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Microstructure, Adhesion, and Erosion Wear of Plasma Sprayed Alumina–Titania Composite Coatings

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ABSTRACT: Plasma spray technology is being widely used for the development of protective coatings to prevent degradation of critical components working under severe conditions. Plasma sprayed alumina–titania have many industrial applications. These coatings provide a dense and hard surface which is resistant to abrasion, corrosion, cavitation, oxidation, and erosion. Plasma sprayed alumina–titania coatings are regularly used for wear resistance, electrical insulation, thermal barrier applications, etc. Alumina pre-mixed with titania powder is deposited on mild steel substances by atmospheric plasma spraying. Microstructure of the coating is analyzed by SEM. Adhesion strength of alumina–titania coatings are measured. The response of plasma sprayed alumina–titania coatings to the impingement of solid particles has been presented in this study. The erosion rate is calculated on the basis of 'coating mass loss'. It is observed that the erosion wear rate varies with erodent dose, angle of attack, the velocity of erodent, standoff distance, and size of the erodent. Cumulative coating mass loss varies with time of erosion.

KEY WORDS: alumina–titania coating, plasma spraying, adhesion strength, solid particle erosion.

INTRODUCTION

Thermal spraying is a technique of coating manufacturing implementing a wide variety of processes and materials. Atmospheric plasma spraying (APS) is one of these processes based on the creation of a plasma jet to melt a feedstock powder [1]. Powder particles are injected with the aid of a carrier gas; they gain their velocity and temperature by thermal and momentum transfers from the plasma jet. At the surface of the substrate, particles flatten and solidify rapidly forming a stack of lamellae. Micro-cracks appear also in the microstructure as a consequence of stress accommodation due to the high spray temperature and a large difference in thermal dilation coefficients between the substrate and coating. This is mainly the case for ceramic coatings deposited on metallic substrates. Plasma sprayed ceramic coatings, for their higher strength-to-weight ratio and superior wear-resistant properties, are preferred in most tribological applications. The suitability of a ceramic coating on metal substrates depends on (a) the adherence strength

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Figure 3 appears in color online: http://jrp.sagepub.com

at coating–substrate interface, and (b) stability at operating conditions. Critical components in high-tech industries operate under extremely hostile conditions of temperature, gas flow, heat flux, and corrosive media, which severely limit their service life. This problem can be overcome by using composite structures consisting of the core material with a suitable surface coating. Plasma spray technology, the process of preparing overlay coating on any surface, is one of the most widely used techniques to prepare such composite structural parts with improved properties and increased life span [2]. Composite coatings are defined as the deposits produced by thermal spraying containing at least two distinctive, intentionally present phases apart from porosity. Al_2O_3–TiO_2 composite coatings are composed of a matrix Al_2O_3 and second TiO_2 phase called reinforcement. The role of the matrix is to distribute the stresses homogeneously inside the composite material. The role of the second phase in the coating is mostly to reinforce the material mechanically. These types of coatings can be prepared by blending the matrix powder with reinforcement and by plasma spraying [2,3]. The use of the composite in preference to pure aluminum oxide has certain advantages. Titanium oxide has a lower melting point and effectively binds alumina grains leading to higher density and wear resistance coating. Al_2O_3 with low wt% of TiO_2 coatings provide high electric resistance and are suitable where good insulating properties and high electric strength are required, but the coatings of mixtures with high wt% of TiO_2 possess good electrical conductivity due to its manufacturing process of powder and preparation of coatings.

Coating adhesion to the substrate and wear resistance are important properties of the thermally sprayed ceramic coatings. In this paper, the Al_2O_3–TiO_2 layers are deposited on mild steel substrates using the atmospheric plasma spray technique. Adhesion of the coatings to the substrate and residual stresses generated at the interface are the main characteristics, which influence the structure. Adhesion strength of alumina–titania coatings are measured. Properties of the plasma sprayed coatings are influenced by the microstructure of the coating. The coating morphology is analyzed with SEM studies. Erosion wear tests were carried out on the coatings to ensure its applicability under different operating parameters. Solid particle erosion is a process where particles strike against a surface and cause material loss. During flight, a particle carries momentum and kinetic energy, which is dissipated during impact due to its interaction with a target surface. In the case of plasma spray coatings encountering such situations, no specific model has been developed and thus the study of the erosion behavior has been based on mostly experiment data [4]. Erosion is a non-linear process with respect to its variables: either materials or operating conditions. To obtain the best functional output coatings exhibiting selected in-service properties and the right combinations of operating parameters are to be known. These combinations normally differ by their influence on the erosion wear rate or coating mass loss.

