CHAPTER II
In recent years, the use of plasma sprayed protective coatings has gained increasing acceptance for prolonging the life of critical components exposed to aggressive environments during normal operation. Of all the ceramic materials, the use of plasma sprayed alumina (Al$_2$O$_3$) coatings for applications requiring enhanced corrosion and wear resistance is well recognized and widely established. However, in many of the demanding applications, the low tensile bond strength and the high porosity characteristic of the plasma sprayed Al$_2$O$_3$ coatings have limited their use. For such extreme applications, the use of detonation gun (D-gun) spray technique is a viable option, by virtue of the very high particle velocities that it imparts, thereby leading to dense and well bonded coatings which exhibit excellent tribological properties such as high abrasion and erosion resistance. In view of the perceived advantages of D-gun coatings over plasma spray coatings, a brief literature survey on the properties and tribological performance of Al$_2$O$_3$ coatings deposited by plasma and D-gun spray processes are presented. Of great interest, review has also been made on the utilization of optimization studies and deposit formation dynamics in plasma spraying.

2.1 PLASMA AND D-GUN SPRAYING

Thermal spraying is emerging as an important tool of increasingly sophisticated surface engineering technology. Among all the thermal spray variants, the versatility of plasma spraying is well established and widespread, which allows the application of coating of a wide range of materials, including the most refractory ones. These include metals, their oxides, carbides, borides, nitrides and even composites of different materials. Over the
years, the areas of application of plasma sprayed coatings have grown in an impressive manner, particularly their use to combat wear is evolving rapidly. However, in recent times, deposition techniques such as D-gun and HVOF gained growing interest due to their inherent advantages, particularly for depositing wear resistant coatings [1-3]. The D-gun spraying process is characterized by spray particles, which impact the surface of a substrate or a coating formed previously at the highest velocity realizable for the thermal spraying process available at present. Although high power plasma spraying equipment and HVOF devices are reported to accelerate particles to velocities comparable with those of D-gun [4], the actual velocity has not been found to be so high. Typical measured particle velocities for WC-Co powder are reported to be about 600-700 m/s [5,6], 400-500 m/s [7,8] and 100-200 m/s [9] for D-gun, HVOF and plasma spraying respectively.

In a thermal spraying process, the parameters of the spray particle affecting coating formation and the structure and properties of the coating-substrate system are considered to be the size, temperature and velocity of the particle for a certain spray material. Generally, it is considered that a sufficiently high particle velocity will lead to the production of a dense coating with low porosity. Consequently, a high particle velocity is associated with good coating performance; in particular erosion and abrasive wear resistance. Therefore, it can be considered that D-gun coating is the best technique from the viewpoint of coating density and high wear resistance [1-3]. However, because of the limited availability of D-gun spraying equipment from commercial sources, it is recognized that the literature published on the D-gun process is very limited compared with the other processes such as plasma spraying and HVOF.

Oxide ceramics such as aluminium oxide (Al₂O₃ - traditionally referred as alumina), chromium oxide (Cr₂O₃), and zirconium oxide (ZrO₂) are mainly used on an industrial scale. The most extensively used plasma coatings are those of Al₂O₃, because this ceramic material is
distinguished by its chemical stability, high strength, good heat and electrical insulating properties and is, at the same time, abundant and cheap. Although it is widely recognized that plasma sprayed Al₂O₃ coatings can provide many successful solutions to engineering problems [10-13], its ability to satisfy requirements, where high wear resistance is of great importance has to be raised. For such requirements, the use of D-gun spraying is a viable option, since D-gun coatings exhibit higher bond strength, hardness and density as compared to plasma sprayed coatings. In general, a D-gun coating is more wear resistant than plasma coating of the same composition. The high bond and intrinsic cohesive strength of D-gun coatings allow them to survive under severe conditions of any wear mode that could destroy plasma coatings. However, the recent literature reveal that there have been very few studies ascertaining the relative performance of plasma and D-gun sprayed Al₂O₃ coatings and are reviewed in the following sections.

