Journal of the European Ceramic Society 21 (2001) 493–506

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Optimization of the rheological properties of alumina slurries for ceramic processing applications

Part II: Spray-drying

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Received 30 March 2000; accepted 16 July 2000

Abstract

The present work deals with the preparation of stable alumina, titania and alumina–titania slurries with a high solid content for the production of spray-dried powders. The compatibility of commercial dispersants with various commercial binders, with respect to slurry stability and viscosity, was first studied on alumina slurries. It was shown that binders such as carboxy-methyl-cellulose significantly increase the slurry viscosity whereas acrylic-based binders have a high tendency for foaming. Among the various combinations of the three different commercial dispersants and the four commercial binders studied, it was found that the pair Darvan C–polyethylene glycol (PEG) produced the best results in terms of slurry rheological properties; therefore, this combination was subsequently used for the stabilization of titania and alumina–titania slurries as well. The optimum dispersant–binder concentrations were determined for all three kinds of slurries with the aid of viscosity and zeta-potential measurements. High solid content slurries (70–80 wt.%) of alumina and alumina–titania were spray-dried successfully to produce spherical spray-dried powders with well-defined and uniform size distribution. © 2001 Published by Elsevier Science Ltd. All rights reserved.

Keywords: Al_2O_3; Binders; Dispersants; Drying; Spray–drying; TiO_2

1. Introduction

In ceramic forming processes such as spray-drying and tape-casting, in addition to dispersants, binders have also to be added to the ceramic powder slurry in order to impart good mechanical properties to the green body.[1–5] Binders are polymer molecules that diffuse through the powder particles creating a mesh that holds them together, without the particles themselves being in contact with each other. The most characteristic types of binders are cellulose-based like carboxymethyl-cellulose (CMC), poly-vinyl-alcohols (PVA) and poly-ethylene glycols (PEG).[6–10] The third category (PEGs) are actually plasticizers and are employed in combination with other binders; however they are also frequently used alone since they can impart satisfactory properties to both the powder slurry and the green body. Recently, polyacrylic emulsion binders (PAE) have been suggested[11–14] which are dispersions of 0.05–0.5 μm polymer particles in water, and are reported to provide satisfactory slurry properties (high solid content with moderate increase of viscosity, low foaming tendency) and produce spray-dried granules less sensitive to humidity.

Usually binder addition results in a significant increase in slurry viscosity. Comparative studies among the various kinds of binders on the effect of binder addition on slurry viscosity for spray-drying applications, have shown that for the same binder concentration, there exist dramatic viscosity differences from one kind of binder to another.[13,15] Busch et al.[15] evaluated nine commercial organic binders (PVA, PEG and CMC derivatives) with respect to slurry viscosity, granule diameter, and green density of compacted specimens and concluded that PEG and PVA produced slurries with the lowest viscosity, whereas CMC produced the hardest grains. However, the slurries tested did not contain any dispersant and the solids content in the slurry was not maximized. With respect to the properties

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PII: S0955-2219(00)00232-6

of pressed objects, PVA binders usually provide high green strength, whereas PEG binders provide higher green density.[13] The tensile strength of green compacts prepared from spray-dried powders was higher for the specimens containing PVA compared to specimens containing PEG and was correlated to the evolution of Young's modulus with forming pressure.[16] In order to improve the strength of granules produced with PEG as a binder, the use of co-binder systems e.g. substitution of a part of PEG with hyd roxy-ethyl-cellulose has been proposed.[17]

Dispersant–binder compatibility is necessary in order to ensure optimal slurry rheological properties. Binder addition can cause de-stabilization of slurries already stabilized with a dispersant. Several studies have addressed the interactions between dispersants and various kinds of binders and their effect on the slurry rheological properties.[18–22] The slurry rheological properties, in turn, affect the quality of the granules produced. Even though the influence of the slurry on the character of the granules has been emphasized,[4] studies that correlate the slurry characteristics to the granule properties have appeared only recently in the literature.[23–26]

In Part I of this work,[27] we have investigated the conditions for the preparation of stable, processable alumina slurries with high solid content for slip-casting applications, studying the effects of the kind and the amount of dispersant added. Three of the most commonly used commercial dispersants were compared, and the optimum dispersant concentrations leading to high solids content slurries with good stability and low viscosity were determined. Slurry viscosity was shown to affect the casting rate and, through that, the properties of the cast specimens such as density and mechanical strength. The present work is a continuation of that study, aiming to identify the conditions for the preparation of stable slurries with high solid content for the production of spray-dried powders. However, since spray-drying can be a very effective method for mixing and homogenization of multi-component systems, the present work is extended to two-component systems and specifically to alumina–titania. The final objective was the preparation of alumina–titania spray-dried granules with controllable size which will be subsequently used for the production of aluminum titanate objects. The course of the work firstly involved determining the optimum conditions for the stabilization of slurries with high solids content for alumina and titania separately. Dispersant–binder compatibility studies were performed, and with the aid of viscosity and slurry stability measurements, dispersant–binder systems that could produce high-solids-content slurries suitable for spray-drying were identified. Conclusions from these sets of experiments were employed for the stabilization of alumina–titania slurries of high solid content. Subsequently, optimized slurries of alumina–titania powders were spray-dried in order to test their appropriateness for such an application.

2. Experimental

The α-alumina powder as well as the dispersants employed (Darvan C, Dolapix CE64, Duramax D3005) were the same as in Part I of this work.[27] The titania powder employed was rutile, supplied by Rhone–Poulenc. The properties of the as-received powders are reported in Table 1. The size and morphology of the as-received alumina and titania powders can be compared in the respective SEM photographs in Fig. 1. The much finer dimensions of the titania powder are obvious. Particle size analysis (Malvern E-3600 laser particle size analyzer) indicated that 88% of the titania powder had a characteristic diameter smaller than 1 μm, a fact that can also be observed in Fig. 1b

The dispersants and the binder types and properties are summarized in Table 2. All three dispersants are completely water-soluble and were provided from the manufacturers in the form of aqueous solutions. Taking into account the active polymer species concentrations in these solutions (reported by the manufacturers and given in Table 2) the dispersant concentrations reported hereafter, are expressed as mass of active polymer per mass of dry ceramic powder (wt.%).

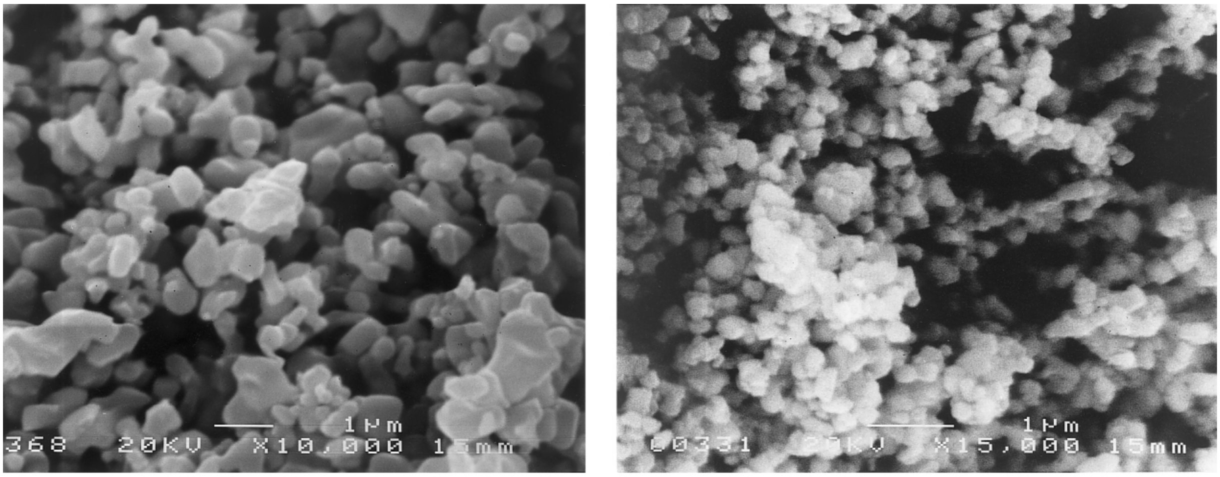
The binders used in this part of the work were carboxy-methyl-cellulose (CMC), poly-ethylene-glycol (PEG), poly-vinyl-alcohol (PVA — commercial name Optapix 4G) and a polymeric emulsion binder (styrene/acrylic copolymer — commercial name Duramax

