

Article

A Comparative Study of YSZ Suspensions and Coatings

Fariba Tarasi, Elnaz Alebrahim, Ali Dolatabadi, Christian Moreau*

Concordia University, Montreal QC Canada

*Corresponding author: Christian Moreau Email: Christian.Moreau@Concordia.Ca phone: 1-514-848-2424 (7921)

Abstract: The demand for suspensions used in thermal spray processes is expanding from research labs using the lab-prepared suspensions toward actual coating production in different industrial sectors. Industrial applications dictate reduced production time and effort which may in turn justify the development of the market for ready-to-use commercial suspensions. To this end, some of the powder suppliers have already taken steps forward by introducing to the market suspensions of some of the most used materials such as yttria-stabilized zirconia (YSZ), alumina and titania. There is, however, a need to compare the suspension characteristics over time and the resultant coatings when using these suspensions as compared with the freshly prepared home-made suspensions. In this work, such comparison is done using YSZ suspensions of the sub-micron to a few micron powders. In addition, some changes in the suspensions' formula were performed as a tool to vary the coatings' microstructures in a more predictable way, without variation of spray parameters. The coatings were generated using both radial and axial injection of the suspensions into Oerlikon-Metco 3MB and Mettech Axial III plasma spray torches, respectively. A clear effect of suspension viscosity on the coating microstructure was observed using the 3MB torch with radial injection of suspension (i.e. cross flow atomization). The viscosity role, however, was not dominant when using the Axial III torch with axial feed injection system (i.e. coaxial flow atomization).

Keywords: axial and radial suspension plasma spray, commercial suspensions, viscosity, surface tension, coatings microstructures

1. Introduction

Suspension plasma spray (SPS) process is considered as a technique that enables variations of thermally sprayed coatings e.g., from highly dense and vertically cracked (DVC) to porous, feathery and columnar microstructures [1]. There is a growing demand for yttria-stabilized zirconia (YSZ) suspensions to deposit thermal barrier coatings (TBC), either to generate the main TBC ceramic layer or as a repair method [2]. In both cases, the preferred microstructure contains large globular pores and connected cracks that can potentially yield high strain tolerance and low thermal conductivity [1,3].

Accordingly, to satisfy the needs of the industry, the suppliers have offered to the market the ready-to-use suspensions of yttria stabilized zirconia-YSZ powders. It is, therefore, a matter of interest to identify first the differences (if any) of the commercially available suspensions with those freshly made in laboratory. A major difference while comparing commercial suspensions with the home-made ones is the freshness of the latter. Therefore, whether the "aging" of a suspension could affect its properties is a question to be addressed in this work. In addition, the commercial suspension formula target highly demanding applications that require coatings with specific microstructure and properties produced in a consistent manner. Therefore, it would be important to verify the flexibility of such commercial formula toward fabrication of different types of microstructure mentioned above (columnar, DVC, etc.).

While numerous studies have been conducted for controlling the coating microstructure by optimizing the spray parameters [4,5], this work focusses on investigating the influence of the suspension characteristics on the coating structure while keeping the other spray parameters constant.

VanEvery et al. [6] suggested a mechanism for variation of the SPS coating microstructures based on the impacting particle size that has a direct influence on the particle velocity and direction prior to impact [7,8] and showed a transition from planar (APS-like) deposition to columnar coatings as the average particle size decreases. The size of the suspension droplets atomized by the plasma jet has a strong influence on the size of the in-flight particles in SPS process [9-11]. The control of the resultant coating microstructure is therefore dependent, among all, on the size of the droplets generated during the atomization/fragmentation of the suspension as it determines the size of the impacting particles that are formed following to the evaporation of the suspension solvent [12]. In addition to droplet size, a variety of morphologies of the in-flight suspension droplets during drying can be formed such as solid or hollow spheres, as well as large inflated shapes depending on their heating and drying history [13]. Such intermediate shapes of the particles following the solvent evaporation that occur before deposition on the substrate shall affect the coating microstructures [14].

Literature on atomization phenomena recognizes the importance of the viscosity and surface tension of the liquid phase (solvent and suspended solid particles in this study) in either cross flow [15,16] or coaxial flow [17]. These parameters become fundamental especially when other parameters are identical, that is to say, when the densities (similar solid loading and carrier liquid) and the gas and liquid velocities (using identical spray parameters) during fragmentation of the suspensions are kept constant. Therefore, in this work apart from particle size studies, the viscosity and surface tension of the suspensions are the main parameters of investigation.

2. Experimental

2.1. Suspensions and Feed Material

Overall, five different YSZ suspensions were deposited in this experiment as presented in **Error! Reference source not found.** They included two commercial suspensions (as received), one commercial suspension with an amended formula, and two home-made (HM) suspensions, all at 25 wt% solid. The commercial suspensions were supplied by Innovnano (4YSZSE.4, Porto Salvo, Portugal) named C1 in this work and Treibacher (YSZ suspension, Althofen, Austria) named C2. The amended commercial suspension is called C3. It was produced by adding 5 wt% of the solid content of PVP (Poly vinyl pyrrolidone) in the C2 suspension continuously agitated with a magnetic stirrer. There is no surfactant identified in the composition of both C1 and C2 commercial suspensions. The home-made suspensions had the formulation presented in **Error! Reference source not found.** The surfactant used was with an amount of 5wt% of the solid (equal to 1.25wt% of the suspension). The HM1 suspension was produced by firstly mixing the surfactant with the ethanol followed by gradual addition of the powder while both magnetic and ultrasonic mixing were in process (during about 30 minutes). The HM2 suspension was generated the same way as HM1, except that in this case no surfactant was used.

