Towards an aerogel-based coating for aerospace applications: reconstituting aerogel particles via spray drying

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Abstract. Silica aerogel is an ultralight and highly porous nano-structured ceramic with its thermal conductivity being the lowest than any solids. Although aerogels possess fascinating physical properties, innovative solutions to tackle today's problems were limited due to their relative high manufacturing cost in comparison to conventional materials. Recently, some producers have brought forward quality aerogels at competitive costs, and thereby opening a panoply of applied research in this field. In this paper, the feasibility of spray-drying silica aerogel to tailor its granulometric property is studied for thermal spraying, a novel application of aerogels that is never tried before in the academic arena. Aerogel-based slurries with yttria stabilised zirconia as a secondary ceramic were prepared and spray-dried according to modified Taguchi experimental design in order to appreciate the effect of both the slurry formulation and drying conditions such as the solid content, the ratio of yttria stabilised zirconia:aerogel added, the amount of dispersant and binder, inlet temperature, atomisation pressure and feeding rate on the median particle size of the resulting spray-dried powder. The latter was found to be affected by all the aforementioned independent variables at different degree of significance and inclination. Based on the derived relationships, an optimised condition to achieve maximum median particle size was then predicted.

1. Introduction
Aerogels [1], invented by Samuel Stephens Kistler 85 years ago, are highly porous nanostructured materials with an open-cell network. Aerogel is generally characterized as a gel in which the liquid phase has been replaced by a gas in such a way that the solid framework is being retained with only a slight or no shrinkage in the gel. It can be argued that there is no austere definition for aerogels. For example, according to the International Union of Pure and Applied Chemistry (IUPAC), an aerogel is a gel which is comprised of a microporous (<2nm) solid in which the dispersed phase is a gas, but yet mesoporous (2-50nm) aerogels are acknowledged within the community. As time evolves, different types of aerogels have been synthesized from the very first silica aerogel produced at the stage of invention in 1931. Within the classes of aerogels, silica aerogel is still considered to possess the most
fascinating physical properties such as low thermal conductivity, ultra low bulk density, optical transparency in the visible spectrum, high specific surface area, low dielectric constant, low refractive index and low sound velocity. Up to now, the latter is the solid with the lowest thermal conductivity ever existed but no more the lightest material as this property has been surpassed after the invent of graphene aerogel in 2013. In terms of commercialisation, silica aerogel is lagging behind significantly because of its relatively high manufacturing cost due to overpriced precursor and high energy required in supercritical drying. As a result, driven by the potential applications of silica aerogels are almost illimitable, extensive studies ranging from modelling to experiments, in both academia and industries, have been conducted during the past two decades in the quest for affordable silica aerogels.

After tremendous efforts, numerous producers have brought forward different forms of aerogels that are derived from different sources of silica and modified drying conditions. Silica aerogel is now experiencing a renaissance and is tracing its way into various applications like thermal and acoustical insulation, kinetic energy absorption, electronics, optics and biomedicine, amongst others, with the former as the most preferred and versatile one. Consequently, industries are perpetually developing innovative solutions to existing problems by the use of silica aerogel as a super insulative material. High-performance insulation or super insulation is attributed to aerogel based on its attractive R-value, which is usually the factor considered when taking into account the thermal insulation performance of a system. By definition, R-value is a measure of resistance to heat flow through a given thickness of material. The higher the R-value, the more thermal resistance the material has and therefore, the better its insulating value. This value is inversely proportional to thermal conductivity and hence, being the solid with the lowest thermal conductivity, implies that silica aerogel possesses the highest R-value than any material for a fixed length. Furthermore, it should be appreciated that a lower thermal conductivity means the same insulation performance is achieved with a thinner layer or that the same thickness of super insulation can be used to ensure far better insulation performance. Up to now, two thermal insulative solutions are being used widely: in centimetre-thick flexible blankets wherein silica aerogel particles are dispersed into a reinforcing fibre matrix such as glasswool and in millimetre-thick paints as additives wherein aerogel granules are mixed with the alcohol-based solvent. It is worthwhile to note that aerogel-based blankets are already in use in astronomical applications whereas aerogel-based paints are mostly opted for architectural uses. Due to the space and weight constraints, thick insulation is not favoured in aeronautics and thus it is imagined that aerogels could be integrated as a form of micrometre-thick protective coating that can resist substantial mechanical loads and thermal cycling. The issues, challenges and applications of aerogels in aerospace have been detailed in [2].

