Chapter 5
Agglomeration of Al$_2$O$_3$ powders by spray drying for plasma spray coating

5.1 INTRODUCTION

Alumina (Al$_2$O$_3$) coatings having superior hardness, chemical stability and refractory character are commonly utilized to resist wear caused by friction and solid particle erosion (Hawthorne et al; 1997, Ramachandran et al; 1998, Abdel-Samad et al; 2000). As a surface modification technique, atmospheric Plasma Spraying (APS) has been well-established to deposit various ceramic coatings (Westergard et al; 1998, C.J.Li et al; 2004, Shunyan Tao et al; 2010). Recent works on nanoceramic coating show enhanced tribological behavior when compared to the conventional micron sized powder coatings (Zeng et al; 2002, Jordan et al; 2001, You Wang et al; 2000, Kabacoff et al; 2002). However, it is difficult to achieve good flowability using plasma spray gun. The sub-micron/nano sized ceramic powders (<1µm) cannot be sprayed by particle injection into the plasma as it lacks the momentum necessary to penetrate into the plasma or to impinge on the surface while the plasma sweeps over the substrate. In order to fulfill plasma spray process requirements, it is essential to have suitable particle size, morphology and density even though, in this process, the advantageous property due to large surface area of nanoparticles is lost to some extent. Hence for the coating to be performed, it has been found that the powder should consist of dense agglomerated particles in the size ranging from 10-20 µm in diameter with bulk density of around 1.7 g/cc. Hence, it becomes necessary to process the procured nano particles to achieve appropriate size range as mentioned above. This can be easily accomplished by spray drying the slurry consisting of appropriate concentration of solid loading of alumina particles, dispersant and the binder. Spray drying is a process by which a fluid feed material (slurry) is transformed into a dry powder by spraying the feed into a hot medium. Spray drying is considered to be the best technique employed for agglomerating the nano powders which can be further used as the raw materials for plasma spray coating (Minoshima et al; 2001). When making agglomerated powders, the slurry (ie) the water based suspension has to be atomized into the discrete droplets in a hot drying medium. The water present in the
suspension will be evaporated due to the large surface area to volume ratio of the droplets, thereby resulting in dry agglomerated powder. Various parameters such as droplet size, atomizer design, solid loading, pH of the slurry, hot air inlet and exit temperature, atomizing air flow rate and feed rate of the slurry control the morphology of the granules. Among all the parameters, the most important parameter to be considered is the slurry preparation. The factors which govern the slurry preparation are the percentage of solid loading, binder, the dispersant and its pH’s of the slurry (Liang et al; 2001, Pagnoux et al; 2000) Several workers have varied the percentages of both the solid loading (Al₂O₃) and the binder (Poly vinyl alcohol) at different pH values and concluded that the percentage of binder plays a paramount role in the preparation of agglomerated powders. The work carried out by Bertrand et al also suggested that the agglomerated powders prepared from slurry having pH value of 4 (flocculated) resulted in solid, spherical shape granules while the slurry obtained from slurry with 9 as the pH resulted in hollow granules. The work carried out by Bertrand et al also showed that the atomizing air flow rate and feed rate of the slurry have the most effective influence on particle sizes whereas the tapped density and flowability highly depend on slurry flocculation (Bertrand et al; 2002).

Diez et al and Hamacha et al have developed spray dried powders for thermal barrier coating (TBC) application. These spray dried powders offer an advantage in the application of thermal barrier coatings where a high porosity (10-20%) is required (Diez et al; 1993, Hamacha et al; 1996). Apart from this, these particles obtained by spray drying are usually spherical and free flowing in nature which allows the ease with which the plasma spraying process can be affected (Allen et al; 2001). Hence these powders can be easily fed by plasma spraying gun. The work of Wigren et al showed that the coating whose powders were prepared by spray drying had longer thermal shock resistance than those coatings whose powders were prepared by precipitation, sintering/crushing (Wigren et al; 1996). Betrand et al have extensively studied the influence of dispersant level, pH and binder addition on the slurry characteristics and observed that the flocculated slurry leads to solid granules while the dispersed suspension leads to the formation of hollow granules (Betrand et al; 2003). Walker et al have shown the correlations between the aqueous alumina slurry formulation, slurry yield stress and granule characteristics and their studies revealed that high deflocculant level which corresponds to low slurry yield stress leading to the
formation of hollow granules (Walker et al; 1997). Cao et al have obtained high dense agglomerated powders with larger particle size and good flowability using polyethyleneimine (PEI) as a binder and dispersant emphasize the importance of the factors related to the suspension preparation (Cao et al; 2000). Most of these works were based on polyvinyl alcohol (PVA) binder and poly acrylic acid dispersant. But it is also evident from these works that PVA reduces the density of the spray dried powder. Apart from the particle size of the powder, the agglomerated powders should have sufficient density (1.6-1.7 g/cc) for plasma spraying. This made us to use polyethylene Glycol (PEG) as a binder. Hence, the objective of this work is to study the effect of polyethylene glycol (PEG) binder and sodium hexametaphosphate dispersant on the agglomeration characteristics of spray dried Al₂O₃ powder.