Table 1
Properties of the alumina and titania powders used

Powder characteristics	Alumina	Titania
Manufacturer	VAW aluminium AG	Rhone-Poulenc
Type	NABALOX 625-30	RCL 535
Phase	>95% α-alumina	>95% rutile
Characteristic particle diameter d_{50} (μm)	3	0.7
Characteristic diameter d_{90}	6	1.3
Density (g/cm^3)	3.9	4.25

B1020). The binders Optapix 4G and Duramax B1020 were recommended by the suppliers of the dispersants Dolapix CE64 and Duramax D3005 respectively, for maximum compatibility between dispersant/binder. The binders PEG and Duramax B1020 were supplied as aqueous solutions whereas PVA and CMC were in the form of water-soluble granules. For the preparation of an aqueous PVA solution, the PVA granules were dissolved in water at 80°C (proportions: 20 wt.% granules–80 wt.% distilled water) and the homogeneous solution obtained was subsequently added to the respective alumina powder slurries. The CMC granules were added in solid form during the slurry preparation stage, after the addition of the alumina powder and the dispersant aqueous solution in the distilled water and were dissolved and homogenized during ball-milling. Thus, the binder concentrations reported hereafter, are expressed as mass of binder aqueous solution per mass of dry powder, with the exception of CMC, which is expressed as mass of solid binder per mass of dry powder.

Alumina slurries with solid content 40, 60, and 80 wt.% (corresponding to 14.6, 27.8 and 50.6 vol.%) were prepared with the addition of a pre-weighed amount of powder in distilled water, with the ultimate goal of determining the optimum conditions for stabilization of slurries at high solids content (80% wt). Immediately after powder addition, the dispersant solution was added and the slurries were conditioned by ball-milling with alumina grinding media for 8 h. Then (with the exception of CMC described previously) the binder solution was added and milling was continued. Viscosity measurements were used in order to optimize the milling time. Slurry viscosity was determined with a rotating-spindle viscometer (Brookfield RVT DV — II). Sets of measurements with a specific spindle were taken at all shear rates (rotational speeds) where a reading of the viscosity value could be obtained. The slurry stability was evaluated in a sample of the slurry, by measuring the particle settling rate inside glass test tubes (sediment height as a function of aging time).



(a) (b)

Fig. 1. SEM photographs of the as-received powders, (a) alumina, (b) titania powder.

Table 2
Properties of the dispersants and binders used

Commercial name	Darvan C	Duramax D 3005	Dolapix CE 64	
Dispersants				
Manufacturer	R. T. Vanderbilt co., Norwalk, CT, USA	Rohm and Haas, Lauterbourg, FRANCE	Zschimmer & Schwarz, Lahnstein, GERMANY	
Active matter (wt.%)	25	35	70	
Density (g/cm^3)	1.11	1.15	1.10	
pH	7.5	6.5	7.0	
Binders				
Chemical basis	Carboxy-methyl-cellulose CMC	Poly-vinyl-alcohol PVA	Poly-acrylic emulsion PAE	Poly-ethylene-glycol PEG
Commercial name	–	Optapix PA 4G	Duramax B1029	Carbowax 400
Manufacturer	AKZO	Zscimmer & Schwarz, Lahnstein, Germany	Rohm and Haas, Lauterbourg, France	Union Carbide Corp., Danbury CT, USA
Form received	Granules	Granules	Aqueous solution	Aqueous solution

The production of spray-dried granules took place in an ICF model 1 C/5 DF-T spray-dryer (inner diameter 0.9 m, chamber height 0.95 m, capacity 3–6 l/h, maximum air inlet temperature 300°C). Atomization was achieved by spraying the slurry through a pneumatic nozzle (orifice diameter 0.1 mm), employing compressed air. The size and quality of the granules produced was evaluated with the aid of Scanning Electron Microscopy (JEOL JSM-6300 microscope) and their composition by X-ray microanalysis (EDS — LINK Isis 300B).

Having identified the optimum dispersant–binder combination for the spray-drying of high-solid content alumina slurries, the work was extended to titania and alumina–titania slurries. First, titania and alumina–titania slurries with only the particular dispersant (without the presence of binder) were prepared and the conditions for their stabilization were determined with the aid of viscosity measurements as well as by zeta-potential measurements (MALVERN Zetasizer 2000 instrument). In order to study the effect of dispersant concentration, small samples from slurries prepared with the addition of various amounts of dispersant were diluted in aqueous solutions of 0.001 M NaCl. Samples of these NaCI solutions were injected into the electrophoresis cell and the average values of four samples and two measurements per sample were obtained.

Then, the effect of binder addition on slurry stability was studied. The optimum dispersant–binder concentrations were determined based on both viscosity and zeta-potential measurements. Slurries prepared with these optimum concentrations were finally spray-dried for the production of titania and alumina–titania granules in the spray-dryer described above.

3. Results and discussion

3.1. Alumina slurries

3.1.1. Optimization of slurry properties

Binder addition to the slurry is necessary for spray-drying applications where the formation of coherent spherical granules is required. However, on one hand, binder addition results in a significant increase in slurry viscosity, and on the other hand it may impart instability to a slurry already stabilized with a particular dispersant. Thus, the first part of the present work involved compatibility testing among various dispersant–binder combinations so that stable slurries with high solid content and minimum viscosity could be prepared. Darvan C was tested with three binders: CMC, PVA and PEG, whereas the other two dispersants, Duramax D3005 and Dolapix CE64 were tested in combination with only the binders recommended from the respective suppliers, i.e. with Duramax B1020 and Optapix PA4G respectively. The concentration of each dispersant was kept constant and equal to the value that resulted in minimum viscosity for the respective slurry solids content, determined in Part I of the work[25] (for example slurries with 80 wt.% solid content were prepared with concentrations of Darvan C, Duramax D3005 and Dolapix CE64 of 0.1, 0.14 and 0.28 wt.% respectively). As already mentioned, these concentrations refer to the weight of active matter of dispersant (i.e. weight of active polymer solids) per weight of dry alumina powder.

Addition of binders to alumina slurries stabilized with Darvan C affects the slurry stability. The sediment height after 2 h vs the kind of the binder used is plotted in Fig. 2, for two slurries with solid contents of 40 and 60 wt.% (corresponding to 14.6 and 27.8 vol.%) and it is compared to the sediment height percentage without the presence of binder. In these two slurries the amount of Darvan C was 0.25 and 0.175 wt.% respectively, determined from the settling and viscosity measurements reported in Part I of the work. The binder concentration in all slurries was 1 wt.% (as defined in Section 2 above). It can be seen that addition of either PVA or PEG de-stabilizes the slurry, increasing the settling percentage at each solid content, whereas, on the contrary, addition of CMC diminishes the sediment height.