EXPERIMENTAL DETAILS

Coating Deposition

Alumina–13% titania used as feed stock for coating are first sieved and size range powder 35–80 μm are taken. This mixture is sprayed on mild steel substrates of 25 mm diameter and 3 mm thickness. Spraying is undretaken using a 40 kW APS (atmospheric plasma spray) system in the thermal plasma laboratory (Thermal Plasma Section, L&PTD, B.A.R.C, Bombay).

Table 1. Operating parameters used during the plasma spraying process.

Parameter	Range
operating power	1–21 kW
Current	250–500 A
Voltage	40–45 V
Plasma gas (Ar) flow rate	28 lpm
Secondary gas (N_2) flow rate	3 lpm
Powder feed rate	11.5 gm/min
Powder carrier gas (Ar) flow rate	12 lpm
Torch to base distance	100 mm

This is a typical plasma spray system operating in the non-transferred mode. The major components of this set-up include the plasma torch, power supply, power feeder, plasma gas supply, control console, cooling water, and the spray booth. Prior to spraying, the substrates are grit blasted by compressed air at a pressure of 3 kgf/cm^2. A current regulated dc power supply is used. A four stage closed loop centrifugal pump at a pressure of 10 kgf/cm^2 supplies cooling water for the system.

The primary plasma gas (argon) and the secondary gas (nitrogen) are taken from normal cylinders at an outlet pressure of 4 kgf/cm^2. The plasma torch input power is varied from 11 to 21 kW by controlling the gas flow rate, plasma arc current, and the arc voltage. The powder feed rate is kept constant at about 11.5 g/min by a turntable type volumetric powder feeder. Operating parameters used during the spraying are given in Table 1.

Microscopic Observation

A scanning electron micrograph of the coating surface is examined with a JEOL JSM-6480 LV scanning electron microscope.

Adhesion Strength

To characterize the coating, coating interface bond strength is measured with coating pull-out method using Instron 1195, confirming to ASTM C-633 standard. To evaluate the coating adhesion strength, a special type jig is fabricated. Cylindrical mild steel dummy samples (length 25 mm; top and bottom diameter 12 mm) are used. The surfaces of the dummies are roughened by punching. These dummies are then fixed on top of the coating with the help of a polymeric adhesive (epoxy 900-C) and pulled with tension after being mounted on the jig. The coating pullout test is carried at a crosshead speed of 1 mm/min. The moment the coating gets torn off from the specimen corresponds to the adhesive strength of the coating and is recorded.

Erosion Wear Test

Solid particle erosion is usually simulated in the laboratory by one of two methods; the 'sand blast' method, where particles are carried in an air flow and impacted onto a stationary target; and the 'whirling arm' method, where the target is spun through a chamber of falling particles. In the present investigation, an erosion apparatus (self-made)

of the 'sand blast' type is used. It is capable of creating highly reproducible erosive situations over a wide range of particle sizes, velocities, particles fluxes, and incidence angles in order to generate quantitative data on materials and to study the mechanisms of damage. The test is conducted as per ASTM G76 standards.

The jet erosion test rig used in this work employs a 300 mm long nozzle of 3 mm bore and 300 mm long. This nozzle size permits a wider range of particle types to be used in the course of testing, allowing better simulations of real erosion conditions. The mass flow rate is measured by a conventional method. Particles are fed from a simple hopper under gravity into the groove. Velocity of impact is measured using the double disc method [5]. Some of the features of this test set-up are:

- Vertical traverse for the nozzle: provides variable nozzle to target standoff distance, which influences the size of the eroded area.
- Different nozzles may be accommodated: provides ability to change the particle plume dimensions and the velocity range.
- Large test chamber with sample mount that can be angled to the flow direction: by tilting the sample stage, the angle of impact of the particles can be changed in the range of 0–90° and this will influence the erosion process.