2.1.1 Performance of Al₂O₃ coatings deposited by plasma and D-gun spraying

Microhardness, bond strength, density and porosity are the important physical properties of the coating, and their measures are often used for the first approximation of coating wear resistance. The hardness of D-gun coatings is generally higher than that of equivalent coatings produced by any other thermal spray process. This is basically due to the very dense structure achieved by the high impact velocity of the spray process. The bond strength of D-gun coatings to their substrates are also extremely high for the same reason. D-gun was used to spray Al₂O₃ and the resulting coating was significantly harder than that of the coating obtained with APS by Tucker [7]. Guest [14], also showed that the possibility of getting higher hardness (1100 Hv₀.₃) and tensile bond strength (68 N/mm²) for the Al₂O₃ coatings by D-gun. For APS process, hardness is 850 Hv₀.₃ and tensile bond strength is 52 N/mm². Al₂O₃, Al₂O₃+30%MgO, Al₂O₃+3-40%TiO₂ and Cr₂O₃ coatings deposited by atmospheric plasma spraying and detonation gun spraying were studied and compared by Vuoristo et al. [15,16].
Obtained results clearly showed that the D-gun sprayed coatings had more homogeneous microstructures and higher microhardness values than the corresponding plasma sprayed coatings. The enhanced performance of D-gun coatings over APS coatings using Al₂O₃ (of ranging size from 22.5 to 45 μm) have been thoroughly reviewed by Niemi et al. [17-19]. The coatings had hardness in the range 1040-1340 Hv₀.₂ and bond strength of 31 N/mm², which is 2.2 times greater than that of APS coatings. Recently, Sundararajan et al. [20], reported a higher hardness (1141 Hv₀.₂) and lower porosity (1.18 vol.%) for the D-gun coatings while for APS, the hardness is 693 Hv₀.₂ and the porosity is 4.55 vol.%. All these researchers confirmed that improved coating quality could be achieved by D-gun over APS for the same coating material: Al₂O₃. The following Table 2.1 shows a brief survey on the properties of Al₂O₃ coatings deposited by APS and D-gun spray processes.

<table>
<thead>
<tr>
<th>Spray process</th>
<th>Coating characteristics</th>
<th>References</th>
</tr>
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<tbody>
<tr>
<td>APS D-gun</td>
<td>3 825 52 (7500 psi) 3.40</td>
<td>R.C. Tucker et al., 1974 [3]</td>
</tr>
<tr>
<td>APS D-gun</td>
<td>2 1100 69 (10,000 psi) 3.38</td>
<td>Y.Wang et al., 1989 [22]</td>
</tr>
<tr>
<td>APS D-gun</td>
<td>3 850 52</td>
<td>C.J.S.Guest, 1986 [14]</td>
</tr>
<tr>
<td>APS D-gun</td>
<td>2 1100 68</td>
<td></td>
</tr>
<tr>
<td>APS D-gun</td>
<td>1020 972-1142</td>
<td>P.M.J.Vuoristo et al., 1992 [16]</td>
</tr>
<tr>
<td>APS D-gun</td>
<td>780±58 1023±52</td>
<td>K.Niemi et al., 1994 [18]</td>
</tr>
<tr>
<td>APS D-gun</td>
<td>6.8 904</td>
<td>K.Niemi et al., 1995 [17]</td>
</tr>
<tr>
<td>APS D-gun</td>
<td>2.3 1196</td>
<td></td>
</tr>
<tr>
<td>APS D-gun</td>
<td>3.7 1010 12</td>
<td>K.Niemi et al., 1995 [19]</td>
</tr>
<tr>
<td>APS D-gun</td>
<td>1.5 1045 31</td>
<td></td>
</tr>
<tr>
<td>APS D-gun</td>
<td>4.55 693</td>
<td>G.Sundararajan et al., 1998 [20]</td>
</tr>
<tr>
<td>APS D-gun</td>
<td>1.18 1141</td>
<td></td>
</tr>
</tbody>
</table>