Table 1: Formulation of the investigated suspensions

Supplier	Suspension name	Formulation
Innovnano	C1	25wt%YSZ in ethanol
Treibacher	C2	25wt%YSZ in ethanol
Treibacher- amended	C3	25wt%YSZ in ethanol + 5 solid wt.% PVP
Home-made 1	HM1	25wt% YSZ + 5 solid wt.% PVP in ethanol
Home-made 2	HM2	25wt%YSZ in ethanol (similar to commercial formula)

The size distributions of the particles in the suspensions were measured using the Spraytec particle size analyzer (Malvern Worcestershire, UK) having a measurement range of 0.1 to 2000 μm . The system uses a wet cell in which a dilute suspension of the particles in ethanol is circulated. The suspension viscosities were measured using an Anton-Paar MRC 502 rheometer system (provide Anton-Paar company's info) using double cylinder method with shear rates varying from 10 to 1000 s^{-1} . The measurements were done on fresh or magnetically re-mixed suspensions for at least 30 minutes or after bottle mixing (manual shaking) for the commercial suspensions. For further characterization of the suspensions, a thin layer of suspension was spread on a glass plate and dried at room temperature. The

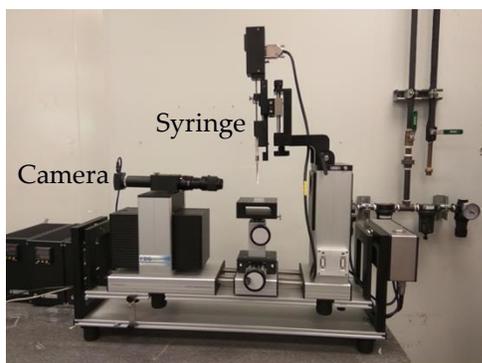


Figure 1 Setup for surface tension measurement

particles and agglomerates were then observed by SEM microscopy. Surface tension measurements were performed using an arrangement shown in Figure 1, consisting of a droplet flow syringe ending to a needle. The specified size of the tip of the needle allows the suspension droplet to fall and the camera takes a video of the phenomena. Using the recorded images, the moment of droplet detachment and the diameter and volume of the droplet are calculated and based on the density of suspension (0.95 g/mm^3) translated to the surface tension by the software. A minimum of five measurements were taken and the related standard deviations were calculated as error bars.

The five suspensions were used to compare the commercial suspensions with home-made ones having either different formula and/or different time of life (previously prepared commercial or freshly prepared). In addition, they made it possible to investigate if the microstructures of coatings produced with the commercial suspensions can be tailored for other applications than TBC.

2.2. Coatings Generation

The coatings were generated using two commercial plasma spray systems including a 3MB torch (Oerlikon-Metco, Pfäffikon, Switzerland) with radial injection; and a Axial III (Northwest Mettech Corp., North Vancouver, BC, Canada) with axial injection of the suspension. In both cases, the suspension was fed into the plasma torch using a NanoFeed™ Liquid & Suspension Feeder (Northwest Mettech Corp., North Vancouver, BC, Canada). The spray conditions are summarized in Table 2 and Table 3 for the two plasma spray torches. The substrates were $2.54 \times 2.54 \text{ cm}^2$ and 3 mm thick stainless steel 304 plates blasted with alumina grit 20. The approximate roughness of the substrates was 5-6 μm . The radial injection was normal to the flow axis.

Table 2: Spray conditions using 3MB torch with radial injection and no prior suspension atomization

Sample #	Supplier	Plasma gas (L/min)	Gas pressure (psi)	Current (A)	Feed rate (mL/min) (set = 20)	Robot Speed (m/s)	Spray distance (mm)	Injector dia. (μm)	# of Passes
1	C1	Ar+He (25,25)	60	600	19-20	1	30	150	69
2	C2				21-23				80
3	C3				20-23				80
4	HM1				20-24				80
5	HM2				22-24				80

Table 3: Spray conditions using Axial III with axial injection and atomization

Sample #	Supplier	Atomizing gas (N ₂) (L/min)	Plasma gases (L/min)	Total gas (l/min)	Current (Amp)	Feed rate (ml/min) (set=40)	Robot speed (m/s)	Spray distance (mm)	# of Pass
1	C1	15	Ar/N ₂ /H ₂ (75/10/15)	245	190	32-48	1	50	40
2	C2								30
3	C3								30
4	HM2								30

It can be pointed out from Tables 2 and 3 that some deviations from the set point value in the feed rate were observed. These deviations were more pronounced when using the axial injection plasma torch (Table 3). The suspension densities, as measured during spraying, varied between 0.95-1.1 g/cm³.