Because of this behavior with respect to slurry stability, CMC was further tested in combination with Darvan C. Addition of CMC (as well as of any other binder) first of all, results in a significant increase in slurry viscosity. This behavior for two slurries with 1% CMC is shown in Fig. 3, where the apparent slurry viscosity is plotted vs the rotational speed of the viscometer spindle (which is proportional to the shear rate) and it is compared to the respective slurry viscosity without binder addition. In addition to the significant viscosity increase (one to two orders of magnitude) with the presence of CMC, it can be observed that the slurries with binder addition exhibited shear-thinning behavior, their viscosity decreasing with increasing shear rate. This shear-thinning behavior was common to all slurries with binder addition, irrespective of the kind of binder used, and is desirable for slurries that are to be used for spray-drying, since the slurries will be subsequently subjected to high shear in the spraying nozzle of the spray-dryer.

Since CMC was supplied in the form of solid granules, ball-milling was required for its homogeneous dispersion in the slurry. However, extensive ball-milling reduced the alumina particle size and consequently increased viscosity, due to flocculation, because of stronger particle–particle interactions. Thus, optimization of the milling time with respect to slurry viscosity was required, so that a homogeneous slurry with low viscosity could be obtained. The effect of milling time on slurry viscosity for a slurry with 60 wt.% solids content with the addition of 0.175 wt.% Darvan C and 0.7 wt.% CMC is shown in Fig. 4. For every shear rate, as the milling time increases, first a steep decrease in viscosity is observed. Viscosity reaches a minimum value at 16 h of ball-milling and thereafter a slow rise in the viscosity values with increasing milling time takes place. Particle size distribution measurements on slurries milled for 16 h did not indicate any decrease in the size of the alumina powder; thus, in all subsequent experiments with CMC as well as with every other binder, the ball-milling time was kept constant at 16 h.

The next step involved viscosity measurements of the various slurries. The viscosities of three slurries stabilized with Darvan C and with the binders CMC, PVA and PEG respectively, as well as these of slurries with the dispersant–binder pairs Duramax D3005/Duramax B1020 and Dolapix CE64/Optapix PA4G were compared. The concentration of binder was varied in the range 0–5 wt.%, depending on the particular kind of binder used. The comparative results for slurries with 60

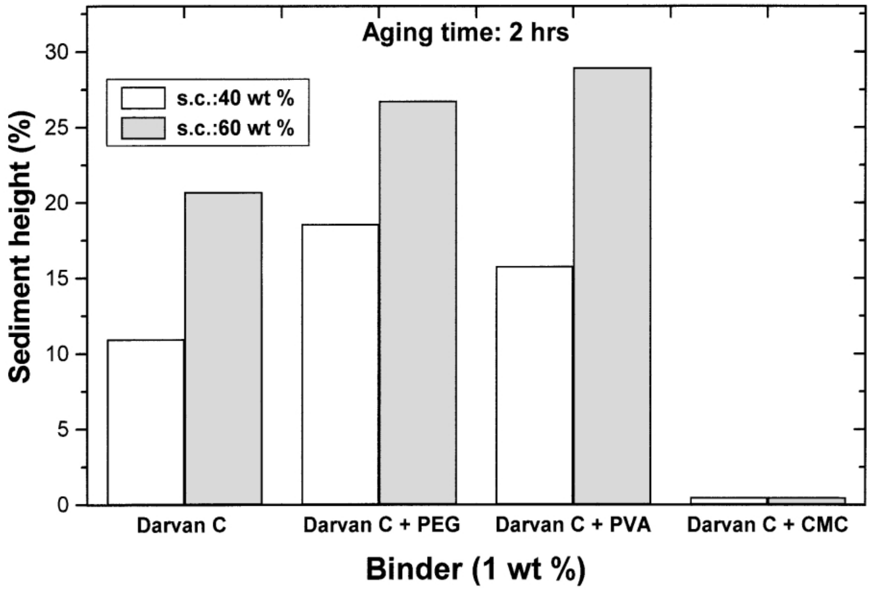


Fig. 2. Effect of binder addition on slurry stability, for two slurry solid contents, 40 and 60 wt.%.

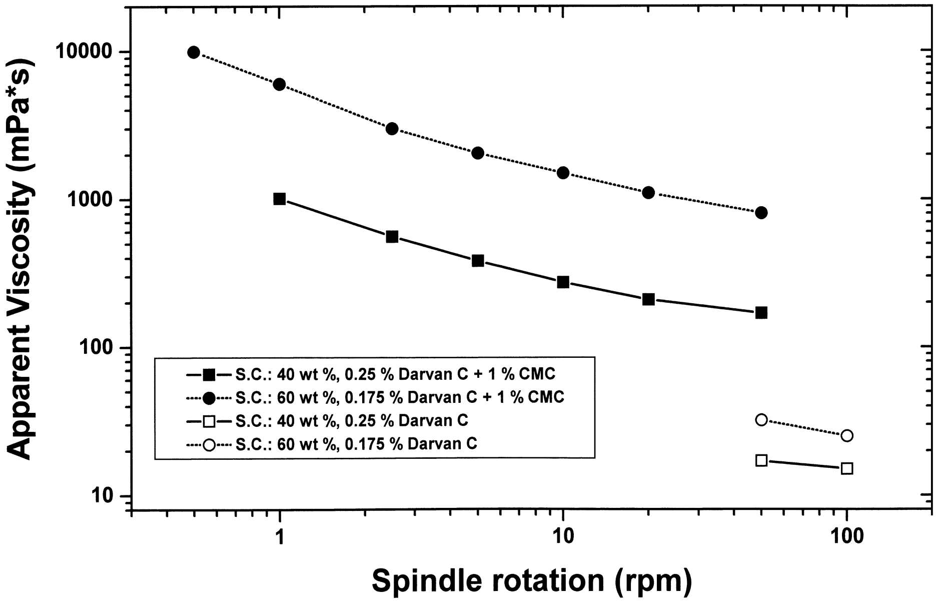


Fig. 3. Effect of binder (CMC) addition on slurry viscosity for two slurry solid contents, 40 and 60 wt.%.

wt.% solid content are summarized in Fig. 5 and for slurries with 80 wt.% solid content in Fig. 6. A lower rotational speed (50 rpm compared to 100 rpm) was required in the second case, so that reliable viscosity measurements could be obtained. The combination Dolapix CE64/PVA(Optapix PA4G) was employed only in the case of slurries with 80 wt.% solid content.

It is evident from Fig. 5 that among the various binders tested, addition of CMC had a dramatic increase on slurry viscosity. Slurries with 60 wt.% solid content could not be handled when CMC exceeded 0.9 wt.%, whereas processable slurries with 80 wt.% solid content could not be prepared at all with CMC addition, even in quantities as low as 0.1 wt.%. On the contrary, for slurries with 60 wt.% solids content, PEG and PVA combined with Darvan C resulted in similar, low viscosity values, even for high binder concentrations (up to 5 wt.%). Only in the upper limit of binder concentration (3–5 wt.%) slurries with PEG exhibited slightly lower viscosity than the respective slurries with PVA.