APS - air plasma spraying; D-gun - detonation gun spraying
2.1.2 Wear resistance of plasma and D-gun sprayed Al$_2$O$_3$ coatings

Plasma and D-gun sprayed Al$_2$O$_3$ coatings are primarily used for their wear resistance and many authors have made generalized statements about the relative merits of coatings or presented data from a wide variety of wear tests. In general, a D-gun coating is more wear resistant than a plasma coating of the same composition, because of its higher density and cohesive strength. The high bond and intrinsic cohesive strength of D-gun coatings allow them to survive under severe conditions of any wear mode.

There have been many studies of plasma sprayed Al$_2$O$_3$ coating as well, e.g., sliding wear tests have been reported by Ding et al. [21], Wang et al. [22], and Fernandez et al. [23]. Further, the enhanced tribological performance of Al$_2$O$_3$ coatings by D-gun has been compared with APS by several authors [19,20,24,25]. A dry sliding wear test was conducted at a normal load of 320 N; test of duration 3 h; sliding speed of 1.18 m/s by Wang et al. It was observed that the D-gun sprayed Al$_2$O$_3$ coating exhibited higher wear resistance (wear rate = 9.8 mm$^3$/N m) than that of plasma sprayed coating (wear rate = 18.9 mm$^3$/N m). Niemi et al. [19], evaluated the wear characteristics of Al$_2$O$_3$ coatings using rubber-wheel abrasion test, pin-on-disc test and particle erosion test. The results showed that the D-gun coatings have better wear performance over corresponding coatings deposited by conventional APS. Similar study has been conducted by Sundararajan et al. [20], who observed that the D-gun coatings were superior to the APS coatings. The tribological performance studies of Al$_2$O$_3$ coatings done by some of the authors using APS and D-gun are tabulated in Table 2.2. All these researchers confirmed that with the Al$_2$O$_3$, the D-gun method produced clearly more wear resistant coatings than those by the APS method. However, there have been a very few studies that attempted an elucidation of the mechanism of wear of these coatings.
Table 2.2 Tribological performance of the Al₂O₃ coatings deposited by APS and D-gun

<table>
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<tbody>
<tr>
<td></td>
<td>APS</td>
<td>D-gun</td>
<td>APS</td>
<td>D-gun</td>
</tr>
<tr>
<td>Abrasive wear:</td>
<td></td>
<td></td>
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<tr>
<td>Wt. loss (mg)</td>
<td>--</td>
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<tr>
<td>Vol. loss (mm³)</td>
<td>--</td>
<td>--</td>
<td>115</td>
<td>32</td>
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<tr>
<td>Erosive wear:</td>
<td></td>
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<td></td>
<td></td>
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<tr>
<td>Wt. loss (mg)</td>
<td>--</td>
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<tr>
<td>Sliding wear:</td>
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<tr>
<td>Wt. loss (mg)</td>
<td>--</td>
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</tr>
<tr>
<td>Wear rate x 10⁻⁸ (m⁢³/N m)</td>
<td>18.90</td>
<td>9.80</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Friction coefficient</td>
<td>0.75</td>
<td>0.70</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

APS - air plasma spraying; D-gun - detonation gun spraying

2.2 UTILIZATION OF DOE TECHNIQUES IN PLASMA SPRAYING

A key to the successful exploitation, especially commercial, of any coating system will lie in the generation and acceptance of appropriate quality assurance i.e., a repeatable achievement of high quality coatings. Hence, there is an urgent need to characterize and fully understand and interpret the reported enhanced performance of such coatings. Design of experiments (DOE) is an effective method for conducting experiments to enhance thermal spray coating properties through finding optimum spray parameters and for obtaining a better understanding of the physical mechanisms involved in the coating. Further, DOE techniques have been shown through many studies to be an efficient method in learning the effects of various parameters on coating properties.

