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Preparation of zirconia granules with a low molecular weight dispersant

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Abstract

In the present work, different conditions, such as PVA content as a high molecular weight polymer, Dolapix CE64 level with a lower molecular weight and pH adjusted by HCl, were investigated for the preparation of the yttria-stabilized zirconia (YSZ) granules from nanosized YSZ particles. It was found that the suspension prepared at pH = 4 and with 0.1 wt.% Dolapix CE64 has a reasonable value of viscosity for spray drying. The morphology of granules and their cross-sections were characterized through microstructural observation. The flowability of the prepared granules and the Hausner ratio were also evaluated. The results indicated that the addition of only 0.1 wt.% of PVA binder and the use of Dolapix can produce the YSZ granules with good flowability. Replacement of PAA by Dolapix has the benefits of achieving uniform granules with a dense shell layer, decreasing the amount of binder and accelerating the feeding rate of suspensions. The mechanism of the solid and hollow granule formation by a low molecular weight dispersant was suggested.

Keywords: *YSZ granules, Dolapix, PVA binder, flowability*

I. Introduction

Yttria-stabilized zirconia (YSZ) is generally used as a thermal barrier coating (TBC) with desirable properties such as low thermal conductivity at high temperatures, a high thermal expansion coefficient and high thermal shock resistance [1–6]. In order to obtain a high-quality coating, it is necessary to produce granules with appropriate characteristics, such as good apparent density, fluidity, distribution of granular size, etc. The first step in enhancing the TBCs properties is the control and optimization of the powder morphology [7–9]. For this purpose, the primary powder has been prepared as a suitable suspension for injection in a spray dryer [10,11].

Spray drying is one of the most efficient ways for transferring ceramic suspensions into a free-flowing powder (granule) to render them suitable for industrial coatings [12–14]. To optimize the behaviour of granules, the slurry rheology should be controlled [1,15]. Further, by studying the effect of suspension parameters on the granules obtained by spray drying, the best conditions can be selected for the preparation of granules. Thus, it is important to examine the morphology of granules in order to choose the best one for coating.

Commonly used dispersants have a high molecular weight and they are poly acryl amide (PAA) (5000–8000 g/mol) [2,5,8,11,14] or Dispex A40, an acrylic polymer [17]. Together with a dispersant for preparing a stable suspension and providing an appropriate dispersion, a binder such as PVA, PEG or Latex (which are commonly high molecular weight materials of about 10000–20000 g/mol) should be added to the suspension to achieve self-standing compact granules [2]. Usually, organic volatile binders are used for spray drying to keep the particles attached together. The importance of the binder and its related problems regarding the granule characteristics have been discussed in the literature [18]. Although many studies have been conducted on the effect of suspension characteristics on granules [5,7,8,11,16], there is still a problem with a binder used in spray drying process which has largely remained understudied. The type and the amount of binder, as well as the pH of the suspension are among the main factors affecting the production of granules [7]. The binder composition, binder content, binder distribution and binder aggregation have been reported [19] as important parameters affecting the spray dried zirconia powders. Thus, the binder should not be neglected

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in production of granules. To the best of the authors' knowledge, all studies on the spray drying of zirconia suspensions have been performed based on applying PAA as a dispersant and a high amount of a binder up to 15 wt.% (PVA, Latex or PEG).

Binders usually enhance the suspension viscosity causing some technical problems in the spray drying process. In addition, the uneven distribution of the binder may cause its migration toward the granule surfaces which results in cracks or incomplete cohesion of the granules after sintering [16]. Also, an undesired rigid layer or gel shell rich in binder has been reported on the surface of granules [2]. There has been an attempt to prepare granules with a low binder content (1 wt.%), but the researchers did not obtain the desired properties. However, when the authors increased the binder content to 3 wt.%, the produced granules did not have any defect [16]. The other problem in using a high molecular weight binder is the formation of undesired granules with large craters [13]. Viswanathan *et al.* [18] even reported that PVA is not a good binder to be applied in spray dried powders in plasma spray coatings and they used PEG as a binder for producing alumina granules.