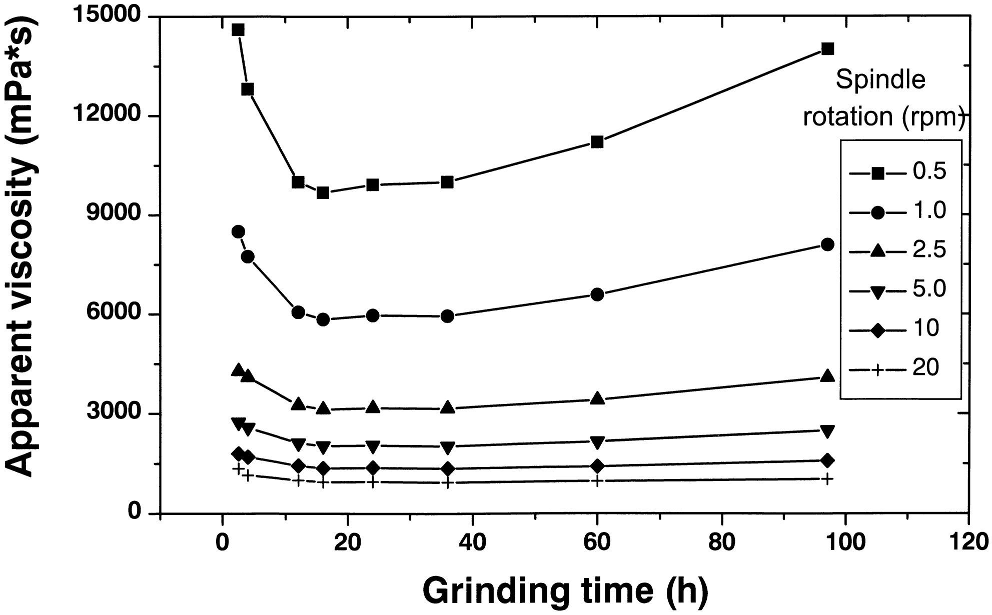


Fig. 4. Darvan C/CMC slurries: effect of ball-milling time on slurry viscosity.

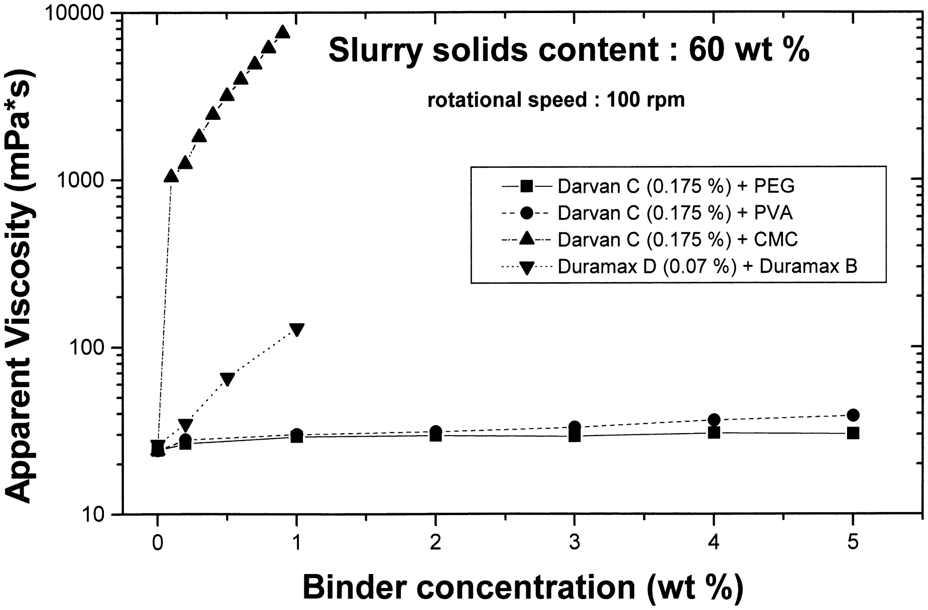


Fig. 5. Effect of kind and concentration of binder on slurry viscosity for slurries with 60 wt.% solid content.

At the same solids content (60 wt.%), the combination Duramax D3005–Duramax B1020 resulted in stable slurries with intermediate viscosity values (between those observed with CMC and with PEG). Compared to PEG and PVA, these slurries exhibited a steeper increase in viscosity with an increase of binder concentration, accompanied by a strong tendency for foaming. These results are in agreement with those of Barnes et al.[17] who also observed that alumina slurries with acrylic binders (Duramax B1020) exhibited much higher viscosities compared to slurries with PEG. At binder concentrations exceeding 1 wt.%, foaming was so intense that reliable viscosity values could not be obtained. When the slurry solids content for this dispersantlbinder pair was raised to 70 wt.%, foaming was intense at binder concentrations as low as 0.25 wt.%, and therefore slurries with even higher solid content (80 wt.%) were not prepared.

When the slurry solid content was raised to 80 wt.% the maximum amount of binder that could be added was, in every case, reduced. The respective viscosity measurements are depicted in Fig. 6. Slurries with PVA more than 2 wt.% suffered from intense settling and a high tendency for foaming. Slurries with Dolapix CE64/PVA could not accommodate more than 1.0 wt.% of binder; beyond this point intense foaming was observed. The best rheological performance (low viscosity at high solid content, combined with satisfactory stability) was achieved with slurries with Darvan C/PEG. This combination exhibited low viscosity even at PEG concentrations as high as 3.0 wt.%. Thus, among the various slurries prepared, slurries with this particular combination of dispersant–binder (0.1 wt.% of Darvan C–3.0 wt.% of PEG) were the prime candidates for the spray-drying experiments.

3.1.2. Spray-drying of slurries — granule preparation

Representative slurries from the ones produced above, were spray-dried for the production of alumina granules. As we have mentioned, the viscosity measurements have indicated the slurries with Darvan C/PEG as the first choice for spray-drying, but in order to compare the effect of the binder on the quality of the granules produced, slurries with Darvan C/CMC were spray-dried as well. The effect of solid content was studied by comparing batches of slurries with 40, 60 and 80 wt.% alumina. The air inlet temperature was kept constant at 190°C and the air outlet temperature at 90°C.

The kind of binder had a significant effect on the quality of the granules produced. Granules produced from a slurry with Darvan C/CMC (in proportions 0.175 and 1% wt.%, respectively) with 40 wt.% solid content are shown in Fig. 7a and b (under a magnification of 500 and 2000 times respectively). The combination of low solids content and high air inlet pressure (3.5 bar) leads to granules of small size, with a mean diameter around 25 μm. However, almost all the granules from this slurry suffer from defects such as cracks and void holes (Fig. 7a and b). In addition, the product recovery percentage (at the bottom of the dryer) was rather low (48 wt.%). An increase of the slurry solids content from 40 to 60 wt.% (for the same dispersant–binder pair), increased the mean diameter of the granules but did not significantly improve the quality of the granules produced. Due to the large increase on the slurry viscosity when using CMC, processable slurries

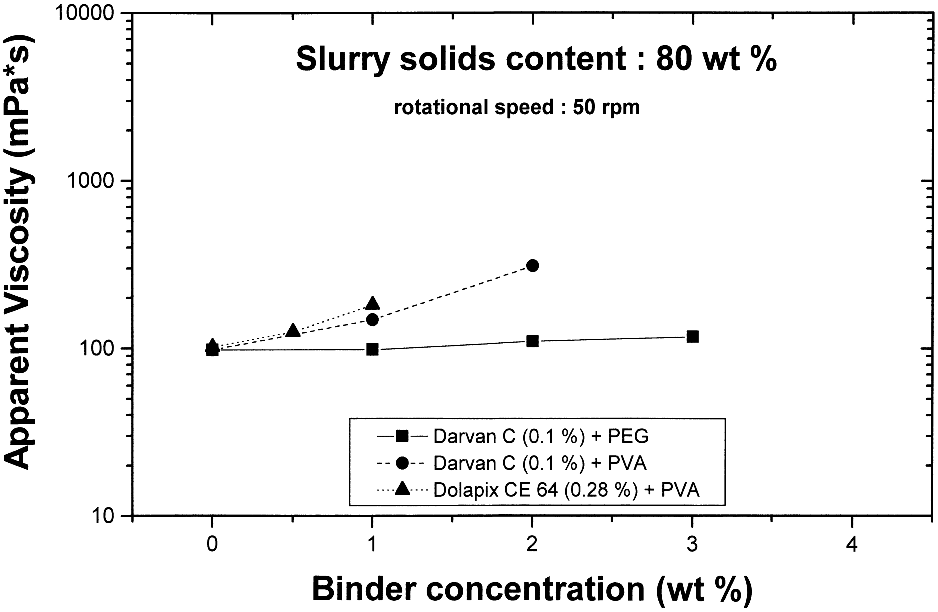


Fig. 6. Effect of kind and concentration of binder on slurry viscosity for slurries with 80 wt.% solid content.

with higher solids content could not be produced. Therefore the quality of the granules produced with CMC could not be improved.