For most of the thermal spray processes, the optimization of the spray parameters is not a trivial task. This is primarily due to the large number of processing parameters or factors involved. Recently, plasma and high velocity oxy-fuel (HVOF) spray parameters have been
successfully optimized using DOE techniques [27-31], particularly the Taguchi method [32-37]; but no such optimization studies have been carried out for D-gun spray process.

A brief survey of the DOE techniques most frequently applied to examine properties of the $\text{Al}_2\text{O}_3$ coatings deposited by the APS and VPS processes is given in Table 2.3.

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Spray process</th>
<th>Coating properties studied</th>
<th>DOE techniques applied</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>APS</td>
<td>Porosity, microhardness and tensile strength</td>
<td>(L8-2$^3$)</td>
<td>J.Walter et al., 1990 [34]</td>
</tr>
<tr>
<td>2.</td>
<td>APS</td>
<td>Microstructure, porosity and microhardness</td>
<td>(L8-2$^3$)</td>
<td>T.Chon et al., 1991 [36]</td>
</tr>
<tr>
<td>3.</td>
<td>APS</td>
<td>Plasma power and porosity</td>
<td>(L27 -5$^3$)</td>
<td>S.L.Chen, 1992 [37]</td>
</tr>
<tr>
<td>4.</td>
<td>VPS</td>
<td>Spray efficiency</td>
<td>(L4-2$^4$)</td>
<td>R.Kingswell, 1993 [29]</td>
</tr>
<tr>
<td>5.</td>
<td>APS</td>
<td>Thickness, hardness, porosity, roughness, dielectric strength and unmelted particle content</td>
<td>(L5-2$^4$)</td>
<td>M.Lynn et al., 1993 [38]</td>
</tr>
<tr>
<td>6.</td>
<td>APS</td>
<td>Thickness, hardness, porosity, roughness, deposition efficiency, dielectric strength and tube resistance</td>
<td>(L8-2$^3$)</td>
<td>T.J.Steeper et al., 1993 [32]</td>
</tr>
</tbody>
</table>

APS - air plasma spraying, VPS - vacuum plasma spraying

A range of $\text{Al}_2\text{O}_3$ and $\text{Cr}_3\text{C}_2/\text{NiCr}$ coatings were produced for the clearance control applications in jet engines using plasma spray process, utilizing (L8-2$^3$) design by Chon et al. [36]. Experiments conducted were eight run, full-factorial design of three independent factors; secondary gas flow, plasma current and spray distance. Microstructural attributes such as, porosity, unmelted or partially melted particles and macrohardness were the coating attributes studied. The following conclusions were drawn from their study: alumina
microstructure and properties can be tailored to meet the specific application requirements utilizing the results of DOE study employed in this investigation, excellent microstructure, tensile and good superficial hardness are attainable using the optimized process parameters. Further, it has been shown that DOE can be utilized to quickly ascertain coating attribute sensitivities to parametric variance.

Lynn et al. [38] conducted experimental and analytical studies to investigate plasma spraying of alumina powder (Alloys International Al-1010) using fractional-factorial statistical parametric approach (L5-2^4). The parameters that were varied for the conducted five experiments include, total gas flow, working gas flow ratio (secondary to primary gas flow), spray distance and power for a plasma spray system (Miller Thermal Plasmadyne SG-100). The measured coating characteristics determined in this study were thickness, porosity, dielectric strength, hardness and roughness. From the results, trends were predicted by the statistical effect analysis. Dielectric strength was most influenced by the total flow rate. Shorter spray distance was the most significant contributor in lowering induced porosity. The unmelted particle volume was most influenced by higher total working gas flow rate. Longer spray distance was the most significant factor in increasing microhardness. An optimized coating design was predicted and verified by the Taguchi analysis employed in their investigation.