The main purpose of the present study is to investigate the properties of YSZ granules prepared by a low molecular dispersant (Dolapix CE64) and to reduce the content of PVA binder. The effects of Dolapix as well as the pH of the suspension on the properties of the prepared granules were studied using microstructural evaluations along with the tapped density, Hausner ratio, cross-section and angle of repose of the granules. Although Dolapix has been known as a good dispersant for the preparation of the zirconia slips, there is only one study on the use of Dolapix for the preparation of granules published in 2018 [20]. Up to now, the authors have not found any systematic study on the effect of this commercial dispersant on the preparation of the YSZ granules and their properties.

II. Experimental

2.1. Materials and methods

Commercial common dispersant Dolapix CE64 with 65% active matter was used for commercial YSZ nano powder (3 mol% yttria, Tosoh, Japan) with an average particle size of 70 nm (Fig. 1). Initially, the dispersant was added to distilled water and stirred for 10 min. Then, the YSZ powder was gradually added to the solution to prepare a 40 wt.% solid loading suspension after which the resultant suspension was stirred again for an additional 20 min. The suspensions were stabilized by ultrasonic treatment for 30 min and HCl was used to adjust the pH of the suspensions. The utilized binder to attach the particles after the spray drying was PVA (hydrosoluble polyvinyl alcohol, Rhodia, France). The spray drying process was performed at the air flow rate of 4.5 l/h, feedstock flow of 1 kg/h, inlet temperature of 220 °C and output temperature of 110 °C. Compositions of the prepared YSZ suspensions in this study are given in Table 1.

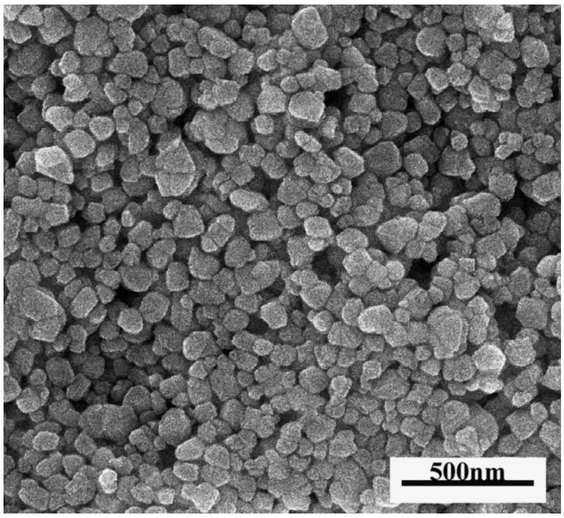

Figure 1. SEM micrograph of the YSZ raw material

2.2. Characterization

The rheological behaviour of the prepared suspensions was evaluated at a temperature of 25 °C using a controlled stress rheometer (MCR301, Anton Paar Physica). SEM microscope (FEI, Quanta) was used to investigate the effect of dispersant on the morphology and the size of the prepared granules. Tapped density measurement was used to determine the interparticle friction and their density. The Hausner ratio (*HR*) which indicates the flowability of granules was also calculated according to following equation [17,21]:

$$HR = \frac{\rho_t}{\rho_b} \tag{1}$$

where, ρ_t denotes the tapped density of the powder and ρ_b is the freely settled bulk density of the powder.

Table 1. Prepared YSZ suspensions

Suspension code	Amount of Dolapix CE64	Amount of PVA binder	HCl addition
S-P	-	0.1 wt.%	without HCl
S-D	0.1 wt.%	-	without HCl
S-DP	0.1 wt.%	0.1 wt.%	without HCl
SH	-	-	with HCl (pH ~ 4)
SH-P	-	0.1 wt.%	with HCl (pH ~ 4)
SH-D	0.1 wt.%	-	with HCl (pH ~ 4)
SH-DP	0.1 wt.%	0.1 wt.%	with HCl (pH ~ 4)

III. Results and discussion

3.1. Rheological parameters

It is well known that the suspension rheology has a great effect on the granule characteristics [16]. Low viscosity (0.5 Pa·s) is required for a suspension to be able to spray [17]. Table 2 outlines the yield stress and viscosity of the prepared suspensions. It can be seen that the highest value of yield stress and viscosity belong to the S-P suspension. High yield stress means the instability and flocculation state of a suspension [11,16,22]. It is of interest to have a deflocculation state in order to obtain hollow granules. The values of the rheological parameters decreased by adding Dolapix (the S-D and S-DP suspensions), by adjusting the pH (the SH and SH-P suspensions) or through both of them (the SH-D and SH-DP suspensions). The stability of these suspensions is due to the electrosteric interaction of Dolapix favouring repulsion among particles [23]. The reasons for the increase in the stability or reduction in the viscosity of a suspension through electrostatic or electrosteric mechanisms have been discussed in the literature [2,13,23,24]. Zirconia is hydrolysed in water and the hydroxide layers containing $Zr(OH)_4$ groups react with protons or hydroxyl ions. The ionization of the hydroxyl groups leads to changes in the surface charge.