In this work, room temperature solid particle erosion test on mild steel substrate coated with alumina–13% titania as feed materials (at 11 kW, 18 kW) is carried out. The coating, made at 11kW power level, is eroded at different impact angles 30°and 90°. The nozzle is kept at 100 and 150 mm standoff distance from the target. Dry silica sand particles of 20 and 40 μm average particle size are used as erodent with an average velocity of 32 m/s and pressure 4 kgf/cm^2 with a feed rate of 50 g/min. The coating deposited at 18 kW power level is eroded at 30, 60, and 90° angles at standoff distance (SOD) of 150 mm. Here, 40 μm size dry silica sand particles are used as erodent with different velocities, i.e., 32, 45, and 58 m/s and at pressures of 4, 5.5, and 6.5 kgf/cm^2, with a feed rate of 50, 58, and 62 g/min. Amount of wear is determined on a 'mass loss' basis. It is done by measuring the weight change of the samples at regular intervals in the test duration. A precision electronic balance with +0.01 mg accuracy is used for weighing. Erosion rate, defined as the coating mass loss per unit erodent mass (g/g) is calculated. The erosion rates are calculated at different erodent size, different erodent velocities, impingement angles, erodent dose, and standoff distances.

RESULTS AND DISCUSSION

Adhesion Strength

Adhesion strength of Al_2O_3–TiO_2 coating on metal substrates is presented in Table 2.

The variation of adhesion strength of alumina–titania coating to the mild steel and copper substrate at different power levels is shown in Figure 1.

From the graph it is clear that adhesion strength value varies with operating power. It is noted that invariably in all cases the interface bond strength increases with the input power of the torch up to a certain power level and then shows a decreasing trend in coating adhesion. Initially, when the operating power level is increased, the melting fraction and velocity of the particles also increases. Therefore there is better splashing and mechanical inter-locking of molten particles on the substrate surface leading to increase in adhesion strength [6]. But, at a much higher power level, the amount of fragmentation and

Table 2. Adhesion strength values of alumina–titania coating on mildsteel, copper substrates at different power levels.

Sl.No	Specimen	Power level (kW)	Substrate	Maximum load (kN)	Adhesion strength (MPa)
1	Al_2O_3-TiO_2	11	Mild steel	0.493	4.35
2	Al_2O_3-TiO_2	15	Mild steel	0.553	4.89
3	Al_2O_3-TiO_2	18	Mild steel	0.612	5.1
4	Al_2O_3-TiO_2	21	Mild steel	0.440	4.2
5	Al_2O_3-TiO_2	11	Copper	0.292	2.58
6	Al_2O_3-TiO_2	15	Copper	0.332	2.93
7	Al_2O_3-TiO_2	18	Copper	0.403	3.5
8	Al_2O_3-TiO_2	21	Copper	0.337	2.98

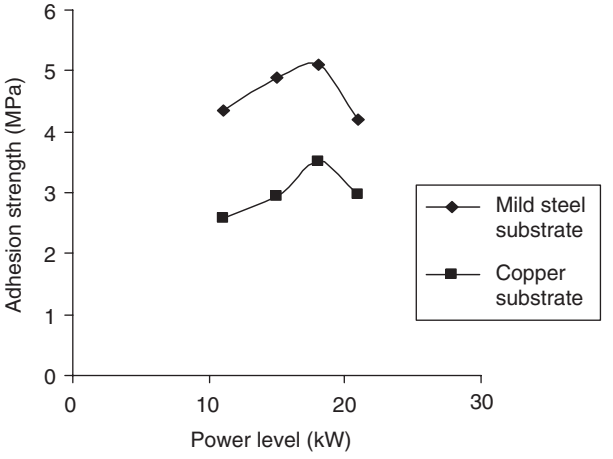

Figure 1. *Variation of adhesion strength of alumina–titania coating to the mild steel and copper substrate at different power levels.*

vaporization of the particles increase. There is also a greater chance of smaller particles (during in-flight traverse through the plasma) to fly off during spraying. This results in poor adhesion strength of the coatings. With increasing power adhesion strength values increase, attaining a plateau/maximum region. A maximum with mild steel substrate; implies the dependence of thermal conductivity for melted particle solidification and/or dissipation of heat at the metal interface [7] and thermal expansion coefficient mismatch.

Erosion Result

The variations of cumulative mass loss of the coating deposited at 18 kW with time is illustrated in Figure 2. The erodent particles having size 40 μm strike the coated samples at 30, 60, and 90° angles of impact with a standoff distance of 150 mm, at a pressure of 6.5 kgf/cm^2. It is seen that the cumulative coating mass loss increases with increasing time length during which the mass loss increases monotonically.