3. Results and Discussion

3.1. Suspension Characteristics

3.1.1. Dried Suspensions

The low magnification SEM images of the dried suspensions from the two commercial and the two home-made suspensions are presented in **Error! Reference source not found.**. It can be observed that there is a higher tendency in the HM suspensions to form large agglomerates of about up to 50 μm . This

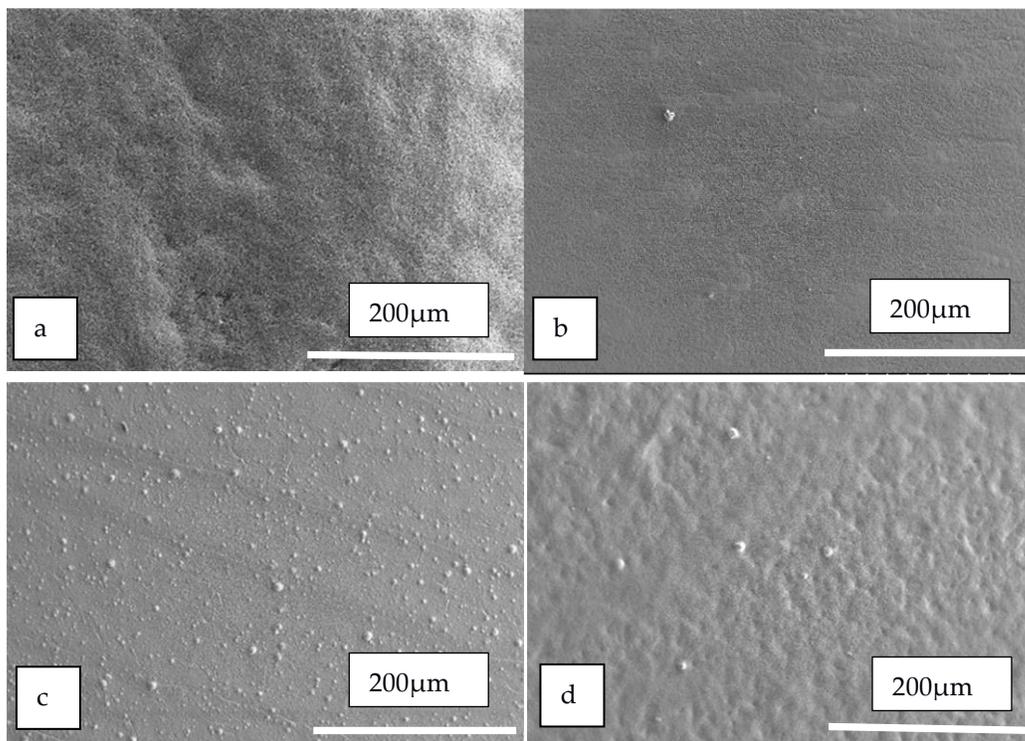


Figure 2: Dried suspensions of a) C1, b) C2, c) HM1, d) HM2

tendency is significantly stronger in case of the HM1 which contains surfactant. It is interesting to note that while the surfactant may provide a better dispersion of particles in suspension and help better stability, it can have a contradictory effect and favor the formation of large agglomerates. Comparing Figures 2.a and b with Figures 2.c and d shows that it is difficult to prepare homogeneous home-made suspensions in the lab. Clearly the processes used by the commercial suspension providers provide a high degree of homogeneity of the suspensions without significant number of large agglomerates as shown in Figures 2.a and 2.b.

Higher magnification SEM images of the same suspensions are shown in Figure 3 revealing further information about the original powders used in each of these suspensions. It can be seen that while the powders in C1 and the HM suspensions are closely similar in morphology (mainly round) and size, the powder particles in C2 are more of angular shape and larger (roughly 2-3 times).