Table 2. Yield stress and viscosity of the prepared suspensions

Suspension	Yield stress [Pa]	Viscosity* [Pa·s]
S-P	1.000	0.071
S-D	0.030	0.002
S-DP	0.046	0.003
SH	0.076	0.005
SH-P	0.079	0.005
SH-D	0.012	0.001
SH-DP	0.017	0.001

* At the shear rate of 10/s

The common amount of binder has been reported to be about 4 wt.% or 15 wt.% of Latex [7,15]. Walker [13] reported that the binder had a little influence on the rheology of alumina suspensions. However, we tried to reduce the binder in this study. Adding 0.1 wt.% of PVA binder to the suspensions led to increased yield stress, while also offering an advantage for their durability. Particles in the suspensions containing PVA binder settled later than in the suspensions without PVA. Enhanced viscosity in the range from 4 to 18 mPa·s has been observed when 5 wt.% of PVA binder was added [12]. Note that polymers cause steric repulsion among particles; however, PVA which has a high molecular weight has long polymeric chains remaining in the suspension media and prohibits the movement of particles, resulting in augmented viscosity [25]. Nevertheless, the data presented in Table 2 show that the prepared suspensions with only 0.1 wt.% of PVA have very low viscosity suggesting that they are suitable for spray drying.

3.2. Microstructural observations

SEM micrograph of the prepared granules from the suspension S-P is shown in Fig. 2a. Since the S-P suspension became very unstable and settled rapidly, it was hard to handle it during the granulation process. Because of that further amounts of PVA binder (0.3 wt.%) were added to the S-P suspension, but a low feeding rate was observed. The morphology of the granules obtained from the S-P suspension was irregular, unshaped, it had particles with sharp edges and contained large agglomerates. The sizes of these granules and/or agglomerates, calculated using *Image J* software, were about 100 µm with a high value of tolerance. Loghman [12] reported that without binders, many non-spherical particles (big facets) would be obtained, like in our case. The granules with an irregular shape suggest the coalescence of drying droplets [13].

The SH-P suspension was somehow stable and showed better durability in the granulation process than the S-P suspension. However, it was hard to spray this suspension, too. Note that this obstruction can be related to the lake of durability of the SH-P suspension. Thus, small amounts of granules were obtained. As shown in Fig. 2b, the morphology of the resultant granules is somehow spherical, but the granules had a wide size distribution and some of them were elongated. Also, the surface of the granules was not very smooth possibly due to the presence of porosity inside the granules. The obtained granules from the SH-P suspension had a desired appearance, but not an ideal symmetry. Note that formation of granules is due to the electrostatic stabilization provided by the pH adjustment. Also, it can be possible to form granules with low PVA contents.

The optimum amount of the binder plays an important role for the suspension to pass through the nozzle and spraying process. Binder increases the viscosity of a suspension and as such the amount of binder should be controlled. In the case of the S-DP suspension, suction and spraying into the chamber was hard and a nozzle with a larger diameter holes was required. According to Fig. 2c, the S-DP granules are more spherical than the SH-P granules, where 0.1 wt.% of Dolapix CE64 has had a positive effect on the morphology of granules. SEM micrograph of the prepared granules from the S-DP suspension indicates that more coherent and spherical granules were obtained using Dolapix. Also, the distribution of granules is uniform and the surfaces of the granules appear to be smoother.

In the case of the SH-DP suspension (Fig. 2d), it was observed that adhesion of the suspension to the walls of the spray dryer device was reduced and the suspension passed more easily through the nozzle. In this suspension, the viscosity did not increase upon binder utilization (Table 2) and this suspension had more durability as well as simpler handling during the spraying process. The obtained granules were spherical and uniform, with approximately the same size (about 50 µm). The viscosity of this suspension was so low that the nozzle could

