1 **Influence of Critical Plasma Spray Parameters on the Properties of Plasma Sprayed**
2 **Coatings Prepared from Spray Dried Alumina Powder**

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9 **Abstract:**

10 Plasma sprayable α -alumina powder was prepared by spray drying process. The powder was
11 characterized by field emission scanning electron microscopy (FESEM), powder X-ray
12 diffractometry, particle size analysis and flowability measurement. In the present work, the
13 influence of three different critical plasma spray parameter (CPSP) values (675, 825 and 937.5
14 W/nl.pm) on the crystallographic forms, microstructure, microhardness, surface roughness, wear
15 and corrosion resistance of the plasma sprayed alumina coatings were investigated. The coatings
16 were characterized by X-ray diffractometry and the analysis revealed the presence of some traces
17 of γ -alumina along with α -alumina for the coating obtained at higher CPSP. The surface
18 roughness, microhardness, corrosion and wear resistance of the coatings were evaluated. Plasma
19 sprayed alumina coating obtained at the highest CPSP exhibited improved wear and corrosion
20 resistance compared to the other two coatings which is attributed to the dense nature of the
21 coating.

22 **Key words:** alumina; spray drying; plasma spraying; wear; microstructure

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1. Introduction

Corrosion and wear problems are still of great relevance in a wide range of industrial applications and products as they result in the degradation and eventual failure of components and systems both in the processing and manufacturing industries and in the service life of many components. Various technologies have been used to deposit the appropriate surface protection that can resist the degradations. Among these, thermal spraying especially plasma spraying is often considered as a potential alternative to traditional coating manufacturing techniques (such as hard chrome electroplating) for the production of wear-resistant coatings^[1-6]. Since the 1960s atmospheric plasma spraying (APS) has been widely used in industry and found applications in many fields like automotive, aeronautical, medical, and paper milling^[7-9]. As far as anticorrosion and antiwear applications are concerned, the most frequently used coating materials are oxide ceramic coatings^[5].

Aluminum oxide, Al_2O_3 , more often referred to as alumina, is an exceptionally important ceramic material which has many technological applications. Plasma-sprayed aluminum oxide (Al_2O_3) coatings offer excellent wear resistance, corrosion resistance, heat, and thermal shock resistance, and have been widely used by the US Navy and other industries^[7]. Plasma sprayed alumina (Al_2O_3) coatings have been used for many applications in textile, electronic, aerospace, and aircraft industries because of their dielectric and wear resistance properties and also nuclear industry^[10,11]. Alumina coatings have several special properties like high hardness, chemical inertness; wear resistance and high melting point. It is reported that the corrosion resistance of alumina coatings are higher than that of cermet and metallic coatings^[12, 13]. Improved wear resistance has been reported for the alumina coatings deposited by low pressure plasma spraying^[14]. The effects of the substrate temperature on the hardness, porosity

and thermal expansion of Al_2O_3 coatings prepared by the plasma spray process have been reported^[15]. Fernandez et al.^[16] studied the influence of sliding speed and normal load on the wear behavior of plasma-sprayed Al_2O_3 coatings. Spraying conditions such as critical plasma spray parameter (CPSP) and distance between the spraying gun and the substrate, which are widely used as variables to quantitatively identify the temperature of spray powders inside the plasma flame, also affect the final coating microstructures and consequently the wear resistance. The critical plasma spraying parameter (CPSP) is expressed as the plasma output power in the numerator and the primary gas (Ar) flow rate in the denominator^[17, 18]. It is well known that when the plasma output power is increased, the particle temperature increases due to increasing plasma jet temperature because it is very sensitive to CPSP. The decrease in the argon flow rate, which leads to an increase in the powder in-flight time, has a similar effect on the particle temperature as the increase in the plasma output power. So CPSP can alter the coating microstructure and properties. Our previous study provided an insight into the wear behavior of plasma-sprayed Al_2O_3 coatings prepared using coprecipitation synthesized alumina powders^[19]. However, such a study has not been reported for alumina coatings prepared by using spray dried alumina powder.

The main aim of this work was to prepare plasma sprayable alumina powder by spray drying process and fabricate coatings with three different critical plasma spray parameters using the spray dried alumina powders. It was also aimed at studying the effect of CPSP on the microstructure, wear and corrosion resistance of the plasma sprayed alumina coatings.

