

Process Development for High Pure, Phase Consistent Yttria Stabilised Zirconia (YSZ) Powders Having Uniform Particle Size Distribution for Thermal Barrier Coating Applications

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ABSTRACT

The advantage of having a ceramic coating on metallic engineering components plays a significant role in improving the overall component life. Yttria Stabilized Zirconia (YSZ) finds major use as a protective ceramic coating in the vast field of thermal barrier coating and related applications. Achieving efficient and better coatings on the substrate depends on the spraying method, gun type, substrate surface, temperature of the carrier gas and molten particle velocity. Apart from these factors, the most important contributor is the feedstock powder characteristics. Parameters such as powder flowability, uniform particle size distribution (PSD), phase purity and stability, melting characteristics of the powder are crucial in selecting feedstock powders for thermal spray applications. This paper discusses industrial scale manufacturing of 8 wt% YSZ micro and nano powders using chemically derived method having uniform PSD, pure and phase stable powders with hollow spherical structure for better melting capability. It also discusses the powder characteristics such as flowability, bulk and tap density, sphericity. Purity, phase stability at different temperatures and evolution of powder microstructure during the thermal stability studies are also discussed. By this process, a 99.9% pure YSZ with above 80% tetragonality and spherical powders of d_{50} 20 microns can be achieved.

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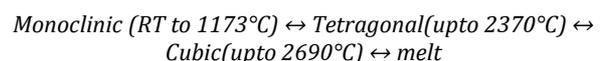
Introduction

Increasing manufacturing efficiency and continuous process improvements have been the watch words of any industry. Extracting the maximum work out of a given scenario, without negatively affecting the overall life of the machine is what any industrial set-up looks for. In that way, to improve the efficiency of high temperature operating gas turbines and engines, thermal barrier coatings (TBC) play a major role. Following Carnot's thermodynamic theorem, to improve the efficiency of a heat engine the input temperature of the engine should be as high as possible, compared to the output temperatures of the engine. Bringing down the output temperature beyond a certain limit is practically not possible. However, increasing the input temperature will help to increase the engine efficiency. To meet the high temperature requirement, Nickel based super alloys are found to be the apt candidate material. It should be noted that the Nickel based super alloys' melting temperature is 1280°C [1]. Beyond this, it can't be put into application. Ceramic coatings on the Nickel based alloys help to address this problem. Specifically, a class of material group, Thermal Barrier Coatings (TBC) are the ideal solution for meeting the working temperature requirements of high temperature engines.

TBCs are basically coatings given on the surface of the super-alloy parts so that those parts are not exposed to the high temperature gases and provide wear and thermal resistance to the substrate material. It is a thin layer of 100

to 500 microns, so that not much weight is added on to the moving parts. Following are the characteristics of a good TBC [2] - 1) very low thermal conductivity value to be a good insulator (around 2 W/m-K at 100°C to 900°C [3]) 2) co-efficient of thermal expansion (CTE) that is very near to the base super alloy (CTE of Nickel based super alloy - $12.5 \times 10^{-6}/\text{C}$). This prevents cracks that will be formed due to dissimilar expansion on heating and cooling. Typically, YSZ based TBC will have a CTE of $13 \times 10^{-6}/\text{C}$ [2]. 3) good wear and thermal resistance 4) good adherence to the bond coat and substrate.

There have been a lot of TBC ceramic materials identified in the market like - Alumina, Alumina Titania, Titania, Zirconia, Alumina Zirconia etc., Zirconia based materials have an advantage in terms of a very near CTE to nickel based super-alloys. They are also chemically inert with high melting points. Also with Zirconia, the wear and thermal resistance properties are pronounced in its tetragonal/cubic phase. Following is the sequence of Zirconia phase transformation [4]:



The phase transition is accompanied by a volume change - Monoclinic to tetragonal involves a volume shrinkage of 3-5%. The tetragonal to cubic transition is accompanied by a slight volume expansion of 0.6%.

