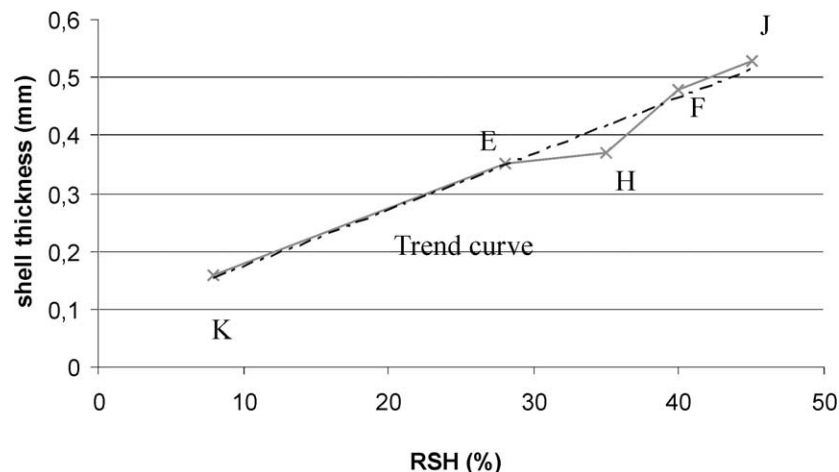


Fig. 12. Shell thickness of hollow granules as a function of sedimentation height.

is not the only reason why the droplet stops its shrinkage, as the phenomenon is also noticed when the slurry does not contain a binder. It seems that in the cases where the particles having an individual behaviour are mobile, which is indicated by the low RSH values (<53%), these particles are able to pack densely at the drop surface as water evaporates. This rearrangement leads to the formation of a microporous solid layer acting like an eggshell, which contributes to maintain a fixed external granule diameter. The liquid–vapour interface remains on the outer part of the crust and drying takes place by capillary diffusion of water. According to the binder segregation on the granule surface, it can be concluded that the particles and the binder were drawn to the droplet surface along with the capillary-induced moisture flow, thickening the granule shell. A linear evolution of the shell thickness with the RSH value reported in Fig. 12 was observed. Simultaneously, an internal void is formed inside the droplet. Finally due to the difference of the pressure a crater may form either from the inward collapse or from an expansion of internal gas. Some authors^{25,26} have shown that in the particular case of fully dispersed slurries, one side of the granule caves in—which was not observed in the present study because of the hemispherical shape of the drop.

4. Conclusion

A systematic study was performed to establish a stability map of highly concentrated zirconia suspensions (solid loading 50 wt.%) based on PAA adsorption saturation levels and sedimentation (RSH) results. Adding a binder to the suspension was shown to change the state of the dispersion depending on the solvent conditions and nature of the binder. The stability map shows stable (fully dispersed) and unstable (focculated) regions as a function of pH.

A single droplet drying device was designed to elucidate the drying mechanism. It was shown that hollow granules are formed in the case of dispersed slurries (low RSH < 53%) whereas full granules are obtained with focculated slurries (high RSH > 62%). The sedimentation height, which represents the state of dispersion of the suspension, is the major factor controlling the droplet drying.

In the case of dispersed slurries, the particles and the binder migrate to the surface of the droplets during the drying process due to capillary forces. A rigid shell is formed at the surface of the granules leading to hollow granules with a limited reduction of the droplet volume. The wall thickness in the case of hollow granules was observed to linearly increase with the sedimentation volume. Full granules, achieved from focculated slurries, reveal the presence of binder in the whole volume,

which indicates a regular shrinkage of the granule. The nature of the binder, which was either latex particles or water soluble PVA, has also an influence on the final volume of the dried granules.

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