Recently, a Taguchi-style fractional-factorial (L8-2^7) design was employed by Steeper et al. [39], to evaluate the effect of seven independent spray process parameters; current, primary gas flow, secondary gas flow, powder feed rate, spray distance, traverse rate and carrier gas flow. Coating qualities were determined with respect to insulator resistance, dielectric strength, porosity, deposition efficiency and microstructure. The study used a plasma spray system (METCO 7 MB) and commercially available spray powder
(METCO 105 SF alumina) ranged in size from 15 to 53 μm. This powder system is being used in the fabrication of heater tubes that emulate nuclear fuel tubes for use in thermal-hydraulic testing. Based on the Taguchi analysis, an optimum coating has been produced for this particular application by employing the optimum levels of the design factors; current 450 A, primary argon gas flow rate of 70 SCFH, secondary hydrogen flow rate of 17 SCFH, powder feed rate of 3.5 lb/h, a spray distance of 3.0 in, a traverse rate of 18 in/s, and a carrier gas flow rate of 41 SCFH.

Other recently reported optimization studies on plasma-sprayed alumina coatings based on (L16) or (L8) Taguchi designs are:

- Universal abrasives 500 # alumina powder, (L16-2⁶ design, 6 independent parameters and the dependent parameter is deposition efficiency) [29],

- Miller Aluminum oxide, (L8-2⁷ design, 7 independent parameters and 3 dependent parameters:- tensile strength, microhardness and porosity) [35], and

- Al₂O₃ powder of size from 5.6 to 45 μm (Amperit 740.1), (L27-5⁵ design, 5 independent parameters and 2 dependent parameters:- plasma power and porosity) [37].

All the above said reports confirm that the utilization of Taguchi methodology is promising for the optimization of plasma spray variables as well as to ascertain parametric sensitivity of the measured coating attributes. However, it is worthwhile to note that such optimization studies have not been exploited for D-gun spraying so far. Since D-gun is an important technique for producing high quality wear resistant coatings, it is necessary to carry out such optimization studies to study the effect of process variables on the coating properties.
2.3 DEPOSIT FORMATION DYNAMICS

Thermal spray deposits are comprised of cohesively bonded splats, which result from high rate impact and rapid solidification of a high flux (millions of particles per cm$^3$/s) of flame-melted particles with sizes in the range from 10 to 100 μm. The physical properties and behaviour of such a deposit will be expected to depend on the cohesive strengths among the splats, the size and morphology of the porosity, the occurrence of cracks and defects and, finally, on the ultrafine-grained microstructure within the splats themselves.

The microstructures of thermal spray deposits are ultimately based on the solidification of many individual molten droplets. A splat results when a droplet of molten material, tens of micrometers in diameter and melted in the flame, strikes a surface, flattens out then solidifies. The collection of these splats forms the deposit. There are numerous considerations relative to the dynamics of deposit evolution during thermal spraying. The mechanistic or physical aspects of splat formation deal with the spreading of the molten droplet, interactions with the substrate, etc. These characteristics are affected by the temperature of the splat, the splat viscosity, its surface tension and other considerations. Splat morphology will depend on a variety of factors; the most important of them are particle velocity, temperature, diameter and substrate surface profile [40].