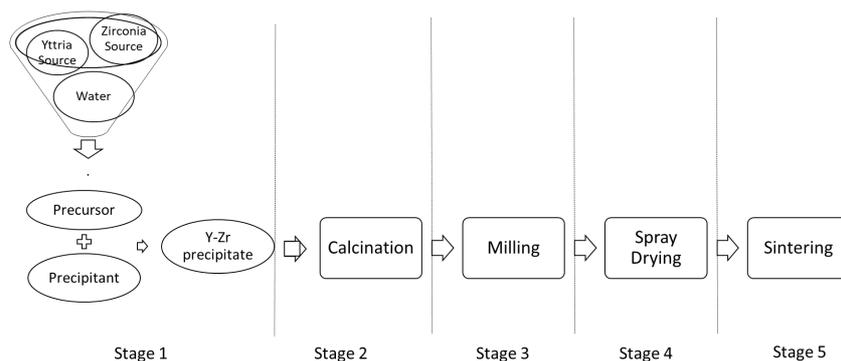


Figure 1: YSZ process flow

The tetragonal phase has more of thermal resistance, whereas the cubic phase exhibits ionic conductivity. The stabilization of these phases in room temperature is achieved by introducing slightly larger metal ions into the matrix of Zirconia, thereby resisting the structural reversion of phases when coming back to room temperature.

Yttria is one such material identified by the scientific community for the stabilization of Zirconia. The stabilization degree varies with the amount of Yttria doped in the system. For the TBC application, tetragonal phase of >80% and a monoclinic content as low as possible is preferred (<15-20%). From the literature it is known that 6-9%, more specifically 8wt% of Yttria is generally used in the industry for achieving the mentioned phase constituency [5]. 8wt% YSZ TBC gives a TC reduction for every micron thickness of the TBC, where the TBCs are usually 400-500µm thick [6].

With stabilized Zirconia coatings, high purity and high phase stability in the TBC material is preferred. As the impurities like other metals or Silica may cause degradation of the phase stability or weaken the structural strength during the heating-cooling cycles. Moreover, monoclinic phase in the feedstock for coating will increase the probability of losing the tetragonal stability during high temperature cycles [7, 8, 9]. Thus, more phase stable, high purity powders are major requirements of coating materials.

Different methods of doping Yttria into Zirconia is adopted for stabilization – 1) Co-milling of Yttria and Zirconia followed by sintering [10] 2) Co-fusion of Yttria and Zirconia [11, 12, 13] 3) Co-Precipitation or wet-chemical method [14, 15, 16]. The stabilization differs in each of these processes.

Advantages offered by the Co-precipitation method compared to the other methods – 1) molecular level mixing of dopants, hence excellent phase stability 2) better control on the impurities in the final product through raw material purity 3) possible to control the particle morphology and thus the particle size distribution.

The starting materials are usually various salts of Zirconia and Yttria dissolved in water and then precipitated with a weak base. The precipitate is then treated to temperatures of 800-1100°C to form the stabilized oxides. Since precipitation is the route of crystal formation, the powders formed will be of fine size and highly pure.

For application of the TBC, generally Air Plasma Spray (APS) is the method widely used. The method employs a plasma gun, where the plasma is fueled by gas. Into this gas

stream, the to-be-sprayed powders are fed into. As the powder passes the plasma flame, input metal oxide ceramic powders are melted. Further due to the velocity of the plasma jet, molten oxide material gets splattered on the substrate [17]. For an effective spraying, a good TBC powder should have good flow-ability. Fine powders generally do not have good flow-ability and tend to choke the flow pipes. Spherical shaped powders are best suited for the coating application [18]. One of the methods is spray drying the fine powders to make spherical agglomerates. This has been explored by various research groups and established that the spray dried powders do not differ in the properties affecting its thermal insulator nature [19, 20].

Good TBC feedstock material needs to be highly pure, phase stable and flowable. The aim of this paper is to combine both the co-precipitation and the spray drying methods to achieve a highly pure, phase consistent YSZ Powders with uniform particle size by optimizing the parameters.

Experimental

The schematic for the method followed in this paper is shown in Figure 1. It has 5 stages to describe the process.

At Stage 1, Zirconium OxyChloride (Source: Bhalla Chemicals) and Yttria (Source: FEILong International Group) as powders are dissolved in distilled water, in necessary ratio to make 8wt% YSZ. The processed samples referred to as 8YSZ. This precursor solution is allowed to rest for >15 h and then precipitated with Ammonia Solution. To understand the effect of pH on the nucleation and crystal growth, two pH values – 7 & 10 are taken.