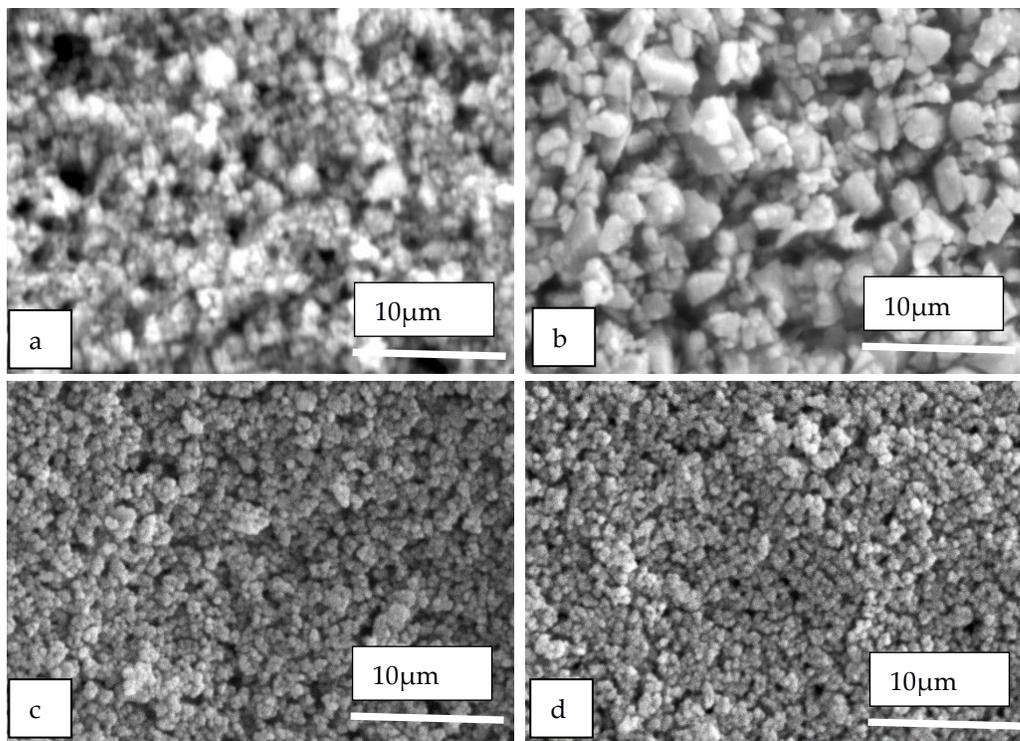


Figure 3 High magnification SEM images of the dried suspensions of a) C1, b) C2, c) HM1, d) HM2, revealing the original powder particle shapes and sizes

3.1.2. Particle Size Distributions

The measured particle/agglomerate size distribution in the suspensions are compared with the original powder size provided by the suppliers in Table 4. The measured size values can be significantly larger than size of the particles as they can form micron-sized agglomerates when suspended in ethanol. The addition of surfactant made it possible to better disperse the particles as seen when comparing home-made suspensions HM1 (with surfactant) with HM2 (without surfactant). Indeed, adding the surfactant resulted in a D50 of 0.4 μm while a D50 of 1.00 μm was obtained for the suspension without a surfactant (HM1).

Table 4: Particle size distribution in original powder and in suspensions

Suspension name	Original powder size (μm)	Particle size distribution in the suspension (μm)		
		D ₁₀	D ₅₀	D ₉₀
C1	0.4-0.5 (D ₅₀)	1.08	2.14	4.07
C2	0.15-0.4, 0.4-0.8, 0.9-1.7 (D ₁₀ , D ₅₀ , D ₉₀)	0.85	1.63	2.97
C3	Same as C2	0.24	0.51	1.06

HM1	0.4 (D ₅₀)	0.15	0.4	0.80
HM2	0.4 (D ₅₀)	0.45	1.00	1.88

3.1.3. Surface Tensions

Surface tensions of six samples were measured including the two commercial suspensions and the home-made ones, both with and without surfactant addition. The results are summarized in **Error! Reference source not found.** Although, the suspension C1 with added surfactant (C1+PVP) was not sprayed, the effect of addition of surfactant to this suspension was investigated for comparison purpose and verification of the behavior observed in commercial suspension C2. As can be readily seen, the changes in surface tension due to surfactant addition in all three suspensions are rather small (less than 6.5%). The highest surface tensions are obtained with the HM suspensions while the lower ones are obtained with the C2 and C3. In addition, the effect of surfactant addition could be either increasing (in case of C1) or decreasing (in case of HM and C2).

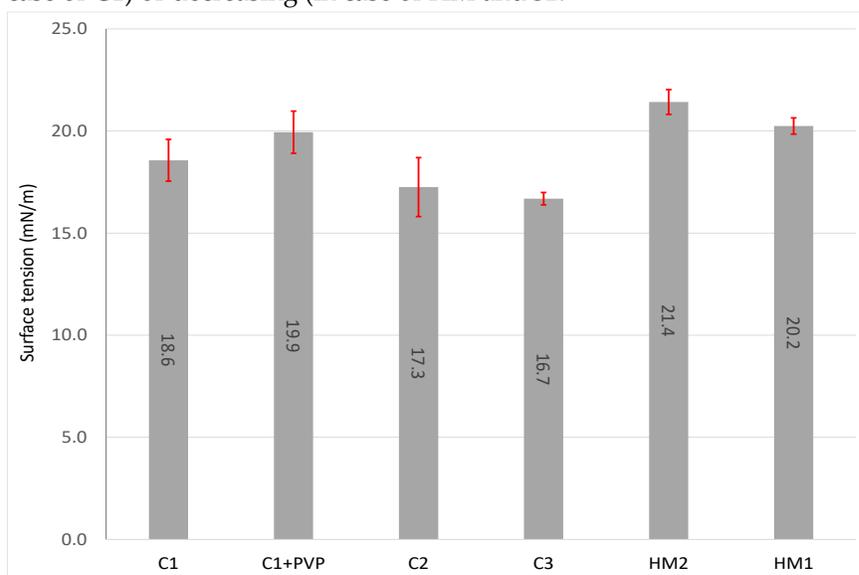


Figure 4: Surface tension of various suspensions

3.1.4. Viscosity

Viscosity of the suspensions was studied to verify the effect of aging of the suspensions as well as to investigate the effect of surfactant addition.

i. Solid particles and surfactant effects

Figure 5 represents the viscosity of the two commercial suspensions, one amended commercial formula (C3) and the two home-made formulas. Both home-made suspensions (HM1 and HM2) present higher viscosities than the commercial suspensions. However, addition of surfactant to the commercial suspension has resulted in an increase of viscosity as observed in C3. A similar increase is observed when comparing the viscosity of HM2 (with surfactant) as compared with HM1 (without surfactant).