5.2 EXPERIMENTAL TECHNIQUES

5.2.1 SLURRY PREPARATION

The present experiment used alumina powder having an average particle size which varies from 0.06µm to 1 µm, procured from Alcoa (grade - A16), polyethylene glycol – 400 (Rolex make) and sodium hexametaphosphate (LOBA Chemie make). In order to obtain appropriate agglomeration, trial runs were made using solid particles (Al₂O₃) whose volume percentages are varied from 20 vol% to 30 vol%, binder (PEG) from 2 wt% to 10 wt% of Al₂O₃ and sodium hexa meta phosphate (NaPO₃)₆ as a dispersant. These ingredients were ball milled in aqueous medium for about 48 hrs. The pH values of the slurries were adjusted with standard analytical grade HCl or NaOH solutions so as to obtain stable sprayable slurry. The viscosity of the slurries was measured using Brookfield rotational viscometer (DV-III ULTRA, Brookfield, U.S.A) at a shear rate of 51 s⁻¹. Further, sedimentation experiments were conducted to study the effect of pH and solid loading. Relative settling height (RSH) of the slurries was measured over duration of 170 hrs.

5.2.2 SPRAY DRYING

Spray drying was carried out with the help of co-current spray dryer (Basic Technology Pvt. Ltd; Kolkata, India). The spray drying apparatus consists of a peristaltic pump which feeds the slurry into the stream of hot gases allowing a rapid
evaporation of the liquid and leaving behind the agglomerated alumina particles. The hot air inlet and outlet temperatures were kept at around 300 °C and 100 °C respectively. The spray dryer essentially consists of pneumatic spray gun with 700 µm nozzle diameter to atomize the slurry. The slurry feed rate was maintained around 10-15 ml/min and spraying was performed at a pressure of 0.9-1.2 Pa (g) of compressed N₂ gas.

5.2.3 SINTERING

Sintering was carried out on the agglomerated spray dried powders at a temperature of about 1300 °C to retain the spherical morphology and improve the handling strength. The powder morphologies of the spray dried and sintered powders were observed using scanning electron microscope (JEOL JSM-360). Phase analysis was performed on these powders using X-ray diffractrometer (Philips 3121) with CuKα radiation. The current and voltage were set at 40 kV and 20 mA and the data were collected in the 2θ ranges 10° to 90° in a step scan mode with a step of 2°/min. Also the particle size of these powders was estimated by particle size analyzer (Sedigraph 5100, M/s Micromeritics, USA make).

5.3 RESULTS AND DISCUSSION

High solid loading is an essential factor for preparing high density agglomerates. Due to the relatively higher surface tension, the solid loading in water is high. In this context it is to be stated that water is preferred over other solvent for slurry preparation. From the preliminary sedimentation experiments on alumina-water system, it was found that very high Al₂O₃ content (>25 vol %) destabilizes the slurry due to flocculation. The concentrations of both the solid loading and binder used were varied (Table 5.1) and finally the optimized parameters were obtained by repeated trials and they are given in Table 5.2. Hence the Al₂O₃ content in the slurry was maintained around 22 vol%. As the viscosity increases with binder content, it is crucial to maintain the binder content as small as possible. It was also evident from our initial trials that the slurry ceased to flow during spraying due to the high binder content (10 wt %). Accordingly the binder content was reduced to 6 wt% with respect to Al₂O₃ content for further experiments. It is important to note that due to the fact
that polyvinyl alcohol binder plays an adverse effect by reducing density and particle size of spray dried powder, poly ethylene glycol (PEG) was used for this study (Yama Shita et al; 1998, Frey et al; 1984).