The formed precipitate is then washed with water till the ionic conductivity of the washed water becomes less than 500µS (as measured in a handheld ionic conductivity meter). The washed cake is then dried at 80°C for >15 h, to completely remove the moisture. Once dried, the dry cakes are then dry milled in a ball mill (Zirconia balls of diameter: 10-25mm, with 1:1 ratio of balls to material in a alumina lined chamber) for <4 h to crush the hard cakes to powders.

At Stage 2, to understand the effect of calcination on the crystal growth and phase transition, study with different temperatures and holding time is done - 950°C, 1000°C & 1100°C for 2 & 4 h.

Once the calcination is completed, at Stage 3, the ceramic powders are then wet milled in an alumina lined ball mill with Zirconia balls of diameter ranging from 0.08 to 0.1mm. Trials with different time periods (3, 5, 7 & 10 h) of

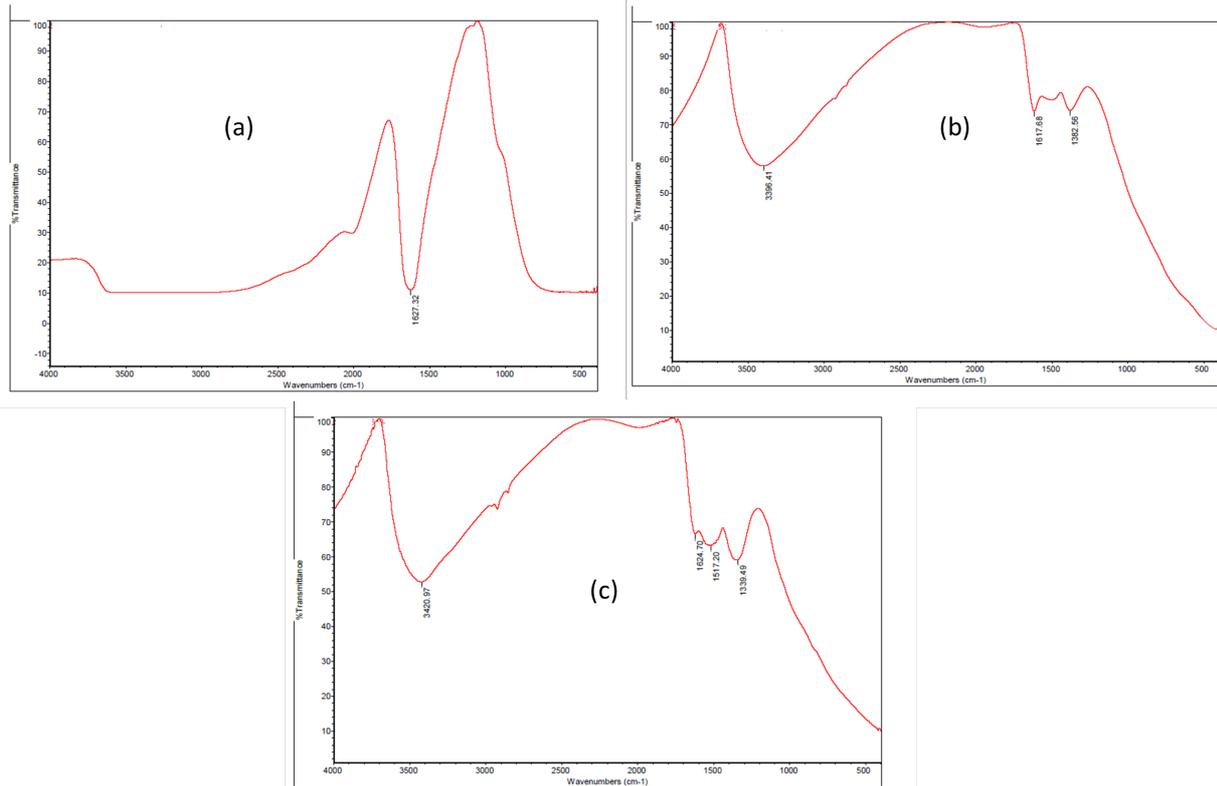


Figure 2: FTIR results of dried cakes of (a) Precursor (b) precipitate at pH7 (c) precipitate at pH10