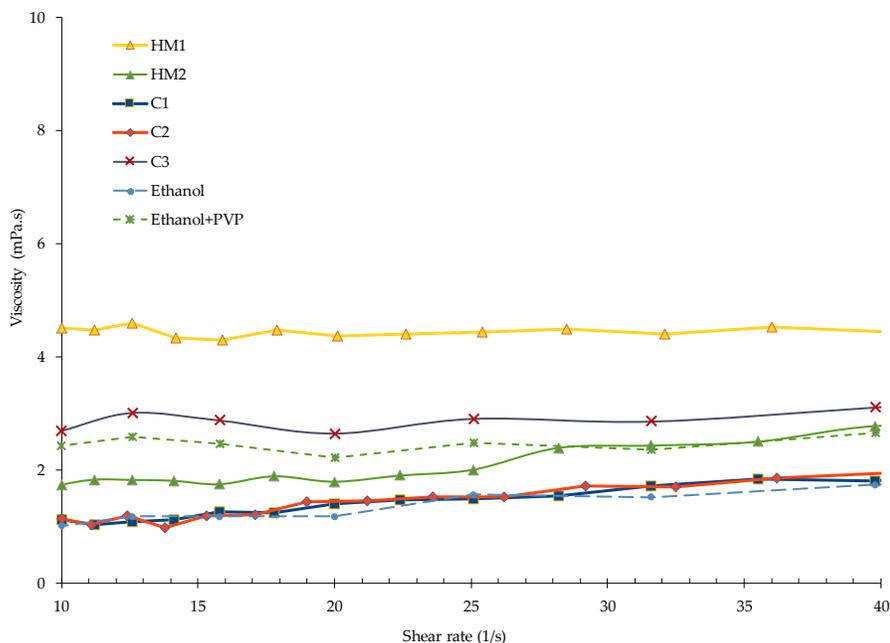


Figure 5 Viscosity vs. shear rate for the two HM (freshly prepared) and the three commercial suspensions (as received and amended), as well as their respective base liquids

In application of either polymeric or ionic surfactants, under-dosed (less than optimum quantity for stabilization) of surfactants can result in increased viscosity [18,19]. It can thus be the low quantity of surfactant used in this experiment that caused the increased viscosity of the suspensions.

It is known that the viscosity of a shear-thickening fluid depends on the shear rate. Key parameters that control the shear thickening behavior comprise; particle size distribution, particle volume fraction, particle shape, inter-particle interaction and continuous phase (solvent) viscosity [20]. Here, to investigate the role of the solid particles on the thickening behavior of the suspensions, the viscosities of the solvents (ethanol and ethanol plus PVP) were measured and are shown in **Error! Reference source not found.** It is also noticeable in this figure, that the viscosity of the ethanol plus PVP is even higher than the suspension with 25wt% solid without surfactant. This comparison emphasizes the non-negligible influence of even small quantities of surfactant on suspension viscosity.

ii. Aging effect

Figure 6 shows the effect of ageing on the suspension behavior. It should be noted that the aged suspensions were well remixed before deposition. The viscosities of two suspensions HM1 (with surfactant) and HM2 (without surfactant) have been measured as fresh as well as after one, three and five months. The viscosity is initially increased by the age of the suspension in one month. However, this relation reverses when the time gets longer. As can be seen for the viscosity of the suspension HM2 from one month to five months the suspension shows a lower viscosity by time. It should be added that the viscosity of the commercial suspensions (aged for long time before testing and remixed in bottle as per the supplier's recommendation) measured in different occasions were showing the same exact curves regardless of the time.