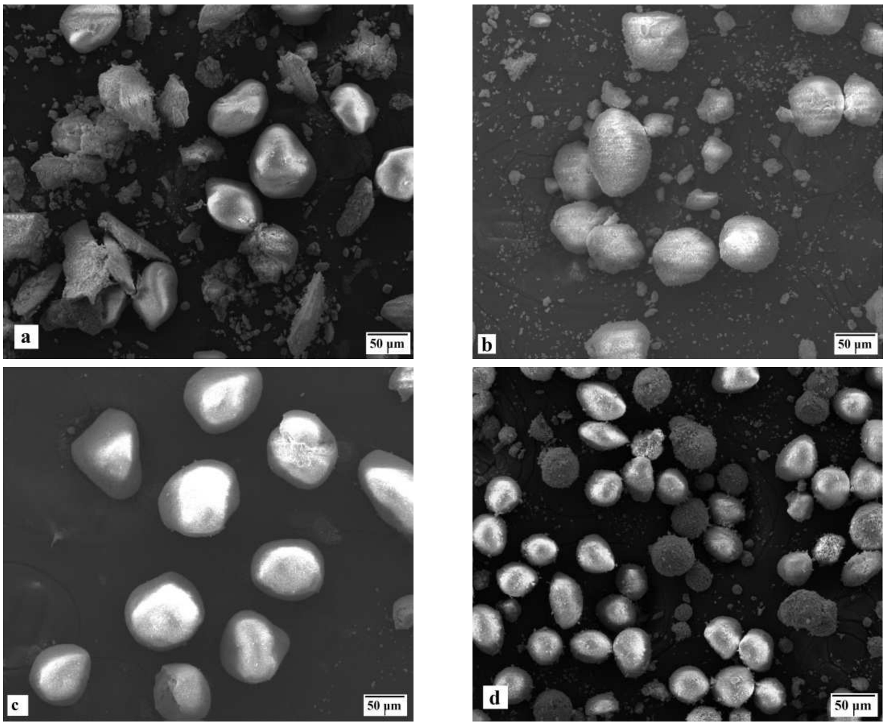

Figure 2. SEM images of the obtained granules from: a) S-P, b) SH-P, c) S-DP and d) SH-DP suspensions

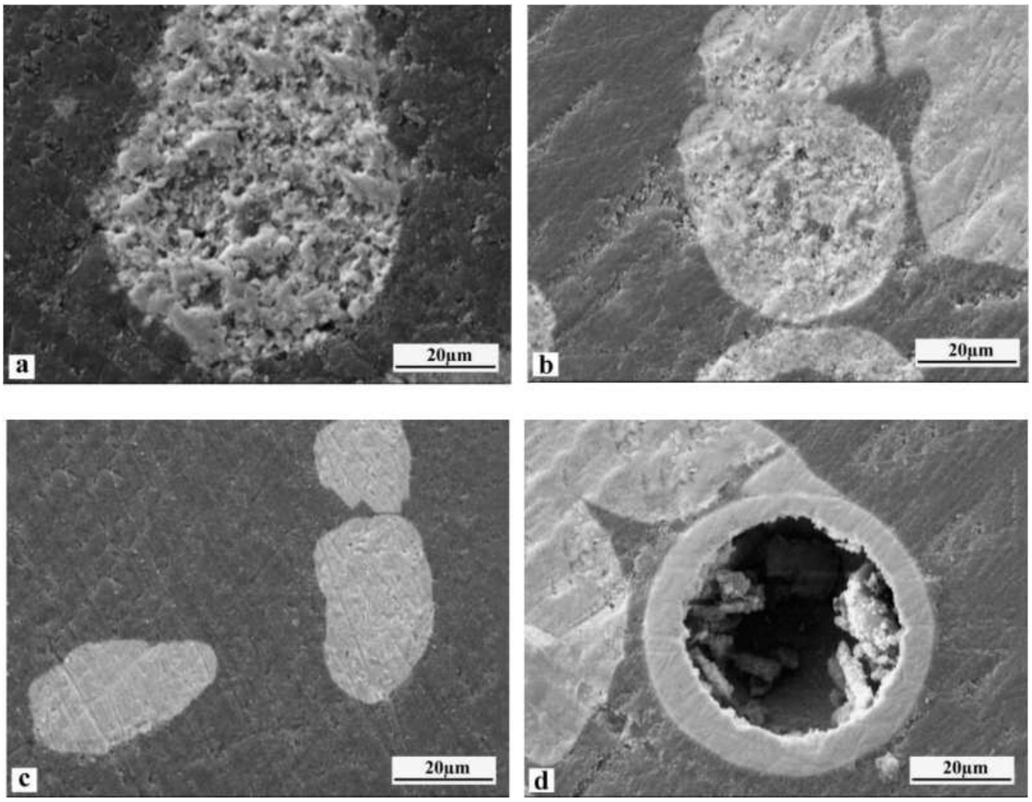

Figure 3. SEM micrographs of the polished cross sections of the granules prepared from: a) S-P, b) SH-P, c) S-DP and d) SH-DP suspensions

be replaced with one having smaller diameter. Also, particles got stuck less inside the device chamber and the rate of spraying was faster. Thus, high amounts of granules could be produced.