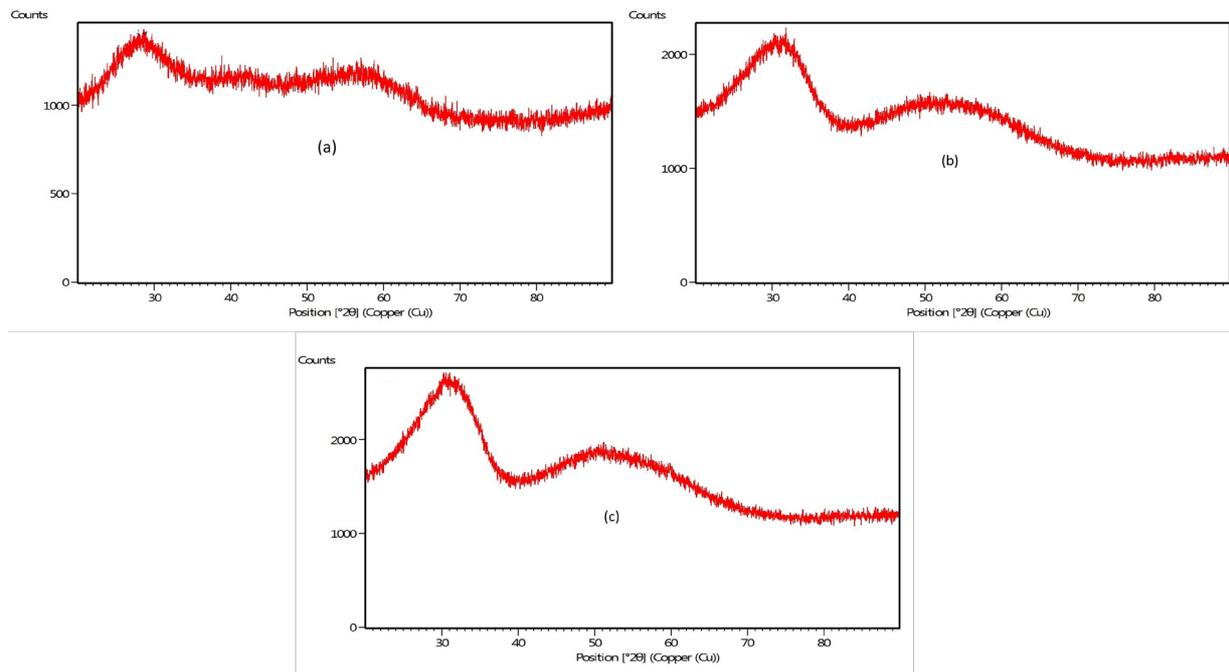


Figure 3: XRD graphs of (a) precursor (b) precipitate at pH7 (c) precipitate at pH10

milling were done to understand the uniformity in PSD of the output.

Stage 4 is the Spray drying process. A slurry of 25 – 50% solid content is preferred for spray drying, to achieve spherical powders of good density [20]. The wet-milled slurry is corrected to the mentioned solid content and spheridised in a rotary atomizer type spray drier of make: Acmeofil Engineering Systems. The input air temperature is

maintained >200C and slurry feed pump operating at around 20-30Hz set in the Variable Frequency Drive (VFD). To understand the effect of atomizer speed on the agglomerate morphology, trials with different atomizer speeds controlled by VFD with frequencies at 35 & 45 Hz were utilized.

These powders are then heat treated at Stage 5, to the temperature ranging between 400 - 1600C for 4 to 5 h, to

give the spherical structure, sufficient strength that does not collapse during handling or transport.

X-Ray Diffraction (Bruker D8) is carried out at each stage of the process, to understand the Phase transformation. Fourier Transform InfraRed Spectroscopy (Thermo Nicolet iS50) is used to understand the precipitation completion. Field Emission –Scanning Electron Microscope. (Carl Zeiss) has been utilized to study the powder morphology and sphericity. Energy Dispersive Spectroscopy (Bruker: Nano XFlash Detector) and Inductive Coupled Plasma – Optical Emission Spectroscopy (Agilent Technologies Model: 700 series) have been employed to study the purity of the 8YSZ. PSD (Malvern Mastersizer 3000E) and Specific Surface Area has also been measured.