On the contrary with slurries with the same solids content (60 wt.%) but with PEG as a binder (0.175 wt.% Darvan C, 3 wt.% PEG), the quality of the granules was improved (Fig. 8a and b) — however the granules are still not defect-free (dumb-bell shape with a crater in the middle). The average granule diameter was around 40 μm. The product recovery percentage was still low (37 wt.%).

However, due to the lower viscosity, use of PEG allows for the preparation of processable, high solid content slurries (80 wt.%). The combination of appropriate binder with high solid content in the slurry can significantly improve the quality of the granules produced. This fact can be clearly seen in Fig. 9 where granules produced from slurries with 80 wt.% solid content with 0.1 wt.% Darvan C and 3.0 wt.% PEG are shown (under magnifications of 450 and 1500 times respectively). First of all, essentially all the granules are spherical. Their size distribution is much narrower (compared to that shown in Fig. 8a) and they exhibit a mean diameter of around 50 μm. With respect to quality, the granules are solid (without voids or craters), much more coherent and essentially free of defects (as can be clearly observed in Fig. 9b). In addition to the granules' quality, the increase on slurry solid content has led to a significant improvement on product recovery which reached 78 wt.% (compared to 37 wt.% achieved with the slurry with PEG but with 60 wt.% solid content).

These observations are in agreement with other recent studies. In addition to the higher solid content, which helps in eliminating the defects,[5] it should be noted that the dispersant level in the two slurries using PEG (60 and 80 wt.% solids) has also been reduced from 0.175 to 0.1 wt.% respectively. Walker et al.[26] have spray-dried

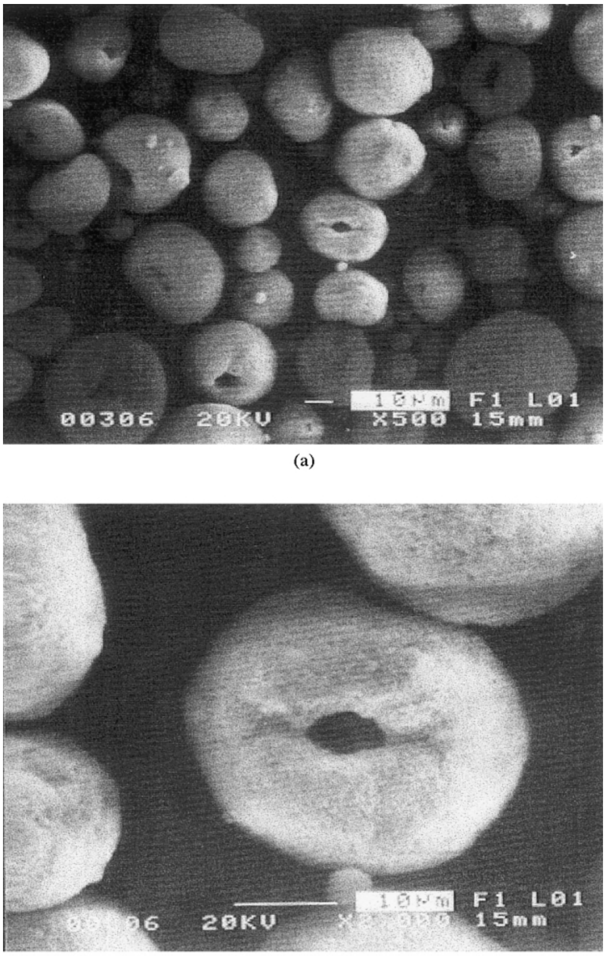


Fig. 7. Alumina spray-dried granules produced from slurries with 0.25 wt.% Darvan C, 1 wt.% CMC, slurry solids content 40 wt.%; (a) magnification 500 times, (b) magnification 2000 times.

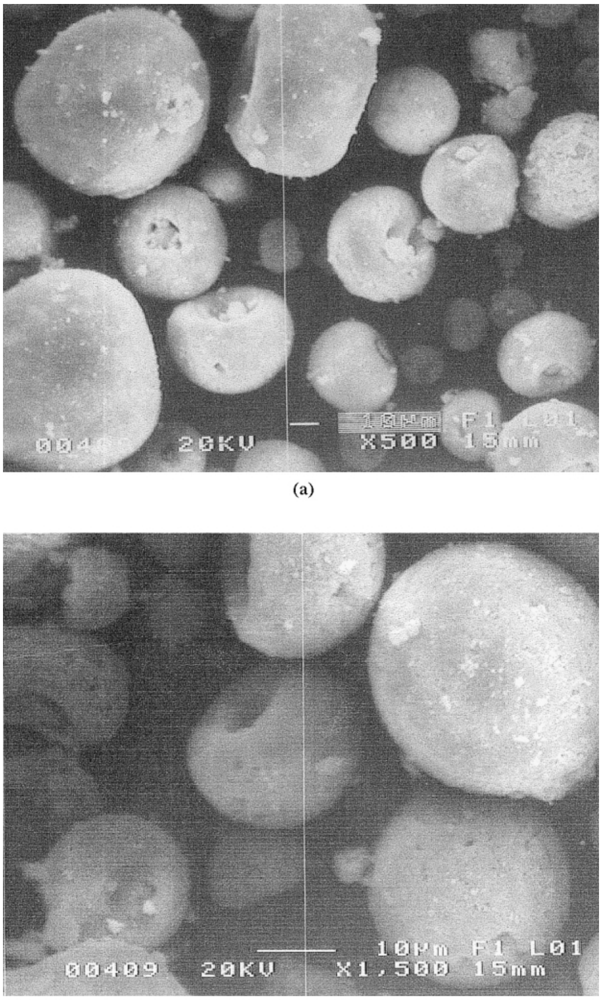


Fig. 8. Alumina spray-dried granules produced from slurries with 0.175 wt.% Darvan C, 3.0 wt.% PEG, slurry solids content 60 wt.%: (a) magnification 500 times, (b) magnification 1500 times.

alumina slurries of up to 72 wt.% solid content, stabilized with Darvan C821 and different types of PEG binders and have found that solid, crater-free granules occurred at low dispersant levels (0.35 wt.%), whereas granules exhibiting craters were formed when the dispersant level was between 0.5–1.0 wt.%. Observations by Lee et al.[23] on silicon nitride slurries, have also indicated similar trends i.e. formation of solid granules at low, and hollow granules at high dispersant levels, respectively.

Since it is clear that the production of superior quality granules at a high recovery rate requires high solid content, such high-solid-content slurries should be prepared — however the high solids content has to be combined with relatively low viscosity, so that the slurries can be easily processed. For that purpose a careful selection of the dispersant–binder pair and their relative proportions, based on rheological measurements, is imperative.

3.2. Titania and alumina–titania slurries

Since the experiments with alumina showed that the combination Darvan C/PEG was good for the preparation of high-solids-content, low-viscosity slurries, it was decided to investigate this particular dispersant–binder pair for the stabilization of titania and alumina–titania slurries.