The common amount of PVA binder used by other researchers was reported as about 2–4 wt.%. Santana *et al*. [14] tried to decrease the amount of PVA; however, porous and non-uniform granules were obtained. In this work, with Dolapix as a dispersant, the amount of the binder is considerably reduced. By lowering the binder

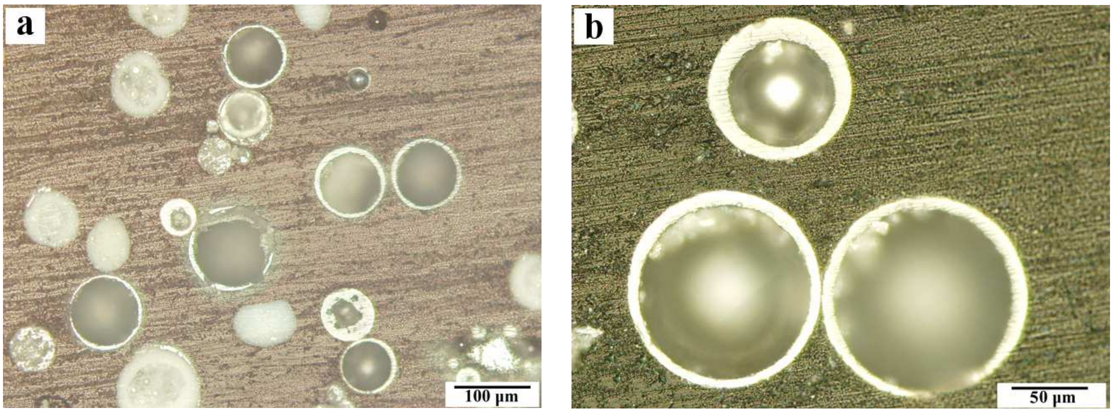

Figure 4. Optical microscopy images of the polished cross section of the granules prepared from SH-DP suspension

content while keeping the suspension stable, it can be seen that the morphology of the obtained granules is spherical and regular. Meanwhile, the suspension waste is reduced during the spray drying. These granules have a smoother surface and more uniformity.

SEM micrographs of the polished cross-sections of the prepared granules are shown in Fig. 3. It can be seen that the S-P, S-DP and SH-P granules have a solid cross-section without any central cavity. It is clear from Fig. 3a that the packing of particles inside a granule is loose and many pores can be seen. Pores are somehow shrunken in the SH-P granules (Fig. 3b) and it seems that the granules are a little denser than the S-P granules (Fig. 3a). It can be concluded that solid compact granules can also be obtained by this suspension. Solid granules are desired for the formation process by pressing, while hollow granules are desired for application of coatings. The completely solid granules can be observed in Fig. 3c. Thus, the use of Dolapix CE64 caused the granules to be dense and more compacted. The SH-DP granules have a different cross section, i.e. they show spherical hollow granules due to the deflocculation state of its suspension (Fig. 3d). Note that the interparticle forces and the viscosity of a suspension determine the shape, density, strength and deformability of the granules. Interparticle attraction causes the particles to be weakly bounded. Thus, the flocculation state of a suspension leads to increased thickness of the granules' wall. On the other hand, in the deflocculation state, the interparticle attraction is negligible and the particles can move rapidly toward the surface of the granules after spray drying, resulting in a hollow shape.

Figure 4 displays the cross-section area of the prepared SH-DP granules, observed by optical microscope in two magnifications. The cross-section of the granules indicates that they are hollow. Many factors such as pH, additives and the amount of solid loading affect the granular morphology. Due to the dispersion of particles in the stable slurry during granulation, single moving particles evolve on the surface during water evaporation and create a layer on the granule, causing the granule to be hollow [15]. It has been reported [16] that unstable slurry with flocculated particles results in solid granules while deflocculated suspension leads to hollow granules. Hollow granules are more fluid than solid granules. Also, they have higher density compared to their solid counterparts [2]. Large voids observed inside granules indicated the deflocculated state of the suspension [1].