2. Experimental

72 Plasma sprayable grade alumina powder was prepared using a laboratory type tall spray dryer
73 (SM Scientech, India) as follows: 350 g alumina powder ($-45\ \mu\text{m}$ sieve, Alcoa) was dispersed in
74 1 litre of water and 50 mL of 6% PVA (Loba Chemie) and was milled for 4 hours using a pot
75 mill and alumina balls. The spray dryer was operated with an inlet temperature of 325°C , outlet
76 temperature of 145°C and air pressure of 2 bars. The obtained spray dried alumina powder was
77 sieved (-25 to $+90\ \mu\text{m}$) to remove larger and smaller sized particles before plasma spraying. The
78 spray dried powder was not subjected to any calcination before plasma spraying. Phase
79 formation of alumina powders were confirmed by X-ray diffraction (XRD) using X`Pert Data X-
80 ray diffractometer. Particle size distribution of the powder was analyzed using laser light
81 scattering method (Mastersizer 2000, Malvern Instruments). Flowability of the powder was
82 measured using a Hall flow meter according to ASTM B213-97. The morphology of the powder
83 and surface and cross-sectional microstructures of plasma sprayed alumina coatings were
84 examined using field emission scanning electron microscope (FESEM, Carl Zeiss). Spray dried
85 alumina powders were plasma sprayed on stainless steel substrates using air plasma spraying
86 system (Sulzer Metco-9M). The plasma spray parameters used for spraying alumina powders are
87 listed in Table-I. To improve the adhesion of alumina coatings to stainless steel substrates,
88 Amdry 962 (Sulzer Metco) bondcoat material was sprayed before spraying alumina powder.
89 EDAX analysis showed the following composition for the bondcoat: Al-9.07 wt%, Cr-23.22
90 wt%, Ni-67.39 wt% and Y-0.33 wt%. Prior to spraying, the substrates were grit blasted (the
91 average size of commercial grit was about $25\ \mu\text{m}$) and degreased ultrasonically in acetone. For
92 convenience, the plasma sprayed alumina coatings sprayed at CPSP (W/nl.pm) values of 675,
93 825 and 937.5 are designated as alumina-1, alumina-2 and alumina-3 respectively.

Microhardness measurements were performed on the cross-sections of the plasma sprayed alumina coatings using microhardness tester (Buehler, Micromet 100) by applying 50 gf load. The microhardness values were measured at ten different places on the cross-section and the average value is reported. For wear studies, alumina powder was plasma sprayed on stainless steel substrates (35 mm x 20 mm x 4 mm). The sliding wear test was carried out using reciprocating wear tester (TR-285 M, DUCOM, India) with reciprocating motion against 6 mm diameter Al_2O_3 ball. The wear test was performed with 2 N load, 1 Hz frequency, and 15 mm stroke length for three and half hours. Wear rate was calculated by dividing the wear volume by the product of load applied and sliding distance. The weight loss of the coating and the counterpart alumina balls was measured using an electronic weighing balance (0.0001 g accuracy). The average of three wear tests is reported. Surface roughness (R_a) of the coatings was measured using a roughness profilometer (Taylor Hobson).

Corrosion behavior of plasma sprayed alumina coatings deposited at three different CPSPs on stainless steel coupons were conducted using CHI 604 2D electrochemical workstation. The test was carried out in deaerated 3.5 wt% (0.6 M) NaCl solution (200 $\pm$ 2 mL). A conventional three electrode cell was used; which was equipped with alumina coated stainless steel coupon with an active area of 1cm^2 as working electrode, platinum foil and saturated calomel electrode (SCE) were used as counter and reference electrodes respectively. The edges of the coupons were also masked using lacquer to avoid crevice corrosion. Prior to the corrosion tests, samples were washed in distilled water and ethanol, and then dried in warm air. The reference electrode was connected to a Luggin capillary and its tip was placed very close to the surface of the working electrode to minimize IR drop. The working electrode was immersed in NaCl solution for an hour in order to establish the open circuit potential (EOCP). The system

was allowed to attain open circuit potential then the upper and lower potential limits of linear sweep voltammetry were set at ± 200 mV with respect to the EOCP. The sweep rate was 1 mV/s. The corrosion potential E_{corr} , corrosion current density i_{corr} and polarization resistance R_p were deduced from the Tafel plot. The polarization resistance was obtained using the Stern–Geary equation:

$$R_p = \left[\frac{b_a b_c}{2.303(b_a + b_c)} \right] \left[\frac{1}{i_{\text{corr}}} \right] \dots\dots\dots (1)$$

where b_a and b_c are Tafel slopes or the Tafel constants, expressed in mV/dec.

3. Results and Discussion

3.1. Characterization of Spray dried Alumina Powder

The spray dried alumina powder had flowability of 70 s / 0.050 kg. The spray dried alumina powder possessed mostly spherical shaped particles as shown in the FESEM images (Fig. 1 a & b). Most of the powders were perfectly spherical in shape. A higher magnification FESEM image (1c) of spray dried single alumina particle consisted of smaller sized particles which indicate each particle to be a constituent of smaller sized particles. Fig. 2 shows the particle size distribution of spray dried alumina powder. The particle size distribution curve of spray dried alumina powder showed a narrow size distribution with an average agglomerated particle size of 41 μm which is suitable for plasma spraying. Fig. 3 shows the powder X-ray diffraction pattern of spray dried alumina powder. The pattern confirmed the formation of 100% α -alumina and the diffraction peaks were sharper and the pattern matched exactly with the starting alumina powder.