Additionally, in a step further, the powders have also been subjected to thermal treatment of 50 h of continuous exposure to very high temperatures. SEM images of the exposed powders have been analyzed.

Results and Discussion

As shown in Figure 1, the mixed precursors are precipitated out by addition of Ammonia Solution. By controlling the volume of ammonia addition, precipitates at pH7 & pH 10 were achieved. The FTIR of the precursor [Figure 2(a)] – dried shows a single peak at 1627 cm^{-1} , this may correspond to the Water O-H bond bending frequency [21, 22]. The dried cake of precipitates at pH 7 and 10 [Figure 2(b, c)], both exhibit peaks at 460 cm^{-1} , which corresponds to Zr-O bond stretching vibration [22]. Peaks at $1330 - 1380\text{ cm}^{-1}$ and around 1520 cm^{-1} correspond to the bridging OH- groups in $\text{Zr}(\text{OH})_4$ [22]. These peaks are weak in pH 7 as opposed to the deeper peaks seen in pH 10. This shows that at pH10, the precipitation of Zirconium salts in water to hydroxides is more complete than at pH7.

This is also substantiated by the increase in the Specific Surface Area (SSA) of the dried cakes of the precipitates, which is shown in Table 1.

Table 1: Specific Surface Area of precipitates at different pH

Sl. No	Sample Description	SSA (m^2/g)
1	pH7 precipitate	103
2	pH10 precipitate	114

Phase transformation & Stability

The XRD results of the precursor and precipitated & washed dried cakes at different pH – 7 and 10 are shown in Figure 3 (a), (b) & (c). It shows the amorphous nature of the material tested.

The precipitate was subjected to Calcination in Stage2, at various temperatures -950C, 1000C & 1100C for 2 & 4 h. SSA and XRD was carried out for each of the temperature and holding times. XRD results are shown in Figure 4. No additional peaks other than Tetragonal is seen in all samples except at 1100C 4 h, where a small peak corresponding to Cubic phase is also seen. SSA was measured for the thermally treated powders and the results are tabulated in Table 2.

Particle size distribution

After the calcination step, the powders are ball milled as shown in Stage 3. Ball milling was carried out at different

milling time – 3, 5, 7 & 10 h. The particle sizes of the powder is measured through a laser diffraction meter that calculates the size of the particles in a stream, based on the diffraction measured from each particle. The results are tabulated in Table 3.

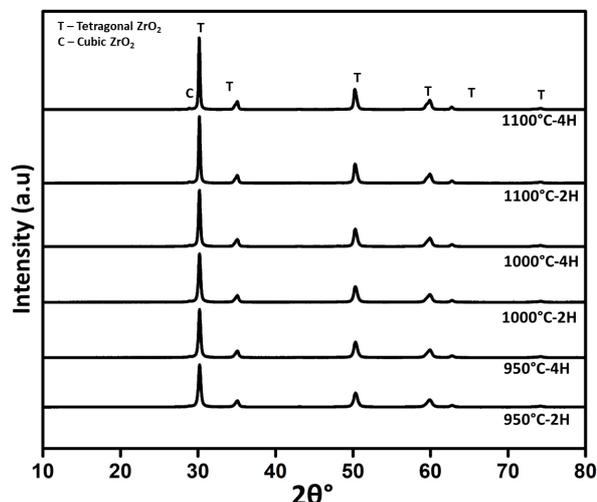


Figure 4: XRD graphs of 8YSZ after Calcination at different temperatures and holding time

Table 2: Specific Surface Area of precipitates at different pH

Sl. No	Sample Description	SSA (m^2/g)
1	950C 2h	25.86
2	950C 4h	18.77
3	1000C 2h	16.86
4	1000C 4h	13.9
5	1100C 2h	8.95
6	1100C 4h	6.2

Table 3: Particle Size Distribution at different milling h

Sl. No	Sample Description	Particle Size Distribution (μm)		
		d10	d50	d90
1	3 h	0.397	1.09	2.86
2	5 h	0.453	1.19	2.81
3	7 h	0.319	0.972	2.98
4	10 h	0.289	0.954	2.36

PSD of $d_{50} - 1.2\ \mu\text{m}$ is achieved with a 3-hour milling and not much change is observed with increasing the duration. To confirm the repeatability of the PSD achieved, the same 3 h milling was repeated for 3 differed batches. Figure 5 shows the uniformity achieved across 3 batches with very minimal differences.