As per authors’ knowledge, no investigation has been carried out until now to study the feasibility of developing an aerogel-based thermally sprayed coating. This paper addresses this technological gap partly since the complete research encompasses different phases before the thermal spraying. The main purpose of carrying out the spray-drying intermediate step prior to deposition is to reconstitute the particles of aerogels to obtain an adhering coating. In consequence, this study employed the Taguchi design to investigate the effect of the different independent variables in terms of the slurry formulation and drying conditions on the median particle size in order to predict the optimum condition to produce aerogel-based powders with maximum particle size with a spherical morphology.

Unlike the spheroidisation, fusing-crushing-cladding or temperature sintering methods [3], spray-drying is a procedure that can reconstitute the granulometric or the morphological properties of a nanostructured ceramic without compromising its microstructures. It is by which a water or organic-based suspension is transformed into dry powder by atomising the slurry into a hot drying medium [4].

2. Experimental specifics

2.1. Materials
Ecological GEAT® 0.125 aerogel was supplied from Green Earth Aerogel Technologies whilst the commercialized yttria stabilized zirconia (YSZ), ZrO$_2$ 8Y$_2$O$_3$ (Metco 240NS-G) was purchased from Oerlikon Metco (previously Sulzer Metco). Polyvinyl alcohol (Mowiol® 4-88) and polyethylene
glycol, \((C_2H_4O)nH_2O\), molar weight 400 were bought from Sigma-Aldrich. On the other hand, Darvan 821-A was provided by Vanderbilt Minerals, LLC. Distilled water was available at AMREC. All the materials were used as-obtained with no further treatment.

2.2. Slurry formulation and spray drying
For a fixed volume of slurry, Darvan 821-A was firstly added to distilled water at 95°C and stirred for 10 minutes. PVA as a hydro-soluble binder was then dropped and mixed for another 20 minutes at the same temperature until it completely dissolved. Next, a specific amount of plasticizer PEG of 0.5 wt.% was dipped and left for mixing until 10 minutes had elapsed. The solution was then left to be cooled at room temperature and was weighted. The loss of water during the heating was compensated. Yttria stabilized zirconia was then mixed gradually and the suspension was blended for another 15 minutes at room temperature. Finally, aerogel was added and commixed for additional 15 minutes. The resulting mixture was ball-milled for longer than 24 hours to attain a well-stabilized slurry. The weight ratio of slurry-to-ball was kept 1:2 at all times.

A LabPlant SD-05 spray-dryer with a two-fluid nozzle was used in this investigation. The heated air was used as the drying medium in the drying chamber. Drying conditions such as inlet temperature, atomization pressure and feeding rate were controlled during the spray drying. Finally, the feedstock was collected in the collecting chamber from the cyclone. In order to study the relationship between slurry properties (powder content, YSZ: aerogel, dispersant and binder) and aforementioned drying conditions upon the particle size of feedstock, an experimental method was designed accordingly.