3.2. Characterization of plasma sprayed coating deposited using spray dried alumina

3.2.1. Microstructure of the coatings

Fig.4 shows the surface FESEM images of the surfaces of as plasma sprayed alumina coatings. The surface FESEM image of spray dried alumina-1 coating exhibited large number of splats along with large number of unmelted particles. Some splats appeared like a custard apple containing well fused particles (Fig.4a). The appearance of such features may be attributed to the explosion of finer and smaller sized particles due to insufficient plasma power. Such features were not observed with plasma sprayed alumina coatings deposited using co-precipitation synthesized powder ^[19]. The presence of such features would have resulted in porous and rougher alumina-1 and alumina-2 coatings. However, the extent of such features was reduced in alumina-2 (Fig. 4b) and finer alumina particles were observed. On the other hand alumina-3 coating exhibited mostly fully melted splats along with very few alumina particles; exploded splats were not observed as in the other two coatings (Fig. 4c). Higher magnification FESEM images of the splats showed some cracks and pores typical of plasma sprayed coatings. Fig.5 shows the cross-sectional FESEM images of plasma sprayed alumina coatings. From the images it is observed that the density of the coatings varied as follows alumina-3 > alumina-2 > alumina-1. Alumina-1 coating had more of unmelted / partially melted regions compared to alumina-2 and alumina-3 coatings. The coating thickness was also slightly higher for alumina-3 coating and this may be attributed to the complete melting of most of the alumina particles in the high temperature plasma. All the coatings showed bimodal distribution.

3.2.2. X-ray analysis of plasma sprayed alumina coatings

Fig.6 shows the XRD patterns of plasma sprayed alumina coatings prepared from spray dried α -alumina powder at different CPSPs. The coating formed with lower CPSP retained α -form of

alumina. Interestingly, the coating obtained with highest CPSP (alumina-3) showed the presence of γ -alumina (400) peak. Commonly γ - Al_2O_3 nucleates in preference to α - Al_2O_3 during rapid solidification of liquid droplets^[20-22]. With increasing CPSP, the intensity of the 100% alpha alumina (113) peak and (024) increased. Interestingly, α - Al_2O_3 (208) peak intensity decreased with increasing CPSP.

3.2.3. Microhardness and roughness of plasma sprayed alumina coatings

Alumina-1 exhibited lowest microhardness followed by alumina-2 and alumina-3 exhibited highest microhardness (Fig. 7). The properties of the coatings were affected by the high incidence of semi-molten/unmelted particles. Porosity was higher at the lower spraying energies, where the semi-molten particles are less deformed. At higher spraying energies, molten material of high diffusivity would fill the asperities and gaps of the previously deposited layers, leading to lower porosities. The microhardness increased with spraying power (Fig.7), possibly as a result of the decreased porosity^[23]. The higher hardness is attributed to the complete melting of the alumina particles at higher CPSP. The lower microhardness of alumina-1 is attributed to the presence of higher fraction of unmelted or partially melted zones present in the microstructure of the plasma coating. The surface roughness of alumina-1 coating was highest and that of alumina-3 was the least (Fig.8).

3.2.4. Wear resistance of plasma sprayed alumina coatings

The wear data obtained for all the three plasma sprayed alumina coatings and the alumina counterpart balls are tabulated in Table-II. Alumina-3 coating and its corresponding alumina ball counterparts exhibited the lowest wear loss. Larger wear rates are usually caused by the removal of entire lamellae or part of them. The low cohesive strength and the presence of inter-lamellar

cracks could have contributed to larger wear rate of alumina-1^[7]. At higher CPSP most of the particles are fully melted in the spray jet. In case of coatings sprayed with medium CPSP, there are sufficient numbers of partially melted or unmelted regions that resemble the constituent alumina particles of the agglomerates.

In general, hardness influences the wear resistance of plasma-sprayed coatings, and microstructure, ductility, toughness, and pores present in the coating also play a role in the wear process. The coefficient of friction (COF) was ~0.7 for all the three coatings irrespective of the different CPSPs used for plasma spraying. The predominant wear mechanism was of abrasive type and caused the material to delaminate owing to the high pressure exerted by the ball on the coating.