Table 5.1 Parameters for Slurry preparation

<table>
<thead>
<tr>
<th>Solid loading vol (%) (Al₂O₃)</th>
<th>Binder (PEG) (wt%)</th>
<th>Viscosity (cp)</th>
<th>Agglomerated particle size (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>2</td>
<td>13.5</td>
<td>2-15</td>
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<tr>
<td>20</td>
<td>6</td>
<td>9.6</td>
<td>2-20</td>
</tr>
<tr>
<td>20</td>
<td>10</td>
<td>14.6</td>
<td>2-20</td>
</tr>
<tr>
<td>22</td>
<td>6</td>
<td>5.1</td>
<td>10-25</td>
</tr>
<tr>
<td>30</td>
<td>2</td>
<td>90</td>
<td>Not flowable</td>
</tr>
<tr>
<td>25</td>
<td>2</td>
<td>72</td>
<td>Not flowable</td>
</tr>
</tbody>
</table>

Table 5.2 Optimized parameters for spray drying

<table>
<thead>
<tr>
<th>Slurry composition and spray drying parameters</th>
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<tbody>
<tr>
<td>Solid loading (Alumina)</td>
</tr>
<tr>
<td>Binder(Poly ethylene glycol)</td>
</tr>
<tr>
<td>Dispersant(Sodium hexa meta phosphate)</td>
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<tr>
<td>Air entry temperature (°C)</td>
</tr>
<tr>
<td>Air exit temperature(°C)</td>
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<tr>
<td>Pressure of N₂ gas(Pa)</td>
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5.3.1 EFFECT OF pH

At lower solid loading, the suspension is less dense which makes the particles to behave as if they are isolated. But in the case of highly loaded slurries, interaction between particles provokes the influence of pH on sedimentation behavior (Mohanta et al; 2008). In addition, the percentage of the binder also changes the state of dispersion of the suspension making either stable or unstable. Consequently 22 vol% Al₂O₃ slurry was prepared with 6 wt% PEG (binder) and 0.08 wt% sodium hexametaphosphate (dispersant) for settling studies.
Figure 5.1 depicts relative sediment height (RSH) with respect to pH of the slurry. It was noticed that RSH remained almost stable at lower pH (<3.85) up to 10 hrs. The slurry with the pH value of 3.85 displayed higher RSH value due to flocculation. Similarly the slurries with higher pH (>5.24), behaved like viscoelastic colloidal gels and got dried over the time. Our studies showed clearly that the pH value must be maintained below 3.85. Moreover slurries with high RSH values are advantageous in achieving dense agglomerates which in turn improves the density of the powder. Further it is evident from the figure 5.2 that the viscosity of the slurries was below 60 cp at the pH in the range of 2.0 to 3.5 which indicated that the slurries were suitable for spray drying. As very low pH, slurries are corrosive in nature and this made the pH to be fixed in the range of 3.2 to 3.5 for the spray drying experiments.
5.3.2 RHEOLOGICAL BEHAVIOR OF THE SLURRY

Rheograph (Figure 5.3) shows the rheological behavior of the Al$_2$O$_3$ slurry whose value of pH was adjusted to 3.2. The experiment was conducted over the shear rate range of 44 s$^{-1}$ to 51 s$^{-1}$ from the upward sweep followed by downward sweep. The viscosity of the slurry was around 21 cp at 51 s$^{-1}$. The difference in the viscosities at any given shear rate gives the information about thixotropy which can be defined as the property of the slurry that are thick under normal conditions and flows over time when it is stressed. From the rheograph, it was evident that the thixotropy was negligible which means that slurry was sufficiently stable. Further, slurry displayed only a mild shear thinning behaviour. The magnitude of shear thinning i.e. reduction in viscosity with respect to increasing shear rate reveals information about inter-particle network formation (Mohanta et al; 2008). High shear thinning behaviour means high inter-particle network which in turn offers more resistance to flow. Accordingly, for the purpose of spray drying, it is preferable to have slurries with weak or no inter-particle network [Mishra et al; 2009]. Hence, the prepared Al$_2$O$_3$ slurry was found to be suitable for spray drying.
5.3.3 SPRAY DRYING OF THE SLURRY

After the optimization of solid loading, binder content and pH of the slurry, the slurries were spray dried under controlled conditions. As the heat capacity of water is relatively higher than the other solvents, it is essential to maintain higher feed rate (Cao et al; 2000). But, it was also found that there is limitation in maintaining higher feed rate as it will otherwise lead to chocking.

However this problem was effectively circumvented by maintaining sufficiently higher temperature during spraying (~300 °C). Spray dried powders were collected from spraying chamber as well as from cyclone filter. The powders collected directly from chamber were coarse and free flowing in nature, whereas, fine powders were obtained from cyclone filter. Accordingly the powders collected from the chambers were found to be more suitable for plasma spraying process.
5.3.4 AGGLOMERATE SIZE AND MORPHOLOGY

The prepared spray dried alumina powder was sintered at high temperature of about 1300 °C to study the effect of sintering on particle morphology.