Figure 6 shows the SEM image of the milled & dried powders. The particle size distribution uniformity is clearly reflected in the SEM micrograph. Individual particle size of the 8YSZ powders was found to be $\sim 50 - 60\text{ nm}$.

Chemical Purity

The purity of 8YSZ material was analysed using an ICP-OES. The results shown in Table 4 are computed to oxide forms of the corresponding metallic elements. EDS results shown in Figure 7. It is evident that the metal ions are in ppm levels and the Yttria content is at 8.5wt%.

From the EDS results, no other element/impurity peak is observed other than Al or Hf.

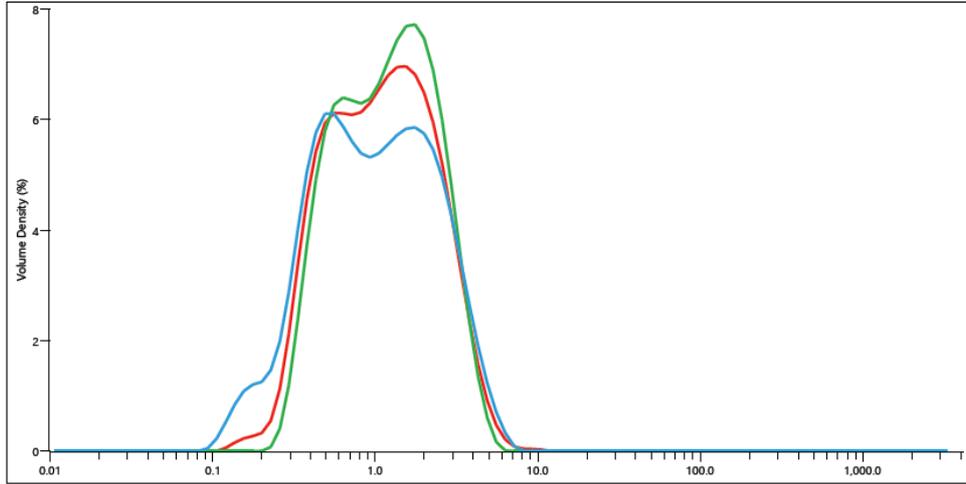


Figure 5: Particle Size Distribution graph of 8YSZ wet milled from 3 different batches

Table 4: Presence of Yttria and other metal oxides quantified through ICP – OES

Oxides	Y2O3 (w/w %)	Fe2O3 (ppm)	Na2O (ppm)	CaO (ppm)	SiO2 (ppm)	TiO2 (ppm)	MgO (ppm)	Al2O3 (ppm)
Presence	8.5	43.8	20.52	328	356	BLQ	71	230