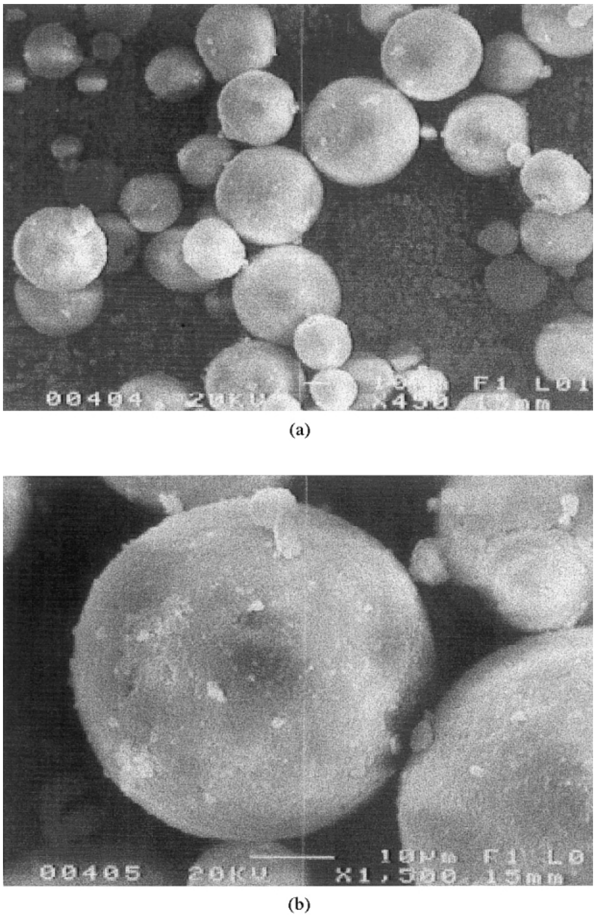


Fig. 9. Alumina spray-dried granules produced from slurries with 0.1 wt.% Darvan C, 3.0 wt.% PEG, slurry solids content 80 wt.%: (a) magnification 450 times, (b) magnification 1500 times.

3.2.1. Slurry stabilization without binder addition

The first step involved the stabilization of titania slurries with the presence of Darvan C only. In contrast to the large number of studies on stabilization of alumina sluries, only few studies deal with the stabilization of titania ones.[28–31] Slurries with solid contents of 60 and 80 wt.% (corresponding to 26 and 48 vol.% respectively) were prepared, according to the procedure described in Part 1.[27] The viscosity of the titania slurries as a function of dispersant concentration is compared to that of the alumina slurries with the same solid content, in Fig. 10. It can be observed that for the same solid content, titania slurries exhibit higher viscosity — obviously because of their finer particle size. This difference becomes much more intense at the highest solids content of 80%. It should be noted that at this solid content, Darvan C concentrations less than 0.125 wt.% were not sufficient to induce deflocculation. Minimum viscosity for both titania slurries was observed at a deflocculant concentration equal to 0.2 wt.%, proving Darvan C an equally effective deflocculant for titania slurries as well as alumina ones. The iso-electric point of rutile lies in the pH range 5–6.[30,31] The "natural" pH of the titania slurries was 6.5; addition of Darvan C shifted the pH to 7.0 (whereas in parallel shifted the iso-electric point to even lower values), where stabilization can be achieved.

The next step involved the stabilization of alumina–titania slurries. In this case, besides viscosity measurements, zeta potential ones were also carried out, since such kinds of mixtures are very little studied and the existing information in the literature is very limited. The proportion of alumina/titania dry powders was kept constant at (1/1) molar ratio (or $1.276/1.0 = 56/44$ weight ratio) in order to achieve the stoichiometric phase of Al_2TiO_5 after sintering. Alumina–titania slurries with a total solid content of 80 wt.% were too viscous and could not be stabilized over the whole range of dispersant concentrations tested. On the contrary, slurries with 70 wt.% solids exhibited an optimum dispersant concentration range, where viscosity was low and slurry stability was achieved as well. This can be clearly seen, both in Fig. 10, where the slurry viscosity as a function of dispersant concentration is compared to that of the alumina and the titania slurries, as well as in Fig. 11, where the slurry viscosity and zeta-potential are plotted against dispersant concentration. Minimum viscosity was observed at a dispersant concentration of 0.2 wt.%. This is also the dispersant concentration above which consistently high values of zeta-potential (> -35 mV) begin to appear, whereas maximum zeta-potential occurred at a dispersant concentration of 0.275 wt.%. From Figs. 10 and 11 it can be concluded that an alumina–titania slurry of 70 wt.% solid content, can be stabilized with the addition of Darvan C in concentrations between 0.2–0.3 wt.%.

3.2.2. *Slurry stabilization with binder addition*

Based on the results above, titania and alumina–titania slurries were prepared with the optimum Darvan C concentration determined above (0.2 wt.%) and the effect of PEG addition on slurry stability and viscosity was determined. The slurry viscosity as a function of quantity of PEG added for alumina, titania and alumina–titania slurries, is shown in Fig. 12a and the respective zeta-potential in Fig. 12b. Similar to the case of alumina slurries, addition of PEG to titania and to alumina–titania slurries, only slightly increased the slurry viscosity; is remained practically constant up to a PEG concentration of 4 wt.%. However, addition of PEG affects the slurry stability, a fact reflected in the significant reduction of the zeta-potential value. This was also observed on alumina slurries where addition of

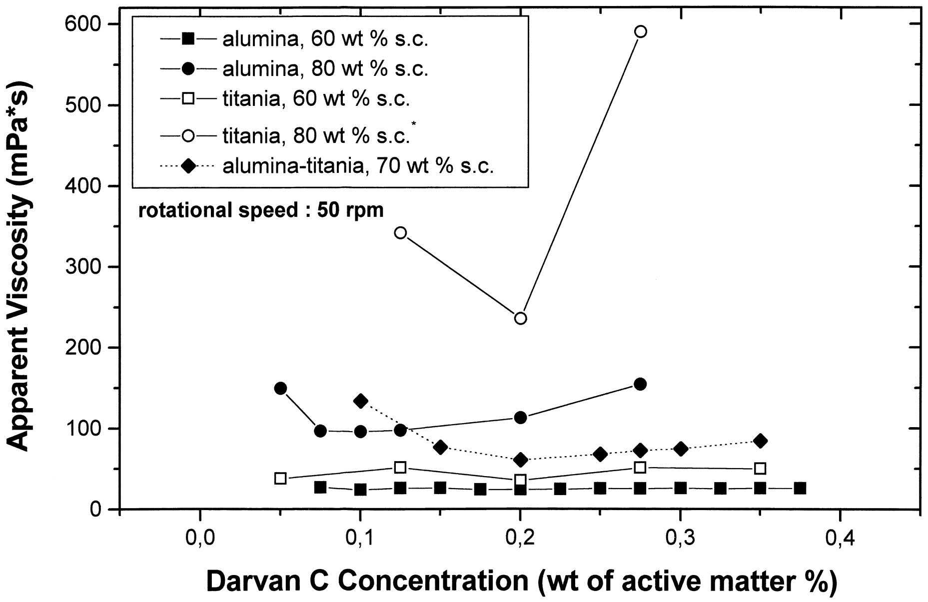


Fig. 10. Effect of Darvan C concentration on slurry viscosity, for alumina, titania,and alumina-titania slurries (*viscosities of all slurries measured with spindle no. 1, 50 rpm, except that of the titania 80 wt.% solids content slurry, measured with spindle No. 2, 100 rpm).