During the spray drying, the particles and the binder are drawn to the surface of granules because of the capillary-induced moisture flow [7,11]. This migration to the granule surface causes granule shell thickening. For the suspensions prepared with the lower molecular weight Dolapix CE64 (320 g/mol), particles have greater mobility as they have no strong attraction to each other. Thus, the migrations of deflocculated particles are easier allowing the particles to move rapidly and making a dense shell. Figure 5 shows the suggested formation mechanism of the solid and hollow granules prepared by high and low molecular weight dispersants. In Figs. 5a and 5c, it is suggested that long chains prohibit the particles to approach each other. The repulsive charges

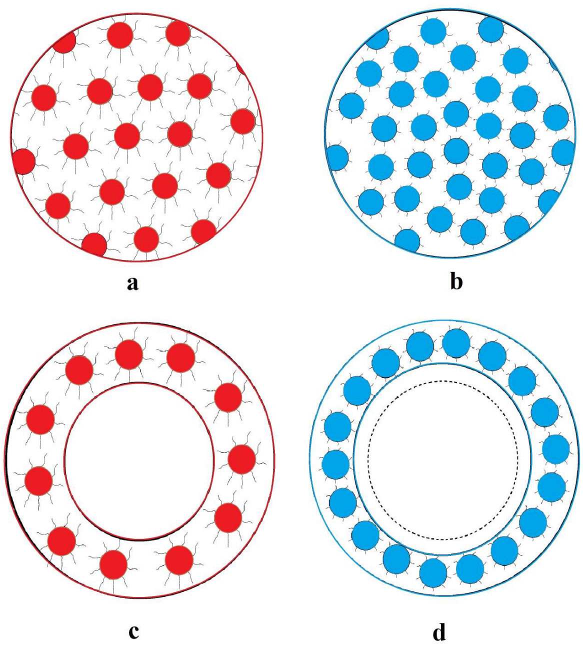

Figure 5. Schematic presentation of the formation of solid and hollow granules using a high molecular weight dispersant (a,c) and a low molecular weight dispersant (b,d)

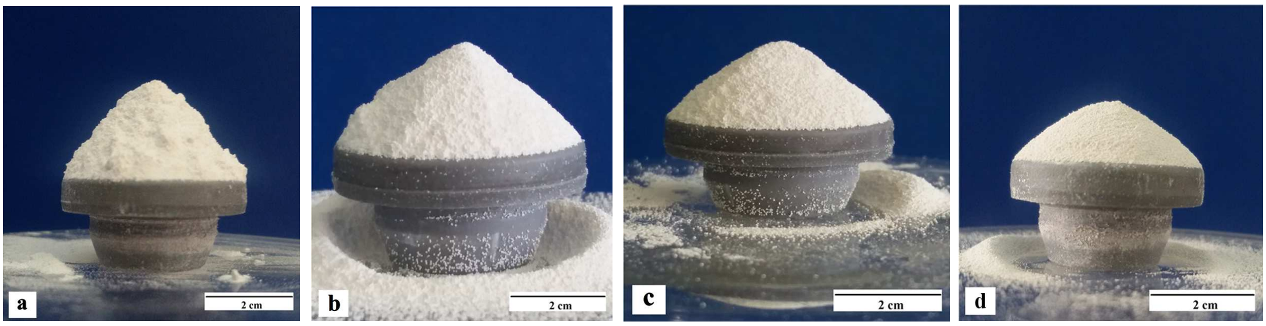

Figure 6. The repose angle of the granules prepared from: a) S-P, b) SH-P, c) S-DP and d) SH-DP suspensions

Table 3. The Hausner ratio and repose angle of the prepared granules

Granules code	Hausner ratio	Angle of repose [°]	Flow property*
S-P	1.33	55	Poor
SH-P	1.30	42	Passable
S-DP	1.24	37	Fair
SH-DP	1.15	34	Good

* According to Ref. 21

of chains repel the other chains whereby porous solid granules are formed. Low molecular weight dispersants have shorter chains and the distances between the particles can be smaller. Short chains of Dolapix allow the particles to approach each other. Thus, Fig. 5b shows that the granules can be more compact. Hollow granules in Fig. 5d are also suggested to be formed with a dense wall. Thin compact shells of granules are an outcome in this case.