The cumulative increment in material loss due to erosion wear of plasma sprayed coatings with exposure time (or erodent dose) has been reported earlier by Levy [8]. It has

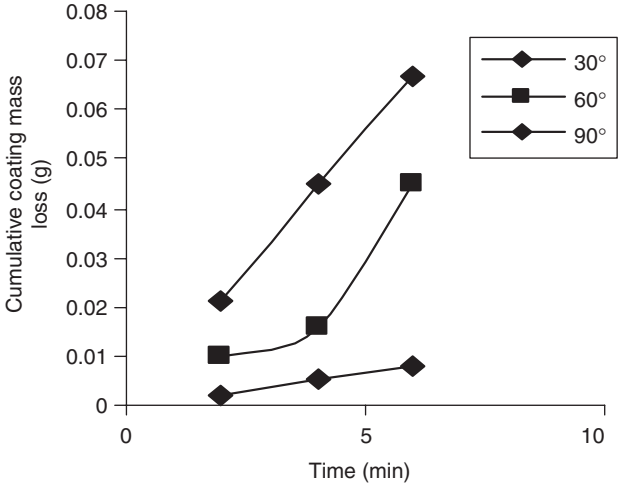

Figure 2. *Variation of cumulative coating mass loss at different time length for 30, 60, and 90° impact angles of 40 μm size erodent at SOD of 150 mm at pressure of 6.5 kgf/cm^2; for the sample coated at 18 kW power level.*

been observed that, the incremental erosion rate curves of brittle materials start with a high rate to a measurable amount of erosion and then decreases to a much lower rate steady state value [9]. In the present study, this trend is also found in the case of all coatings subjected to erosion tests at various impact angles. This can be attributed to the fact that the fine protrusions on the top surface of the coating may be relatively loose and removed with less energy than what would be necessary to remove a similar portion/area of the coating from the bulk of the coating. Consequently, the initial wear rate is high. With increasing exposure time the rate of wear starts decreasing and in the transient erosion regime, a steady state in the wear rate is obtained. As the coating surface gradually becomes smooth, the rate of erosion tends to become steady as shown in Figure 3.

With increase in the erodent dose, the erosion rate is also affected. The erosion with higher erodent dose sharply increases with increasing the angle of impact from 30 to 90°. The increase of erosion rate with erodent dose is because of the cracks formed on the eroded sample. Due to the formation of the cracks on the eroded sample, more coating material comes out with increasing erodent dose, so the erosion rate increases and is maximum for a 90° angle. This is typical for brittle materials.

Figure 4 illustrates the effect of impact angle (α) on the erosion rate of coatings subjected to solid particle erosion. The erosion results for coatings of materials deposited at 18 kW operating power of the plasma torch at impact angles of 30, 60, and 90° for different pressure/force of the erodent attack 4, 5.5, and 6.5 kgf/cm^2 are shown. The erosion rate (mass loss of coating (mg) per unit weight of erodent (g)) is measured after the samples are exposed to the erodent stream for 6 min. It is seen from the graph that irrespective of the feed material, the erosion mass loss is higher at a larger angle of impact and the maximum erosion takes place at $\alpha = 90°$ and is maximum for 6.5 kgf/cm^2. This is typical of all brittle coatings. The relationship between erosion rate E and impact angle (α) is suggested by Bayer [10] as:

$$E = (K_d v^n \cos^n \alpha + K_b v^m \sin^m \alpha) M.$$

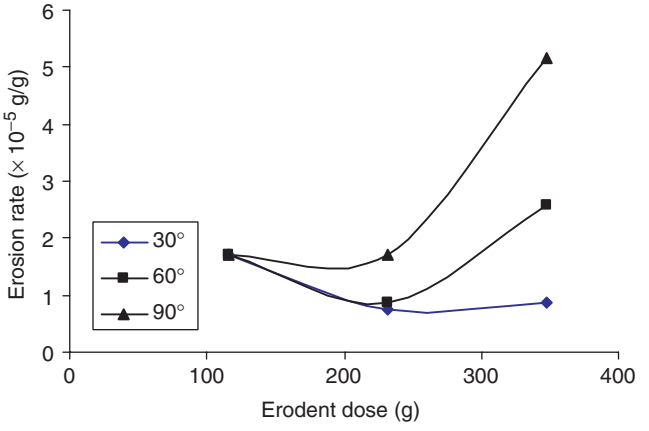

Figure 3. *Variation of erosion rate with erodent dose at 30, 60, and 90° angle of impact of 40 μm size erodent at SOD of 150 mm at pressure of 5.5 kgf/cm^2; for the sample coated at 18 kW power level.*