Houben has described in considerable detail certain physical aspects of splat formation through heat transfer and mechanical models [41]. He has identified the various types of splat morphologies, described broadly as ‘pancake type’ and ‘flower’ type. He has further shown that splat morphology is affected by the velocity of the impinging droplet. An increase in velocity leads to enhanced flattening and spreading of the droplet. Recently, transition behavior of the splat pattern of Ni sprayed particles on a flat substrate was investigated by M.Fukumoto et al. [42] and the following results were obtained through
their study. Splashing tends to occur easier when the solidification is easier and the better the wetting between particle/substrate the more difficult is splashing. From both Auger analysis of the splash splat and SEM observation of the splash splat on the Au coated substrate, they confirmed that the splash is formed by not flowing on the substrate surface from impingement center to periphery, but jetting away from the central disc. They also indicated that the initial rapid solidified layer formed just after the impingement on the substrate plays an important role for the splashing. Montavon et al. [43] further explored the influence of spray parameters on splat formation by utilizing shape factors for the splats. Using optical microscopy and image analysis, they determined the influence of spray parameters and impact angle on the splat characteristics for vacuum plasma sprayed, Ni-based alloy. It was shown that the splat shape factors, especially as influenced by spray angle, have strong effect on deposit characteristics, such as porosity, deposit efficiency and microhardness.

R.Sivakumar et al. [44] have studied the thermal history and velocity of the different spray powders (Mo, NiAl, MgO.ZrO₂ and TiO₂) collected at various distances from the plasma gun using detailed metallographic examination. It was further shown that the optimum spray distance was high for the metal alloy powders compared to that for the ceramic powders. S.V.Joshi et al. [45] have investigated the influence of primary plasma spray variables such as arc current and particle size on the WC-Co powder particle deposition characteristics. Their observation on splat morphology suggests that an increase in arc current leads to satisfactory spreading of the molten droplet and finer size WC-Co particles exhibit better spreading characteristics. They have further shown that such splat morphology lead to a denser microstructure. D.J.Sordelet et al. [46] further explored the relationships among processing, phase structure and splat morphology of certain quasicrystalline coatings (Al₆₃Cu₂₅Fe₁₂, Al₆₅Cu₂₃Fe₁₂ and Al₆₇Cu₂₁Fe₁₇) using plasma and
HVOF spraying. Their study was performed to examine the effects of starting powder composition, substrate thermal conductivity and substrate temperature on the composition and structure of individual Al-Cu-Fe splats formed during spraying. Their observation also showed that the splats obtained by HVOF spraying exhibited similar characteristics to those deposited by plasma spraying.

Though the above said review confirms the viability of evaluating the extent of melting and the relative velocities of coating powders using metallographic examination, such studies are still lacking in the case of Al₂O₃. Recently, the effect of substrate preheating and surface organic covering on splat formation was studied by C.J.Li et al. [47] for Al₂O₃, Al, Ni and Mo powders with stainless steel as the substrate material. However, the effect of primary plasma variables on the splat formation has not been considered in their study.

2.4 SUMMARY OF THE REVIEW

Summarizing the overall review:

1. D-gun spraying is a most promising thermal spray process for depositing Al₂O₃ coating of high quality over APS. However, literature reveal that there have been very few studies ascertaining the relative performance of plasma and D-gun sprayed Al₂O₃ coating, since D-gun spray systems are not yet readily available from commercial sources and only a limited number of systems exist worldwide for carrying out research work.

2. In recent years, the DOE studies have been shown through many studies to be an efficient method in learning the effect of various process parameters on the coating quality characteristics in various thermal spray processes, particularly in plasma
spraying. However, the utilization of such studies is still lacking in the case of D-gun spraying.

3. The flattening and solidification of molten droplets during thermal spraying must be studied for a good understanding of melting and acceleration of powders in the flame, since flattening characteristics of the droplets impacting on a substrate are an important determinant in governing the eventual quality of thermal sprayed coatings. Although this technique has been mentioned in the literature, no detailed work has so far been reported for Al$_2$O$_3$ powder deposition characteristics and such type of studies have not been carried out for the D-gun spraying.

For this reason, the present study aims on the parameter optimization of Al$_2$O$_3$ coatings deposited by plasma and D-gun spraying by utilizing the DOE techniques. Further, an attempt has been made on the melting and acceleration of powders in the flame by probing the as-deposited structure of individual splats formed by both the plasma and D-gun spray processes.
REFERENCES