3.3. Granules flowability

The Hausner ratio and repose angle of the prepared granules are presented in Table 3. The repose angle of the prepared granules was measured based on the photographs given in Fig. 6. Good flowability is indicated by the Hausner ratio lower than 1.18, while a poor flowability has a value greater than 1.35. The measured repose angle of the S-P granules was about 55°. Thus, it can be said that the S-P sample exhibited poor flowability. This behaviour is due to the fact that granules which do not have a spherical or regular shape do not slide on the others, thus accumulating as a mass on each other. The Hausner ratios of the zirconia granules prepared by Carpio [5] were reported to be in the range of 1.11–1.24. Low Hausner ratio (1.22) was also reported for zirconia granules using Dispex A40 as a dispersant [17]. In this study, we attained appropriate values indicating a desired flowability.

Figure 6 shows that the repose angle of the SH-P granules (42°) is in the passable range. These powders which did not contribute to the granule formation filled the spaces among the existing granules; thus less volume of the cylinder would be occupied. Adding 0.1 wt.% of Dolapix CE64 to the S-P suspension increased the stability causing the obtained granules to be more spherical than the SH sample. As a result, the friction between the particles decreased and allowed the formation of appropriate S-DP granules.

The 34° angle between the SH-DP granules and the surface indicates a good flow of these granules, which is a desirable result compared to other granules.

IV. Conclusions

In this paper, application of Dolapix CE64 with a low molecular weight instead of commonly used PAA (dispersant with a high molecular weight) for preparing zirconia granules was investigated. The results indicated that Dolapix can reduce the viscosity and yield stress of a zirconia suspension. Adjusting the pH of the suspension can also help the stabilization and improve the rheological parameters. Microstructural observations revealed that solid spherical granules can be obtained by adding 0.1 wt.% of Dolapix, and hollow granules can be attained by adjusting the pH at 4 and use of 0.1 wt.% Dolapix. The main and interesting benefit of incorporating Dolapix was the reduction of PVA binder amount to only 0.1 wt.%. The prepared granules with Dolapix were uniform and had a reasonable size distribution. Flowability and Hausner ratio of the prepared granules were also measured to lie within the desirable range.

References

1. N.P. Padture, M. Gell, E.H. Jordan, "Thermal barrier coatings for gas-turbine engine applications", *Science*, **296** [5566] (2002) 280–284.
2. H. Mahdjoub, P. Roy, C. Filiatre, G. Bertrand, C. Coddet, "The effect of the slurry formulation upon the morphology of spray-dried yttria stabilised zirconia particles", *J. Eur. Ceram. Soc.*, **23** [10] (2003) 1637–1648.
3. J. Xian-Liang, L. Chun-Bo, L. Min, Z. Hui-Zhao, "Influence of heat treatment on nanocrystalline zirconia powder and plasma-sprayed thermal barrier coatings", *Trans. Nonferrous Met. Soc. China*, **20** [12] (2010) 2272–2280.
4. M.R. Loghman-Estarki, H. Edris, R. Shoja Razavi, H. Jamali, R. Ghasemi, M. Pourbafrany, M. Erfanmanesh, M.