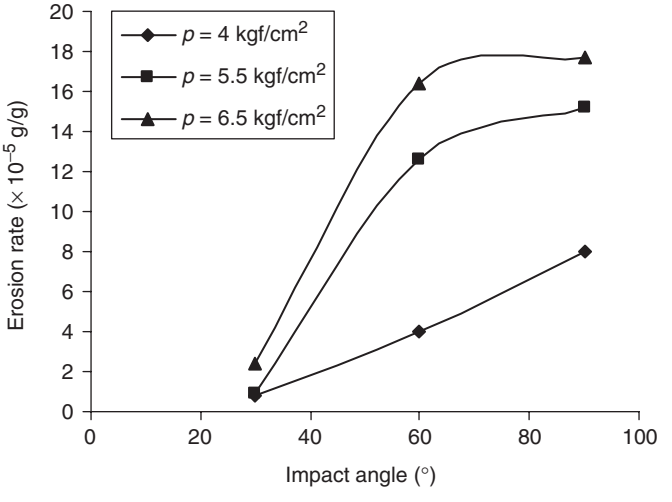

Figure 4. *Variation of erosion rate with angle of impact of the 40 μm erodent at pressure of 4, 5.5, and 6.5 kgf/cm^2 at SOD of 150 mm after 6 min time for the sample coated at 18 kW power level.*

For a particular test condition, velocity of impact v, erodent supply rate M is constant. The constants K_d, K_b, m, and n are determined by fitting the equation to experimental data. For typical brittle materials $K_d = 0$ and the erosion rate is maximum at 90° impact angle. For typical ductile material, $K_b = 0$ and erosion rate is largest at 20–30° impact angles.

The results obtained in the present work show that for 90° impact angle, alumina–13% titania coating loses 29 mg in 6 min at 4 kgf/cm^2 at SOD of 150 mm for the alumina–titania coating deposited at 18 kW power level while the mass loss is only 12 mg in the case of $\alpha = 60°$ and 4 mg for $\alpha = 30°$. This variation of erosion wear loss confirms that the angle at which the stream of solid particles impinges the coating surface influences the rate at which the material is removed. It further suggests that this dependency is also influenced by the nature of the coating material. The angle of impact determines the relative magnitude of the two components of the impact velocity, namely

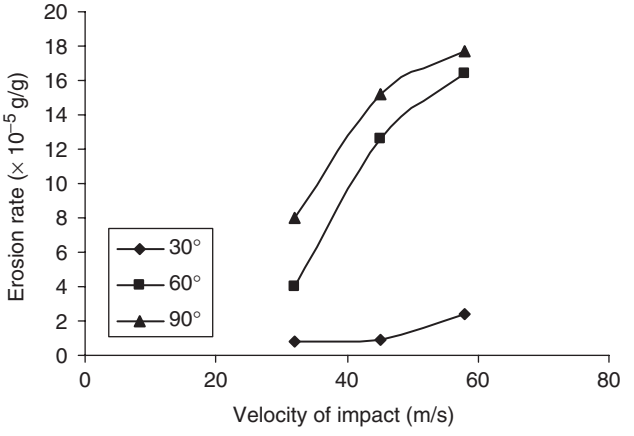

Figure 5. *Variation of erosion rate with impact velocity of the 400 çm erodent at 30, 60, and90° angle of impact at SOD of 150 mm after 6 min for the sample coated at 18 kW power level.*

the component normal to the surface and parallel to the surface. The normal component will determine how long the impact will last (i.e., contact time) and the load. The product of this contact time and the tangential (parallel) velocity component determines the amount of sliding that takes place. The tangential velocity component also provides a shear loading to the surface, which is in addition to the normal load that the normal velocity component causes. Hence as this angle changes the amount of sliding that takes place also changes as does the nature and magnitude of the stress system. Both of these aspects influence the way a coating wears. These changes imply that different types of material would exhibit different angular dependency.

Variation of erosion rate with impact velocity of the 400 μm erodent at 30, 60, and 90° angle of impact at SOD of 150 mm after 6 min for the sample coated at 18 kW power level is shown in Figure 5. Erosion rate increases with increasing velocity. It is obvious that with increasing velocity the particles will have high kinetic energy when transformed at impact and hence remove more particles from the impacted surface [11] and it is maximum for a 90° angle.