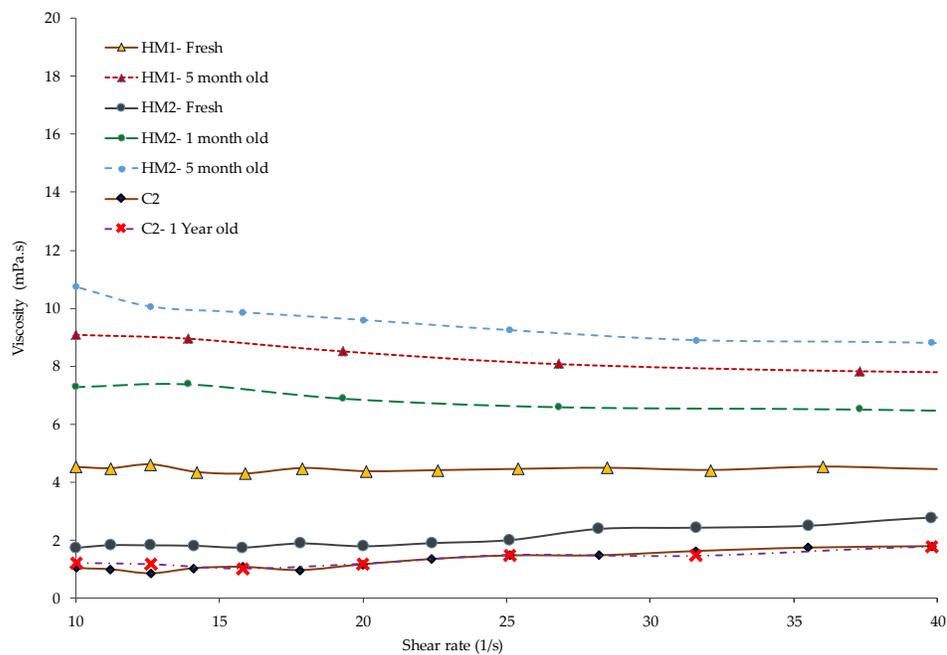


Figure 6 Viscosity vs. shear rate of the two home-made suspensions HM1 and HM2 aged for one, three and five months compared with fresh suspensions

3.2. Coatings Microstructures

The influence of the suspension characteristics on the resulting coating microstructures was evaluated by depositing coatings using two different plasma torches. The microstructures of the coatings generated using the radial injection Oerlikon-Metco 3MB torch are shown in Figure 7. Coatings presented in Figure 7-a and b, generated from the two commercial suspensions with similar viscosities and lowest surface tensions, show similar columnar microstructures. In contrast, home-made suspensions HM1 and HM2 with higher viscosities and higher surface tension resulted in clearly denser microstructures as seen

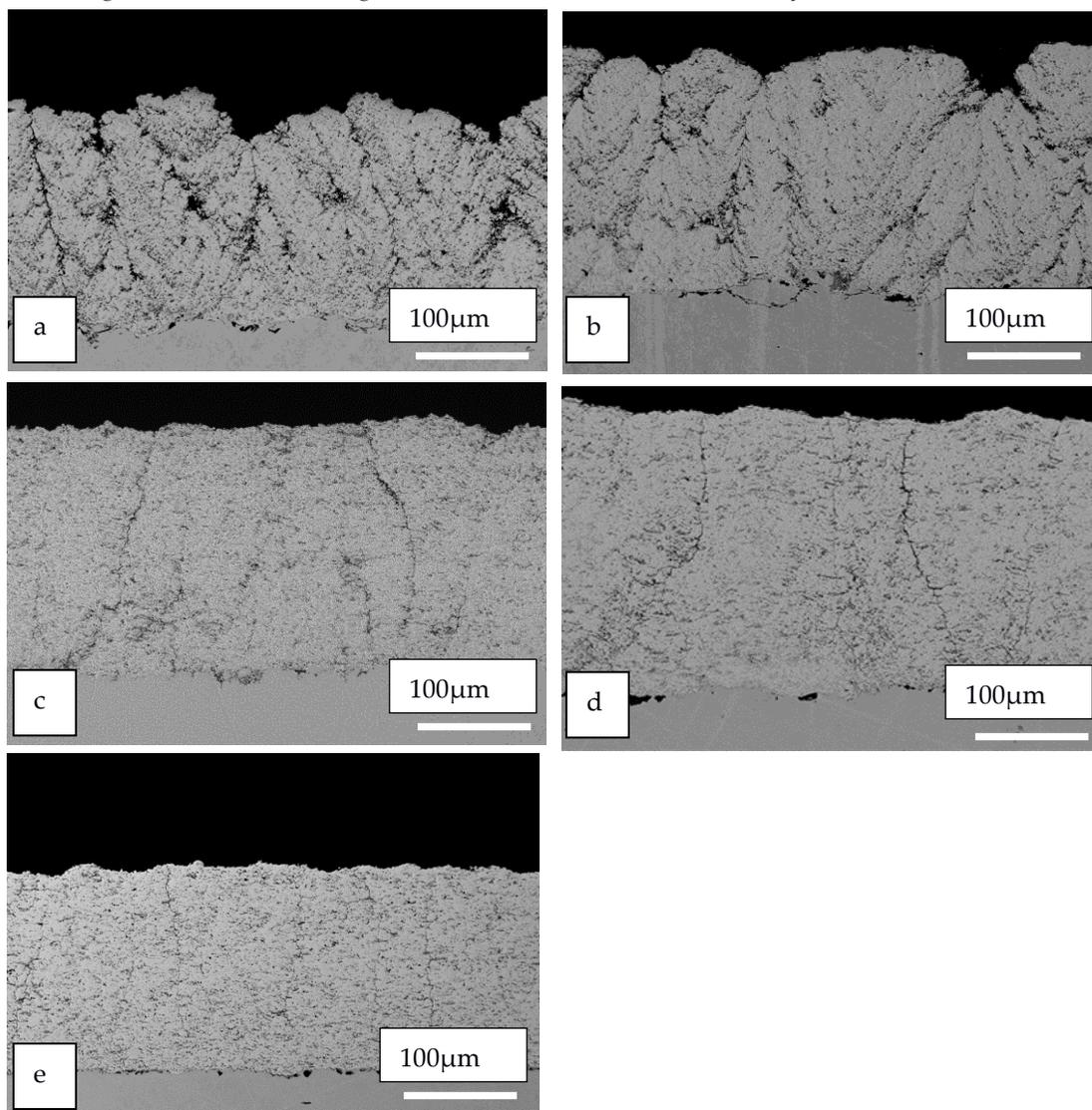


Figure 7: Backscattered SEM micrographs of the coatings deposited by radial injection using various suspensions; a) C1, b) C2, c) HM2, d) HM1 and e) C3