The values of the corrosion potential (E_{corr}) and the corrosion current density (i_{corr}) were extracted from the curves using the Tafel extrapolation method. The corrosion potential, corrosion current density and the polarization resistance obtained for the plasma sprayed alumina coatings by potentiodynamic polarization studies are tabulated in Table-III. The corrosion current density is an important parameter used for evaluating the kinetics of the corrosion reaction. Corrosion protection is inversely proportional to the corrosion current density. Lower the corrosion current density, higher will be the corrosion resistance. The corrosion current density followed the following order: alumina-3 < alumina-2 < alumina-1 < stainless steel substrate. The corrosion current density for the alumina-3 coating was very low which also indicates superior corrosion resistance of the coating. In general the E_{corr} values shifted to more negative side compared to the substrate indicating improved corrosion resistance of the coatings over the substrate. The R_p value of alumina-3 coating was the highest implying better corrosion

resistance of the coating compared to other coatings. The improved corrosion resistance of alumina-3 is attributed to the dense nature of the coating.

4. Conclusion

Plasma sprayable grade alumina powder was prepared by spray drying process. The powders were plasma sprayed at three different critical plasma spray parameters (CPSP). From this study it is evident that CPSP influences the microstructure, microhardness and wear behavior of the plasma sprayed alumina coatings. The surface roughness decreased with increasing CPSP and the density of the coatings increased with increasing CPSP. The wear and corrosion resistance of alumina coatings increased with increasing CPSP. The coating that was plasma sprayed at higher CPSP showed traces of γ -alumina along with α -alumina. The microhardness of the coatings increased with increasing CPSP and was in the range of 1000-2100 HK_{50gf}. The alumina coating, plasma sprayed at the highest CPSP showed lower wear rate and higher corrosion resistance compared to the other two coatings which is attributed to the dense nature of the coating. The surface roughness of the coatings decreased with increasing plasma power.

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Table-I. Plasma spray parameters used for bondcoat and spray dried alumina powder

Plasma spray parameters	Bond coat	Alumina
Argon Flow (NLPM)	40	40
Hydrogen Flow (NLPM)	9	7
Amps (A) /Volts (V)	550/60	450, 550, 625 / 60
CPSP (NLPM)	825	675, 825, 937.5
Carrier gas Flow (SCFH)	15	15
Pre Heat / Spray passes	2/5	2/14
Powder Feed rate (g/min)	10	15
Cooling air Pressure (bar)	2	2
Spray distance (cm)	25	15
Gun speed (mm/s)	800	800

Table. II. Wear rate of plasma sprayed spray dried alumina coatings

Sample ID	Volume loss (mm ³)		Wear rate mm ³ /Nm	
	Coating	Ball	Coating	Ball
Alumina-1	1.859	0.507	1.259 x 10 ⁻³	1.052 x 10 ⁻⁴
Alumina-2	0.728	0.126	5.09 x 10 ⁻⁴	8.76 x 10 ⁻⁵
Alumina-3	0.452	0.101	3.15 x 10 ⁻⁴	7.01 x 10 ⁻⁵

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284 **Table-III. Potentiodynamic polarization data of plasma sprayed alumina coatings**

Samples	OCP(V)	Ecorr (V)	Icorr ($\mu\text{A}/\text{cm}^2$)	Rp ($\Omega \text{ cm}^2$)
Substrate	-0.177	-0.199	9.717	3661
Alumina-1	-0.294	-0.331	0.6864	51399
Alumina-2	-0.236	-0.212	0.3647	54702
Alumina-3	-0.310	-0.214	0.1129	340454

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290 **Figure Captions**

291 Fig.1. FESEM images of spray dried alumina particles taken at various magnifications (a) 1.5KX
292 (b) 6 KX (c) 30 KX

293 Fig.2. Particle size distribution of spray dried alumina powder showing a narrow size distribution

294 Fig.3. XRD analysis of spray dried alumina powder.

295 Fig. 4. FESEM surface images of plasma sprayed alumina coatings at different CPSP s (a)
296 alumina-1, (b) alumina-2 and (c) alumina-3.

297 Fig. 5. FESEM images of plasma sprayed spray dried alumina coatings cross-section at different
298 CPSP (a) alumina-1, (b) alumina-2 and (c) alumina-3.

299 Fig. 6. XRD patterns of plasma sprayed alumina coatings at different critical plasma spray
300 parameter (a) alumina-1, (b) alumina-2 and (c) alumina-3.

301 Fig. 7. Histogram showing the Knoop microhardness of the alumina coatings plasma sprayed at
302 different CPSPs.

303 Fig. 8. Histogram showing the surface roughness of the surface and worn out regions of APS
304 alumina coatings plasma sprayed at different CPSPs.

Fig.1a

Fig.1b

Fig.1c

Fig.2

Fig.3

Fig.4a

Fig.4b

Fig.4c

Fig.5

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Fig.7

Fig.8

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