Variation of erosion rate with a standoff distance of the 400 μm erodent at 30 and 90° angles of impact after 6 min for the sample coated at 11 kW power level at a pressure of 4 kgf/cm^2 is shown in Figure 6. Erosion rate decreases with increasing stand off distance as the impact will be less with increasing standoff distance [12].

Variation of erosion rate with size of the erodent at 30 and 90° angles of impact at a pressure of 4 kgf/cm^2 at SOD of 150 mm after 6 min for the sample coated at 11 kW power level is shown in Figure 7. With increasing size of erodent, erosion rate increases [13] and it is maximum for 90°.

Microstructure of the Coating Surface

The interface adhesion of the coatings depends on the coating morphology and inter-particle bonding of the sprayed powders. SEM micrographs of alumina–titania coating surface (11, 15, 18, and 21) at 500× magnification are shown in Figure 8(a–d) respectively.

From the above figure, coating deposited at 11 kW power level (Figure 8(a)) shows uniform distribution of molten/semi-molten particles. More cavitations are observed,

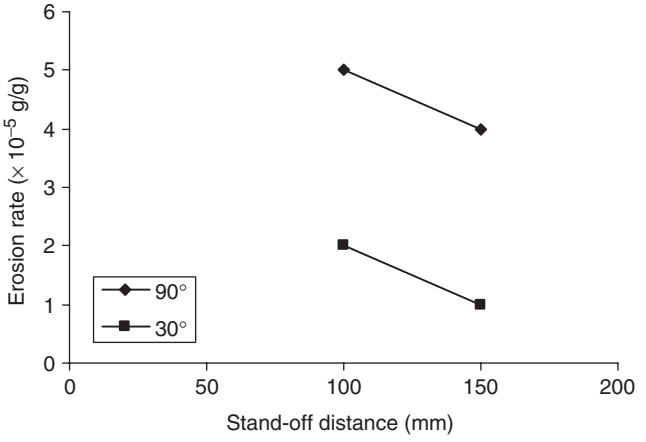

Figure 6. *Variation of erosion rate with stand off distance of the 400 çm erodent at 30, and 90° angle of impact at a pressure of 4 kgf/cm^2 after 6 min for the sample coated at 11 kW power level.*

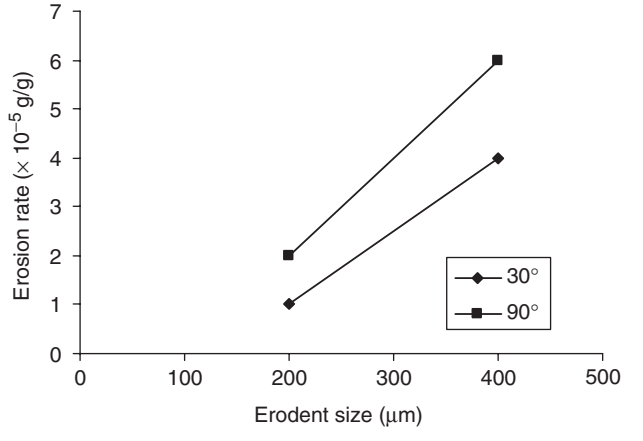

Figure 7. *Variation of erosion rate with size of the erodent at 30°, and 90° angle of impact at a pressure of 4 kgf/cm^2 at SOD of 150 mm after 6 min for the sample coated at 11 kW power level.*

other than some large pores found on the inter-particle boundaries and triple-particle junctions, which may have originated during solidification of particles from un/semi-molten state. The coating made at a higher power level, i.e., 15 kW (Figure 8(b)) bears a different morphology. A large number of globular particles and some flattened regions are indicative of particle melting during spray deposition. The grains/particles are mostly equi-axed type with little boundary mismatch between them. Amount of cavitation is less than that in the previous case. However, some cavity regions are seen along inter-particle/inter-grain boundaries. Coating deposited at further higher power level, i.e., at 18 kW (Figure 8(c)) bears a different morphology. Larger portions of the coatings exhibit flattened regions, which might have been formed during solidification of molten particles that have fused together in lumps. Less cavitation is observed at the inter grain boundary. This may be the reason for increase of adhesion strength and hence is maximum for the coating deposited at 18 kW power level. For the coatings deposited at further