Ramezani, "Spray drying of nanometric SYSZ powders to obtain plasma sprayable nanostructured granules", *Ceram. Int.*, **39** [8] (2013) 9447–9457.
5. P. Carpio, R. Moreno, A. Gómez, M. Dolores Salvador, E. Sánchez, "Role of suspension preparation in the spray drying process to obtain nano/submicrostructured YSZ powders for atmospheric plasma spraying", *J. Eur. Ceram. Soc.*, **35** [1] (2015) 237–247.
6. M. Hajizadeh-Oghaz, R. Shoja Razavi, M.R. Loghman-Estarki, "Synthesis and characterization of non-transformable tetragonal YSZ nanopowder by means of Pechini method for thermal barrier coatings (TBCs) applications", *J. Sol-Gel Sci. Technol.*, **70** [1] (2014) 6–13.
7. P. Roy, G. Bertrand, C. Coddet, "Spray drying and sintering of zirconia based hollow powders", *Powder. Technol.*, **157** [1-3] (2005) 20–26.
8. K. Suwunnasung, A. Nuntiya, "Influence of suspension characteristics on the morphology of 3Y-ZrO_2 granules produced by a spray drying process", *Chiang Mai J. Sci.*, **36** [3] (2009) 340–348.
9. J. Sam Choi, Y.M. Kong, "A case study on sintering characteristics of yttria stabilized zirconia powder prepared by two-fluid spray drying", *J. Korean Ceram. Soc.*, **53** [3] (2016) 332–337.
10. C. Durmus, O.S. Ozgen, "Experimental synthesis of granulated zirconia powders by spray dryer", *Mater. Lett.*, **145** (2015) 243–246.
11. G. Bertrand, C. Filiatre, H. Mahdjoub, A. Foissy, C. Coddet, "Influence of slurry characteristics on the morphology of spray-dried alumina powders", *J. Eur. Ceram. Soc.*, **23** [2] (2003) 263–271.
12. M.R. Loghman-Estarki, M. Pourbafrany, R. Shoja Razavi, H. Edris, S. RezaBakhshi, M. Erfanmanesh, H. Jamali, S. Naveed Hosseini, M. Hajizadeh-Oghaz, "Preparation of nanostructured YSZ granules by the spray drying method", *Ceram. Int.*, **40** [2] (2014) 3721–3729.
13. W.J. Walker Jr., J.S. Reed, "Influence of slurry parameters on the characteristics of spray-dried granules", *J. Am. Ceram. Soc.*, **82** [7] (1999) 1711–1719.
14. L.P. Santana, D.R.R. Lazar, W.K. Yoshito, V. Ussui, J.O.A. Paschoal, "Spray-dried YSZ ceramic powders: Influence of slurry stability on physical characteristics of agglomerates", *Mater. Sci. Forum*, **591-593** (2008) 465–470.
15. G. Bertrand, P. Roy, C. Filiatre, C. Coddet, "Spray-dried ceramic powders: A quantitative correlation between slurry characteristics and shapes of the granules", *Chem. Eng. Sci.*, **60** [1] (2005) 95–102.
16. V. Naglieri, D. Gutknecht, V. Garnier, P. Palmero, J. Chevalier, L. Montanaro, "Optimized slurries for spray drying: different approaches to obtain homogeneous and deformable alumina-zirconia granules", *Materials (Basel)*, **6** [11] (2013) 5382–5397.
17. B.P. Raghupathy, J.G. Binner, "Spray granulation of nanometric zirconia particles", *J. Am. Ceram. Soc.*, **94** [1] (2011) 42–48.
18. V. Viswanathan, K.E. Rea, A. Vaidya, S. Seal, "Role of spray drying of nanoagglomerates in morphology evolution in nanostructured APS coatings", *J. Am. Ceram. Soc.*, **91** [2] (2008) 379–386.
19. P. Pei, S.G. Malghan, S.J. Dapkunas, P.H. Zajchowski, "Characterization and processing of spray-dried zirconia powders for plasma spray application", *J. Therm. Spray Technol.*, **9** [3] (1996) 343–351.
20. P. Hohne, B. Mieller, T. Rabe, "Slurry development for spray granulation of ceramic multicomponent batches", *J. Ceram. Sci. Technol.*, **9** [3] (2018) 327–336.
21. G. Lumay, F. Boschini, K. Traina, S. Bontempi, J.C. Remy, R. Cloots, N. Vandewalle, "Measuring the flowing properties of powders and grains", *Powder Technol.*, **224** (2012) 19–27.
22. H. Majidian, T. Ebadzadeh, E. Salahi, "Effect of SiC particles on rehological and sintering behavior of alumina-zircon composites", *Ceram. Int.*, **36** [5] (2010)1669–1673.
23. F. Zerafati, H. Majidian, L. Nikzad, "Dispersion properties of nano YSZ particles in aqueous suspensions", *Adv. Ceram. Prog.*, **5** [3] (2019) 15–22.
24. H. Majidian, T. Ebadzadeh, E. Salahi, "Stability evaluation of aqueous alumina-zircon-silicon carbide suspensions by application of DLVO theory", *Ceram. Int.*, **37** [7] (2011) 2941–2945.
25. H. Majidian, T. Ebadzadeh, E. Salahi, "Stability properties of alumina-zircon-SiC suspensions by adsorption of Dolapix onto the particles", *J. Ceram. Process. Res.*, **14** [3] (2013) 342–348.