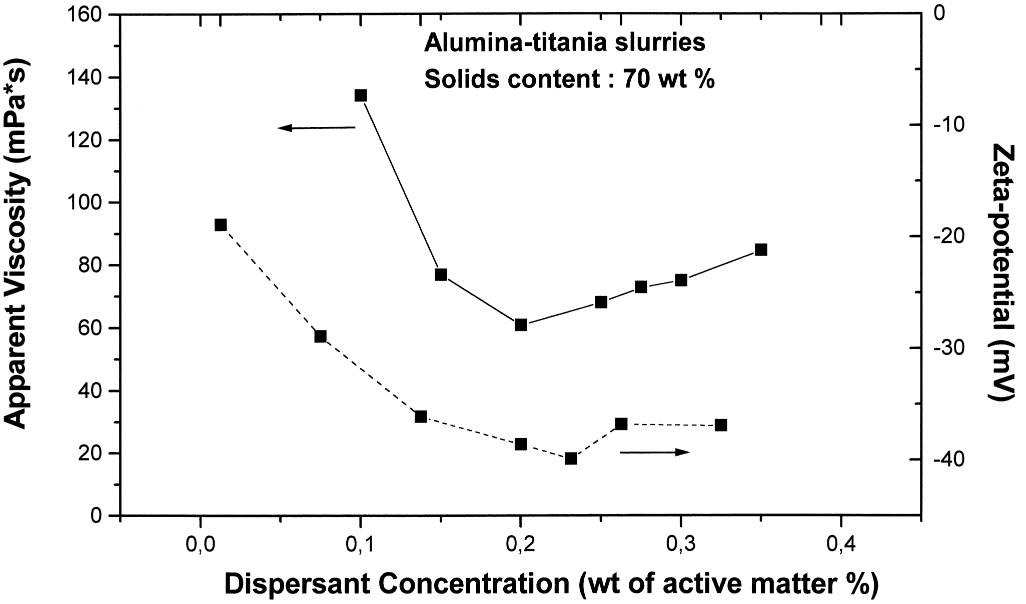


Fig. 11. Effect of Darvan C concentration on slurry viscosity and zeta-potential for alumina–titania slurries.

PEG resulted in an increase of the sediment height (Fig. 2). Therefore PEG concentration should be selected so that it does not de-stabilize the slurry, and from Fig. 12b, it seems that for titania slurries the optimum PEG concentration is 3.0 wt.%, whereas for the titania–alumina ones it is 2.0 wt.%.

Having identified the optimum binder concentration for each kind of slurry, we next investigated whether this quantity of binder affects the value of the optimum dispersant concentration. For this purpose, titania slurries with 60 wt.% solid content and 3.0 wt.% PEG, and alumina–titania slurries with 70 wt.% solid content and 2.0 wt.% PEG (determined from the step above) were prepared with various Darvan C concentrations and the effect of dispersant concentration on viscosity and zeta-potential was investigated. Slurry viscosities, as a function of dispersant concentration, are shown in Fig. 13a, compared to the respective values of the same slurries without PEG (already presented in Fig. 10), whereas the respective zeta potential results are shown in Fig. 13b. It can be seen that for both kinds of slurries with addition of PEG, a higher dispersant concentration is required for the achievement of both lowest viscosity as well as slurry stability than that in the case of slurries without PEG. It should also be noted that addition of PEG to a slurry with Darvan C can either increase or decrease the slurry viscosity, depending on the dispersant concentration, a result also reported by other researchers.[20]

To summarize, from the viscosity and zeta-potential results (Fig. 13a and b), it was shown that in the case of titania slurries of 60 wt.% solid content the optimum Darvan C/PEG concentrations would be 0.30 and 3.0 wt.% respectively, whereas for the alumina–titania slurries of 70 wt.% solid content, the respective values would be 0.35 wt.% Darvan C and 2.0 wt.% PEG.

3.2.3. Spray-drying of slurries — granule preparation

Finally, in order to test the potential of these stabilized alumina–titania slurries to be spray-dried and to produce spherical granules of controlled size, the most stable slurries (70 wt.% solids, 0.35 wt.% Darvan C, 2.0 wt.% PEG) were passed through the nozzle of the spray-dryer. It was confirmed that good quality, spherical granules could be produced by this way. In Fig. 14a and b, the granules produced from the alumina–titania slurry are shown. In these pictures, the spherical shape of the granules, the narrow size distribution (Fig. 14a) and their good quality (Fig. 14b) are clearly seen. Furthermore, both components were very well mixed inside the granules developed. Indeed, in Fig. 15, the structure

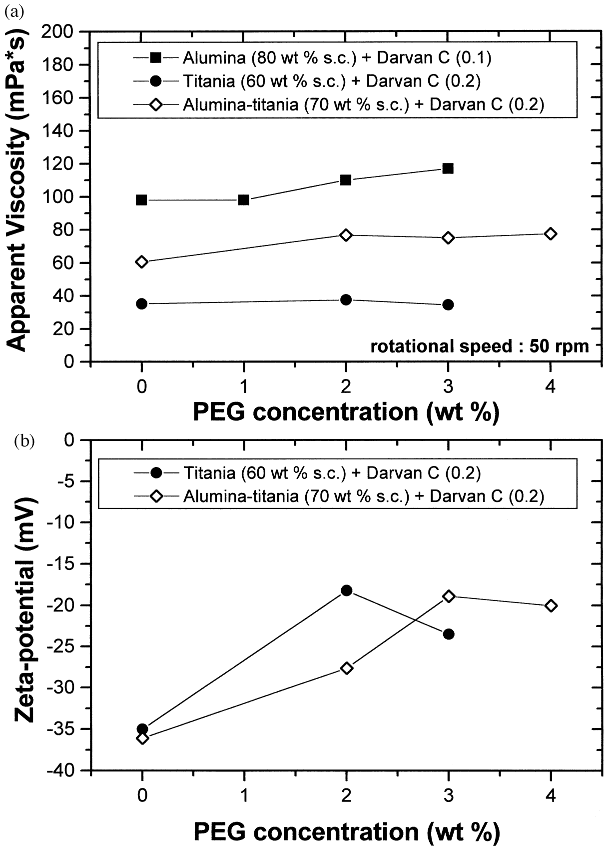


Fig. 12. Effect of PEG concentration on (a) slurry viscosity and (b) zeta-potential, for alumina, titania, and alumina–titania slurries.

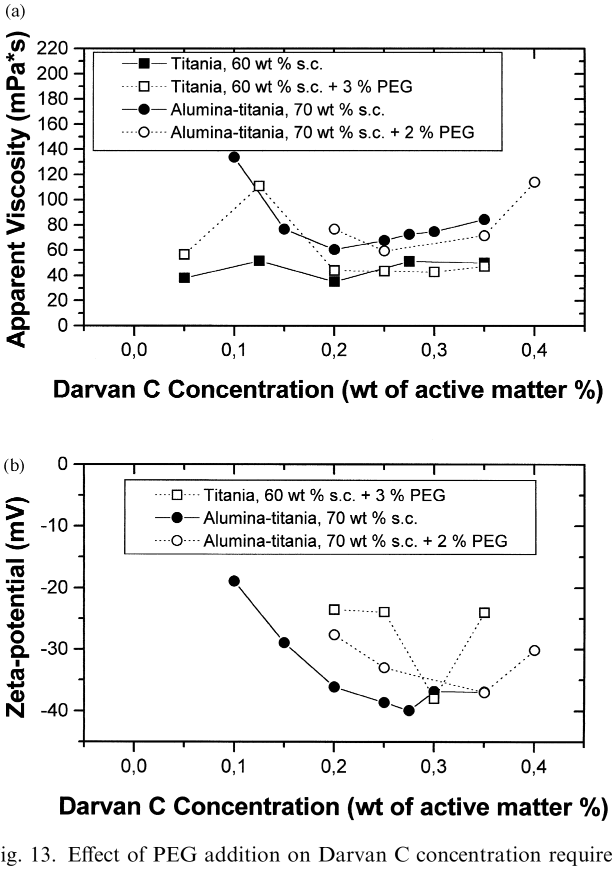
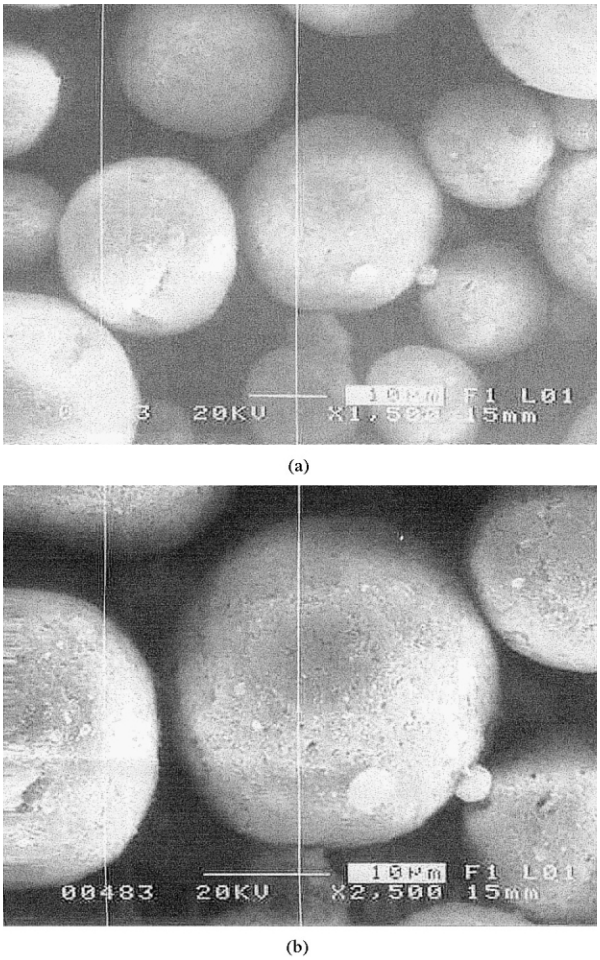