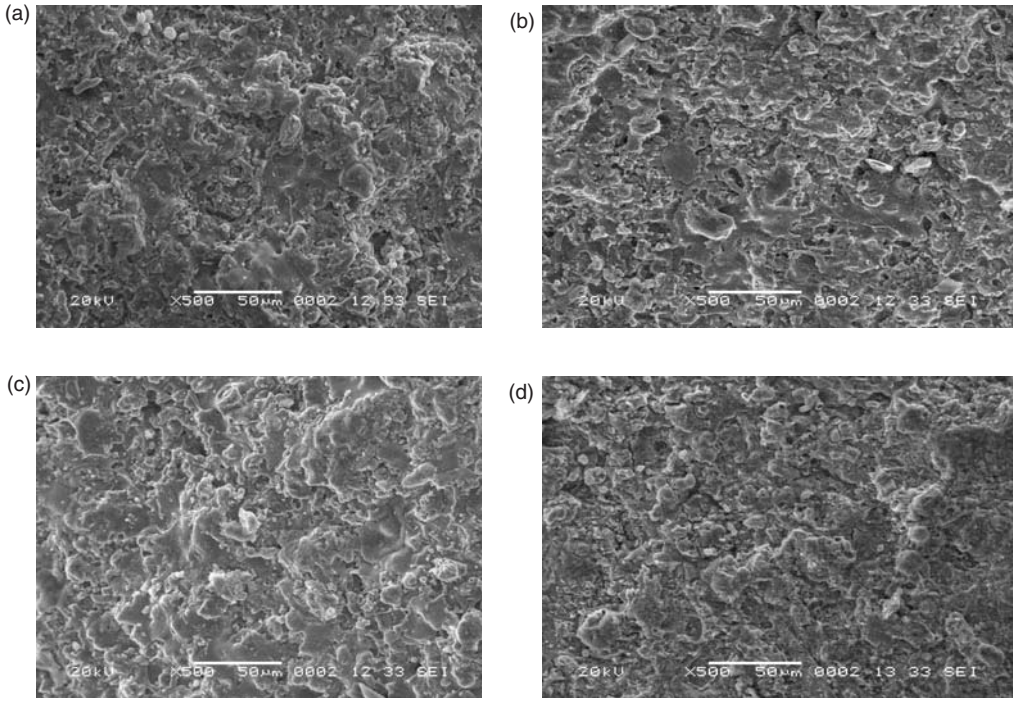

Figure 8. *SEM photograph of alumina–titania coating surface at different power levels, i.e (a) 11 kW, (b) 15 kW, (c) 18 kW, (d) 21 kW at 500× magnification.*

higher power level, i.e., at 21 kW, the surface morphology (Figure 8(d)) is completely different. A large number of spheroidal particles of different diameters are seen, which might have been formed due to breaking/fragmentation of bigger particles and have melted during in flight traverse through the plasma jet. The amount of cavitation is more than that seen in all the previous conditions. This might be the cause for the improper particle-to-particle bonding and poor stacking to the substrate, which have resulted in lower interface bond strength.

Splat formation due to a higher cooling rate leads to maximum adhesion strength for the coating surface made at 18 kW power level. But the protruding surface on the coating might be the cause of increase in erosion rate for the coating made at 18 kW power level. Hence, the erosion is less for the coating deposited at the lower power level, i.e., at 11 kW operating power.

CONCLUSIONS

Adhesion strength value of the coating varies with operating power. It is noted that invariably in all cases the interface bond strength increases with the input power of the torch up to a certain power level and then shows a decreasing trend in coating adhesion. With increasing power adhesion, strength values increase attaining a plateau/maximum region, maximum with mild steel substrate. It is observed that the erosion wear rate is dependent on erodent dose, angle of attack, velocity of erodent, standoff distance, and size of the erodent. Cumulative coating mass loss varies with time

of erosion. Maximum amount/rate of erosion occur with increasing the impact angle from 30 to 90°. The trend of erosion of the coatings seems to follow the mechanism predicted for brittle materials. Coating deposited at 18 kW power level shows a higher erosion rate than that of the sample deposited at 11 kW power level. Erosion is a non-linear process with respect to its variables: either materials or operating conditions. To obtain the best functional output coatings exhibiting selected in-service properties and the right combinations of operating parameters should be known. The solid particle erosion resistance of the alumina–13% titania coatings is fairly good. So, these coatings may be recommended for tribological applications.

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