in Figure 7-c and d. Additionally, coatings produced with suspension C3 (C2 + surfactant) presents a microstructure comparable to that found for the home-made suspensions as shown in Figure 7-e. As shown in Figure 6, the viscosity of suspension C3 is higher than C1 and C2. Accordingly, the observed changes of coating microstructures correlate with the viscosity and surface tension of the different suspensions. The lower viscosity suspensions produced more columnar structures.

This observed relationship can possibly be interpreted in the following manner. During deposition with the 3MB torch, the suspension is injected radially in which the suspension jet is not atomized before interacting with the plasma jet. Consequently, cross flow atomization occurs when the suspension jet penetrates the high-speed high-temperature plasma flow. In such conditions, it is expected that lower suspension viscosity and surface tension produce smaller size suspension droplets and thus, smaller size of the zirconia molten particles after evaporation of the solvent. The trajectories of smaller particles (with reduced mass) are more easily deviated by the presence of the substrate and thus the particles impact with shallower angles on the substrate surface. In such case, the shadow effect has more influence on the coating build-up process resulting in the formation of columnar structures as those shown in Figure 7-a and b for coatings produced with the commercial suspensions. On contrary, one can expect that higher viscosity and surface tension lead to larger particles and thus the formation of denser coatings as observed in Figure 7-c, d and e. The clear variation of microstructures thus supports the expected role of the suspension low viscosity and low surface tension on the atomization process and the resulting microstructure when cross flow atomization plays a dominant role.

Figure 8 shows the cross-sections of the coatings generated using axial suspension injection into the Axial III Mettech torch. In Figure 8-a and b, it can be seen that the two commercial suspensions C1 and C2 produced coatings with significantly different densities and microstructures, despite having the same viscosity and almost similar surface tension values (18.6 and 17.3 mN/m for C1 and C2, respectively). However, the coating produced with the home-made suspension HM2 with higher viscosity and higher surface tension (seen in Figure 8.c) shows columnar microstructure similar to that of C1. Finally, suspension C3 (C2 with surfactant) with relatively high viscosity and low surface tension presents a dense microstructure (Figure 8.d) mostly similar to the coatings from C2.

As seen in Figure 8, the microstructural changes observed with the different suspensions do not correlate in a straightforward manner with the different viscosities and surface tensions of the investigated suspensions in opposition with the results observed with the radial injection (Figure 7). In the axial injection torch, the suspension undergoes two successive atomization steps. The first one occurs in the injector that comprises a coaxial flow atomizer. Indeed, the injected suspension is atomized (primary atomization) before entering in the plasma flow. It is important to mention that if a laminar suspension jet was used (without an air assist atomization as in the radial injection case discussed above), the interaction of this liquid jet with the plasma flow would be very limited as both fluids travel in the same direction leading to extremely large droplets or ligaments of suspensions reducing dramatically the deposition efficiency of the spray process. The second atomization step takes place when the injected suspension droplets interact with the high-speed plasma jet inside the torch. This secondary atomization occurs according to the catastrophic regime where Rayleigh–Taylor and Kelvin–Helmholtz waves (high Weber numbers) play a dominant role in the droplet fragmentation [9,15]. Accordingly, it is expected that the role of the suspension characteristics like viscosity and surface tension be different in the axial injection configuration than in the radial one. What is predictable is that the more the droplets are fragmented, the smaller is the particle size and the stronger the tendency to form coatings with porous and columnar structures. In coatings sprayed with the axial injection plasma torch, other factors (than the suspension rheological properties) influence the development of different coating structures.