Fig. 13. Effect of PEG addition on Darvan C concentration required for (a) minimum viscosity and (b) high zeta-potential, for titania and alumina–titania slurries.

of such a granule in high magnification (15 000 times) can be observed. This granule is comprised, as expected, of the particles of the initial powders in the slurry. EDS analysis in the surface of such granules showed homogeneous distribution of both Al and Ti (Fig. 15b and c) proving the perfect mixing of the powders in the grain.

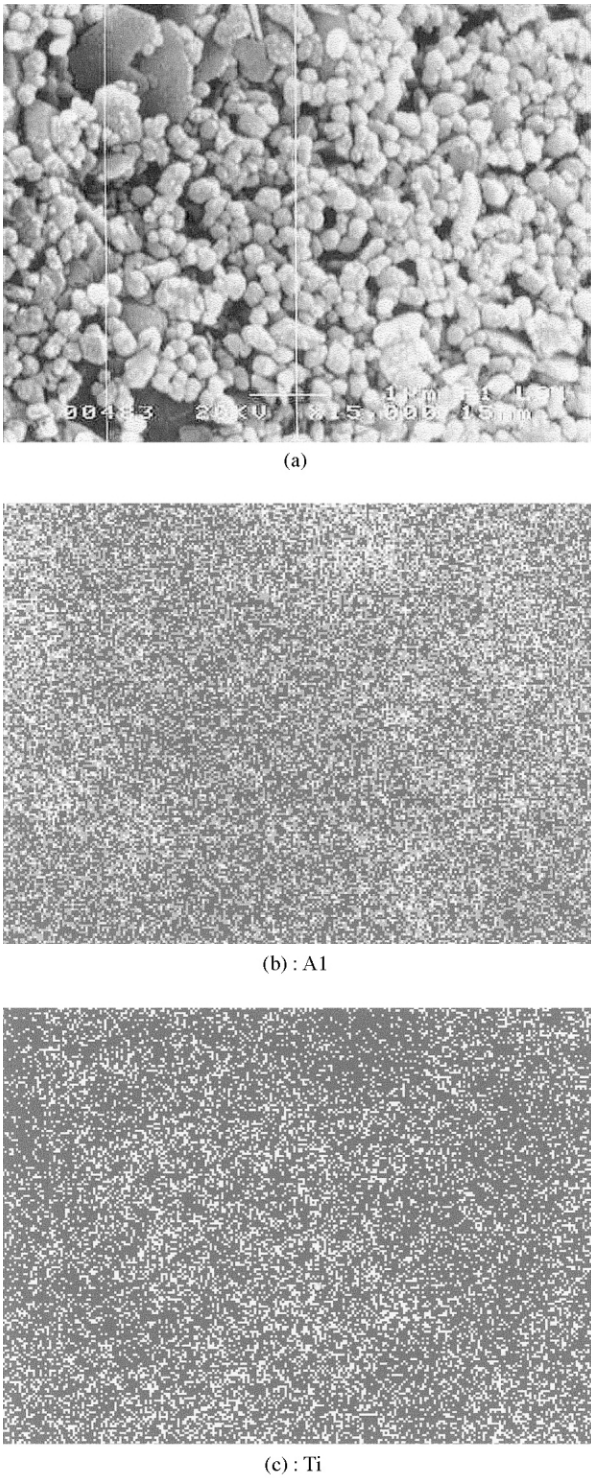
The shape and quality of the alumina–titania granules (Fig. 14a and b) resemble those of the alumina ones (Fig. 9a and b). However, it should be mentioned that due to differences between the two kinds of slurries with respect to both solid content (70 vs 80 wt.%) and viscosity (77.6 vs 110 mPa*s), the spray-drying conditions (such as air inlet pressure and slurry flow rate to the spray-dryer) were different. Therefore Figs. 9 and 14 should be viewed as successful examples of production of uniform, spherical, defect-free granules from each kind of slurry and not as a direct comparison, with respect to granule size, between the two kinds of slurries. The granule characteristics (mean diameter, size distribution, density) can be further fine-tuned by adjustment of the spray-drying parameters such as air inlet pressure, slurry feeding rate, type of atomizer used etc., and correlated to the performance of the spray-dried powder in subsequent operations (flowability, strength, compaction behavior etc.). This work is the subject of a future publication.



(a)

(b)

Fig. 14. Alumina–titania spray-dried granules produced from slurries with 0.35 wt.% Darvan C, 2.0 wt.% PEG, slurry solids content 70 wt.%: (a) magnification 1500 times, (b) magnification 2500 times.



(a)

(b) : A1

(c) : Ti

Fig. 15. (a) Magnification (15 000 times) and (b), (c) EDS X-ray microanalysis of Al and Ti respectively, on the surface of the alumina–titania granules shown in Fig. 14.

4. Conclusions

The present work involved the preparation of high-solid-content alumina, titania and alumina–titania slurries appropriate for spray-drying. In this case, binder addition is required, which drastically increases the slurry viscosity. Among the various dispersant–binder pairs tested on alumina slurries, it was found that, whereas CMC imparts excellent stability on the slurries, it significantly increases the slurry viscosity and therefore could not be used for the preparation of slurries with high solid content. The limitation to intermediate solid content with this particular binder, resulted in the production of defective spray-dried granules.

The combination Darvan C/PEG produced the best results in terms of stability, anti-foaming and viscosity and could be used for the preparation of alumina slurries up to 80 wt.% solid content that could be successfully spray-dried. For constant air inlet pressure, the size of the spray-dried granules produced could be adjusted by varying the slurry solid content. High slurry solid content improved the quality of the granules produced in terms of shape, homogeneity, size distribution and coherence. Spray-drying of high solids content slurries produced spherical granules of uniform size with a mean diameter around 50 μm, with a very high recovery in the dryer.

This combination also proved very suitable for the production of alumina and alumina–titania stable slurries with good rheological properties. Spray-drying of these slurries led to the production of very good quality granules, while in the case of alumina–titania mixtures the mixing of both powders inside the granule was perfect.

In summary, for every case, the effects of slurry rheological behavior on the product properties were demonstrated, and the slurry properties were optimized, so that products with improved properties could be obtained.

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