2.3. Design of experiment
Taguchi's Design of Experiment was used (as in Table 1) as the statistical tool for screening design to ensure a systematic and time-consuming procedure in the pursuit for better morphological properties of aerogels. It is a powerful tool being used within the scientific community for design of high quality systems through screening and optimization by using a strategically designed experiment that is being derived mathematically and empirically. A modified orthogonal array L18 was used to examine seven factor system (A-G) with a combined number of levels wherein one of the factors consists of six levels and the remaining with three levels.

| Symbol | Factors                  | 1  | 2  | 3  | 4  | 5  | 6  |
|--------|--------------------------|----|----|----|----|----|----|
| A      | Powder Content (vol.%)   | 15 | 20 | 25 | 30 | 35 | 40 |
| B      | YSZ: Aerogel (wt)        | 1:1| 1:3| 1:5|    |    |    |
| C      | Dispersant (wt.%)        | 0.3| 0.6| 0.9|    |    |    |
| D      | Binder (wt.%)            | 4  | 6  | 8  |    |    |    |
| E      | Inlet Temperature (°C)   | 150| 175| 200|    |    |    |
| F      | Atomization Pressure (bar)| 0.9| 1.0| 1.1|    |    |    |
| G      | Feeding Rate (ml/min)    | 18 | 21 | 24 |    |    |    |

Note: Each experiment was carried out in triplicate.

2.4. Characterisation
A laser particle size analyser (Mastersizer 2000 E by Malvern Instruments) was utilized to obtain the median particle size. The technique, laser diffraction uses Mie theory of light scattering to calculate the particle size distribution, assumes a volume equivalent of sphere model.

2.5. Facilities
Formulation of slurry and spray-drying were conducted at AMREC, SIRIM while characterization of spray-dried powders was done at the Materials Characterisation Laboratory, UPM.
3. Results and discussion

Figure 1 presents the effect of each control factor, viz. the solid content, the weight ratio YSZ:Aerogel, dispersant, binder, inlet temperature, atomization pressure and feeding rate on the median particle size, $D_{50}$ of prepared spray-dried aerogel-YSZ powders. It was found that the latter ranged from 16.17±0.59 µm to 27.27±0.67 µm with a mean coefficient of variation of 3.90%, hence attesting high consistency and precision among the 18 samples by being under the acceptable value of 15%.

![Main Effects Plot for Means](image)

**Figure 1.** Effect of slurry formulation and spray-drying operating variables on $D_{50}$

In general, granulation process can be divided into three steps: (1) atomization, where the droplets were formed after the slurry had passed by the nozzle that was positioned at the top of drying chamber; (2) drying gas and droplet contact, where evaporation took place and the liquid feed was turned into droplets in the drying chamber; (3) powder recovery, where the dried feedstock was separated from the drying gas stream in the collecting chamber. From Figure 1, it can be seen that each control factor had an effect on the spray-dried granules at different degree of significance and inclination.

Atomisation pressure and feeding rate contributed in the first step of spray drying. It was observed that the particle size was affected in such a way that an increase in pressure led to a decrease in $D_{50}$. Figure 2 depicts the schematic diagram of a two-fluid nozzle with an external mix and the sequence involved during the formation of droplets. First, the slurry was forced into the two-fluid nozzle by the aid of the compressed air, which caused the formation of an air cone covered by liquid membrane, dictated by the cone angle or spray angle, $\theta$. For a constant feeding rate, an increase in the atomisation pressure would enlarge the spray angle, causing the thickness of the liquid membrane to decrease. Consequently, the diameter of droplet would decrease, which in turn would reduce the diameter of the spray-dried particle, in other words, $D_{50}$, as observed in Figure 1. Increasing the feeding rate of the slurry from 18 ml/min to 21 ml/min, on the other hand, would increase the thickness of the membrane leading to the formation of larger particle size, as pointed out in the corresponding diagram. However, when the feeding rate was augmented to 24 ml/min, $D_{50}$ shrank. This phenomenon could be probably because more atomizing air and a higher atomizing air pressure drop was required due to the fact that the mixing and atomization of liquid was taking place outside the nozzle.
The second step in spray drying process was related to the slurry formulation and inlet temperature. It could be observed that increasing the volume fraction of the solid content in the slurry had a strong influence on $D_{50}$. This could be explained by the fact that a rise in the powder content results in an increase of the suspension viscosity, as proposed by Cao et al. [5]. In addition, the particle size is intrinsically the summation of the hollow centre part and the wall-thickness. It was reported in the quoted study that the lower the solid content in the slurry, the larger is the ballooning but the thinner the wall thickness. Adding more solid content could be translated as increasing the density of the solid content as well. YSZ had an apparent density of $2.3 \pm 0.2$ g/cm$^3$ while the aerogel was considerably less dense with a value of $0.2 \pm 0.01$ g/cm$^3$. Therefore, the decrease in $D_{50}$ with an increase in the ratio of YSZ:Aerogel could be possibly justified by the fact that the suspension is less viscous.