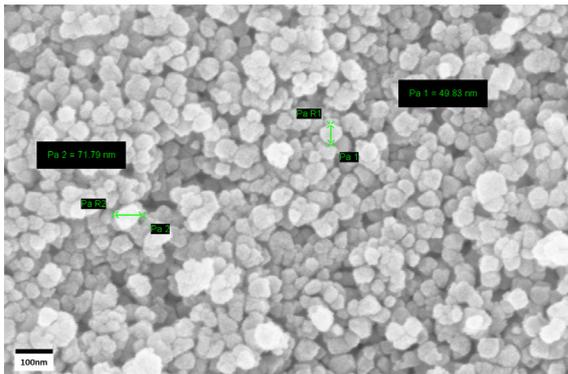


Figure 6: FE-SEM image of 8YSZ produced after 3 h wet milling and dried

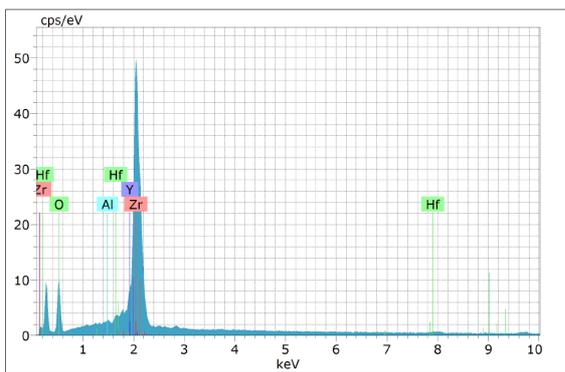


Figure 7: EDS of 8YSZ

Sphericity

In stage 4, the nano powders produced were used to make spherical agglomerated powders. In the spray drier, we understand that the higher the atomizer speed, the smaller and more regular the spheroids are formed. This is because the higher the atomizer speed, the spray droplets formed are small in size. Bigger size droplets tend to break or deform during the drying period in the spray drier.

Frequency of the atomizer was optimized to obtain uniform shaped spherical agglomerates – 35Hz and 45Hz study. The agglomerates produced are sintered at >1500C. To understand the effect of frequency on the shape, SEM was carried out after the sintering step. The results are shown in –Figure 8 & 9.

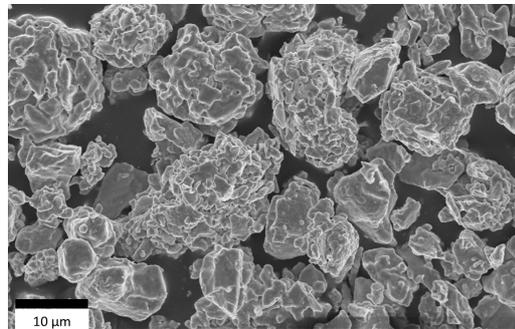


Figure 8: FE-SEM image of sintered spheroids obtained with low frequency (35 Hz) atomization

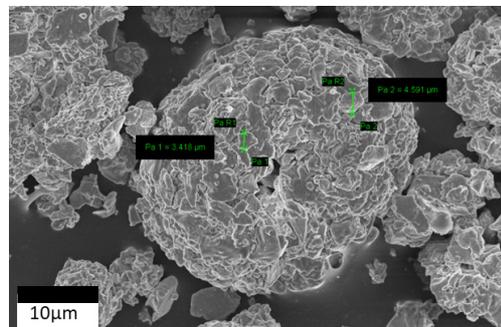


Figure 9: FE-SEM image of sintered spheroids obtained with high frequency (45Hz) atomization

It was found that the high frequency of atomizer gives better shaped agglomerates. After heating to >1500C, the

nano particles have grown and fused together to coarse particles of 1 to 5µm size.

High Temperature Exposure

To further understand the thermal stability of the agglomerated and sintered powders, they have been exposed to very high temperatures for long durations. Figure 10 shows the SEM of high temperature exposed spherodised agglomerates. It clearly shows that the individual crystals have fused together and the number of pores has reduced. Sphericity is intact.

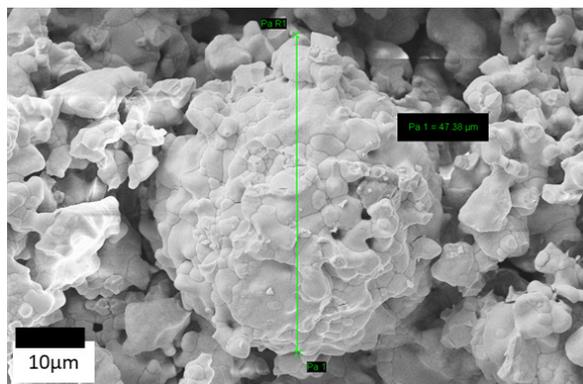


Figure 10: FE-SEM image of 8YSZ spherical powders treated at very high temperatures for 50 h

Conclusions

The majority of the commercial thermal spray industry is today served by fused and crushed (F&C) powders. These powders are by nature blocky and may result in an uneven coating. And PSD, purity and phase stability are difficult to achieve. The below are the concluding remarks of the present study to address the above-mentioned problems –

1. Co-Precipitation method was found to be the better method to manufacture 8YSZ powders.
2. Crystal nucleation can be controlled by varying the pH value of the precipitate process.
3. Calcination temperatures have pronounced effect on the size of the crystals.
4. Spray drying with higher atomizer speed gives better sphericity.
5. By this method better phase stable and high pure nano 8YSZ is possible to manufacture in a bulk scale

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