Sedigraph particle size distribution (Figure 5.4) shows that the median particle size ($d_{50}$) of spray dried powder is around 4µm. Further it showed a narrow unimodal distribution of particles. i.e. the particles were narrowly distributed over the range of 3 – 7 µm. On the otherhand in the case of sintered powder, it was confirmed that particle size ($d_{50}$) was further grown up to 18 µm and about 80% of particles were above 10 µm. This ensures that the sintered powder can be utilized for plasma spraying purpose.

For the sake of comparison between spraying performed with 20 vol% Al$_2$O$_3$ with the varying wt% of binder, SEM micrographs are shown in figure 5.5 (a-c). These reveal that the size of the agglomerated powders obtained were small and highly non uniform in nature.

Scanning electron micrograph (Figure 5.6) reveals that the initial particles were irregular and flaky in nature, whereas, the particles of spray dried powder were dense and exhibited spherical morphology. It was also confirmed that the spherical morphology was retained even after sintering at high temperature. Thus it is evident that sintering increased the particle size without affecting the particle morphology. Further the absence of hollow granules ensured that the dispersant content in the slurry was maintained at an optimum level. These results show that the procedure adopted here has yielded highly satisfactory results.
Figure 5.4 Particle size distribution (a) spray dried and (b) sintered alumina powder
Figure 5.5 SEM Images of agglomerated powders after agglomeration (a) 20 Vol% Al₂O₃ and 2% PEG (b) 20 Vol% Al₂O₃ and 6% PEG (c) 20 Vol% Al₂O₃ and 10% PEG
Figure 5.6 SEM Images of (a) starting powder (b) spray dried and (c) sintered alumina powder
5.3.5 POWDER DENSITY

The bulk densities (g/cm$^3$) of as received spray dried and sintered powders are found to be 1.2, 1.5 and 1.6 respectively. Thus the bulk densities of the spray dried and sintered Al$_2$O$_3$ powders are found to be higher than that of reported values, which are in the range of 0.91-0.97 g/cm$^3$ (Mishra et al; 2009). The higher particle density obtained gives ample evidence for the formation of the solid core particles which is essential for plasma spray process. The porous particle will float on the plasma flame surface or get evaporated by superheating whereas, dense particles will diffuse to the center of the plasma flame which in turn improve the coating efficiency.

5.3.6 X-RAY DIFFRACTION STUDIES

XRD patterns of the as received, spray dried and sintered alumina powders revealed only single phase $\alpha$-alumina structure as could be seen from figure 5.7(a-c). On the other hand, the peaks of the sintered powders showed crystalline nature indicating that some grain growth has taken place and the crystallite size was calculated by the well known Scherrer formula. The crystallite sizes of the as received, spray dried and sintered alumina powders were found to be 62 nm, 116 nm & 1.4 $\mu$m respectively. It is evident from the *in vitro* pattern that the peaks of the as received Al$_2$O$_3$ powder were fairly broadened indicating the nanocrystalline nature of the powder. On the other hand, the peaks of the sintered powders showed crystalline nature indicating that some grain growth has taken place during sintering.

![XRD patterns](image_url)

*Figure 5.7 XRD patterns of (a) Starting Al$_2$O$_3$ powder (b) Spray dried powder (c) Spray dried powder sintered at 1300°C*
5.4 CONCLUSIONS

In order to coat nanoceramic powders using plasma spraying process, the powders are required to be agglomerated to the required size (10-25 µm). In this work agglomerated alumina powder was produced by spray drying process by optimizing solid loading, pH and the concentration of binder. For this purpose, polyethylene glycol and sodium hexa meta phosphate were used as binder and dispersant respectively. The percentage of the solid loading was varied from 20 vol% to 30 vol% and the percentage of the binder was varied from 2wt% to 10wt% of the solid loading and finally the process parameters were optimized and found that slurry with 22 vol% Al₂O₃, 6 wt% PEG and 0.08 wt% sodium hexameta phosphate yielded the good flowable powder. The slurry with pH in the range of 3.2 to 3.5 was found to be very much suitable for spraying. Viscosity of the optimized slurry displayed negligible thixotropy and only a mild shear thinning behavior. Particle size (d₅₀) of the obtained spray dried powder was around 4 µm which was further increased to 18 µm after sintering. Scanning electron micrographs revealed the spherical morphology of spray dried powder. Also it was confirmed that the morphology was retained even after sintering. Thus the obtained powder had bulk density of about 1.6 g/cm³ as required for plasma spraying. Accordingly it was ensured that the prepared agglomerated powder is suitable for plasma spray process.