Changing the amount of dispersant from 0.3 wt.% to 0.9 wt.% increased the median particle size negligibly compared to the other three slurry formulation parameters: solid content, YSZ:Aerogel and binder. Besides, it should be pointed out that ball-milling were carried out for a minimum of 24 hours, which could have enhanced the dispersion of the particles and making it a homogeneous suspension. Mahdjoub et al. [6] studied the effect of the slurry formulation upon the morphology of spray-dried YSZ particles by measuring the relative sediment height (RSH) that represents the state of dispersion of the suspension and is a key factor controlling the droplet drying. It was found that hollow granules were formed in the case of dispersed slurries (low Ratio Sediment Height – RSH < 53%) whereas full granules were obtained with flocculated slurries (high RSH > 62%). Adding binder in the slurry had two effects; $D_{50}$ was increased when Polyvinyl alcohol (PVA) was added with quantity of 0.4 wt.% to 0.6 wt.% whilst a decrease was observed when the amount was brought to 0.8 wt.%. The binder is practically required in order to produce solid compact granules. It was shown in [7] that the RSH value can be drastically modified by the addition of binder and subsequently affecting the state of dispersion of the suspension being stable or unstable and hence the overall granule morphology upon spray-drying. When particles are fully dispersed in a slurry with no interaction between each other, which is the case of a basic suspension (without binder or dispersant), they are very mobile and can pack together. In consequence, particles and binder move to form a dense shell leaving behind an internal void. Because of the difference of pressure between the internal void and the ambient atmosphere, one part of the granule collapses generating hollow powder. In contrast, when the slurry is flocculated, the particles can be considered as immobile; the shell does not appear and granules are formed. Hence, the dual effect due to an addition of PVA in the aerogel-based slurry can be appreciated.

Increasing the inlet temperature resulted in a larger particle size. When the aqueous aerogel-based suspension was forced into the drying chamber, the compressed air converted it into small droplets which contracted as fast evaporation of the water in the slurry took place due to the heated air. During this process of moisture moving from the inside to the outside of the droplet, the solid content, binder and dispersant were also carried along. Inside the droplet, a hollow centre part would be produced.

![Figure 2. Schematic diagram of two-nozzle with external mix and formation of droplets](image-url)
when the evaporation rate of moisture inside the droplet was higher than the diffusion rate through the droplet surface. Overall, for spray drying, increasing the drying temperature resulted in greater loss of water of resultant powder due to the higher rate of heat transfer into particles that is causing faster water removal. However, if inlet temperature was set above 200°C in this study, it could be anticipated that the evaporation rate of moisture inside the droplet would become higher than the diffusion rate through the droplet surface, which would cause a decrease in the resulting spray-dried powder.

4. Conclusion

An attempt was made to tailor the granulometric property of silica aerogel via spray-drying for thermal spray applications. Taguchi experimental design was employed to systematically analyse the effect of the slurry formulation and spray-drying process on the median particle size and to predict the optimal condition to achieve maximum median particle size, which had been found to be 40 vol.%, 1:1, 0.9 wt.% 6 wt.% 200°C, 0.9 bar and 21 ml/min for solid content, YSZ:Aerogel, dispersant, binder, inlet temperature, atomisation pressure and feeding rate, respectively.

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