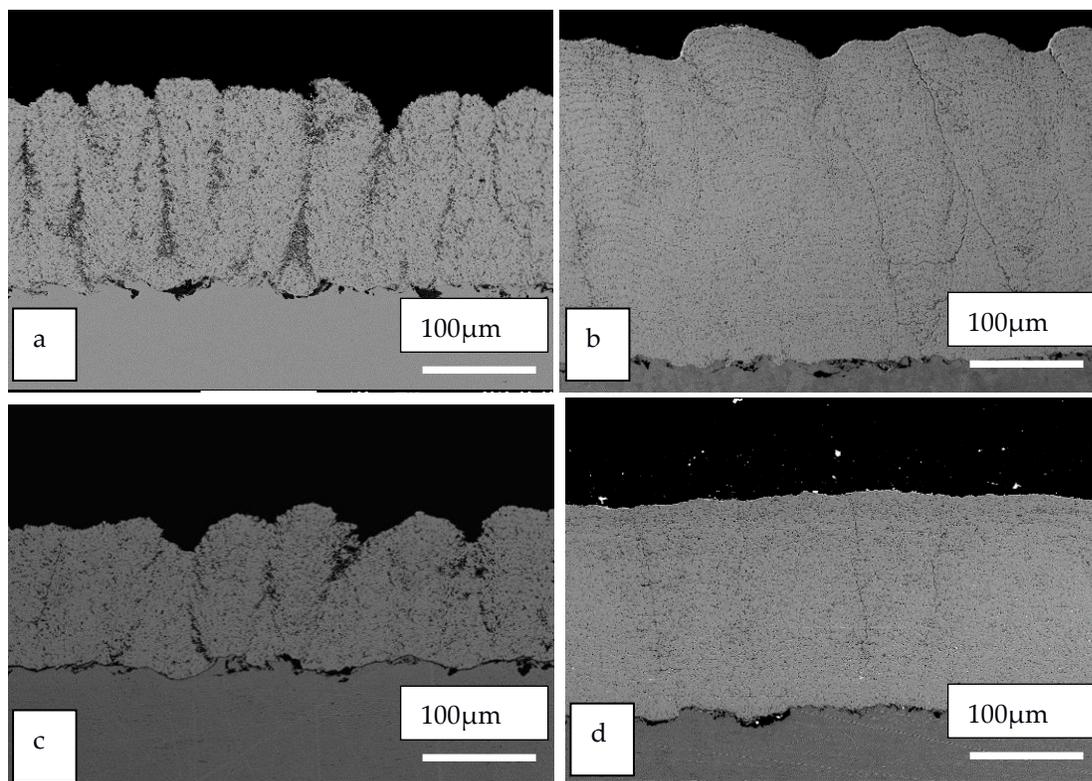


Figure 8: Backscattered SEM micrographs of the coatings deposited by axial injection using various suspensions; a) C1, b) C2; c) HM2, and d) C3

In Figure 3 showing the SEM images of the dried suspensions and the original powders, one can note that the sizes and rounded shapes of the particles in the home-made suspensions and in suspension C1 are very similar. On the other hand, the particles in suspension C2 are roughly 2-3 times larger presenting mainly angular/faceted shapes. As all spray parameters are almost identical for all suspensions and as their rheological properties do not correlate well with the observed microstructures, one can speculate that the different observed structures are linked with the actual particle size and shape that may influence the fragmentation behavior of the suspensions as well as the way particles merge together in flight after the solvent (ethanol) is fully evaporated. These phenomena are not well understood today and can have a significant influence on the final particle size and speed before impact on the substrate.

Finally, it is worth noting in this context that the powder shape can be an important factor influencing the packing density of the solid particles within the droplets as the solvent gets evaporated. A higher solid packing density may result in larger in-flight molten particles and/or result in thicker molten shells that can break up forming much smaller molten ceramic particles. These phenomena need to be further investigated to develop a more complete understanding of the relationship between the suspension characteristics and coating attributes.

4. Summary and Conclusions

The comparison of the suspensions investigated in this study brought up the following summary of observations:

- i.* While in the absence of surfactant, an increase in Dv_{50} ranging 2-4 times of the original particle size is observed, the surfactant addition preserves the original particle size distribution.
- ii.* Freshly made suspensions (HM) leave more floccules during drying than the commercial ones. They meanwhile show higher viscosities than the commercial suspensions. These can play a role on their behavior also during in-flight drying and differentiate them from the commercial suspensions.
- iii.* Surface tension due to addition of up to 5 wt% solid of PVP does not show a large variation.
- iv.* Addition of surfactant even in small quantity clearly increases the viscosity. This influence on viscosity of the liquid carrier (for the present suspensions) is more than that of as high as 25wt% solid content.
- v.* Aging of the fresh HM suspensions increases the viscosity for some time. Then it reduces the viscosity after longer time probably due to more time for better wetting.
- vi.* Radial injection (no atomization during injection- cross flow atomization in plasma plume) showed similar coating structure for the two commercial suspensions with similar viscosities and surface tension values. However, denser structures were formed using the HM suspensions with higher viscosities and surface tensions.
- vii.* Axial injection (atomized injection- coaxial flow atomization) showed great difference in the microstructure of the coatings from two commercial suspensions, despite similar viscosities and surface tensions. However, that of HM shows more similarity to the commercial suspension with similar particle shape and size.
- viii.* Commercial suspensions allow manipulation of microstructure, using small amendment of the formula.

To conclude, the commercial suspensions prepared in industrial scale and with optimized procedures seem to show more stability and provide reproducibility in the coatings. In addition, manipulation of microstructures is always possible. An interesting distinction in the behaviors of suspensions with variation in particle shape (and a small size change) is observed when the axial injection in axial III torch was used. The reasons for varying role of the suspension viscosity and surface tension in the case of radial and axial injection, as observed here, as well as the potential role of the particle shape (and less probably small particle size change) on significant change of the microstructure remain the matter of detailed droplet and in-flight collected particles investigation. Therefore, the exact reason for this difference remains the matter of further investigation.

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