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Plasma sprayed fly ash coating on metal substrates

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ABSTRACT

Rich in metal oxides, fly ash has tremendous potential to be utilized as a coating material on structural and engineering components. Fly ash is basically a solid waste generated in huge quantities from coal fired thermal power stations during the combustion of coal. This work aims at developing and characterizing a new class of such coatings made of fly ash by a novel technique like plasma spraying. Plasma spray technology has the advantage of being able to process various low-grade-ore minerals to obtain value-added products and also to deposit ceramics, metals and a combination of these, generating near-homogenous coatings with the desired microstructure on a range of substrates. In the present investigation, coatings are developed on aluminum substrates using mixtures of fly ash pre-mixed with aluminum powder in different weight proportions at various plasma torch power levels ranging from 9 to 18 kW DC. The coatings are characterized in terms of micro-hardness, interface adhesion strength and deposition efficiency. Maximum adhesion strength of about 35 MPa is recorded with coatings deposited at 12 kW power level. It is noticed that the quality and properties are significantly affected by the operating power level of the plasma. This work establishes fly ash as a potential coating material, suitable for possible tribological applications.

KEYWORDS

Fly ash;
Industrial wastes;
Waste utilization;
Coatings;
Plasma spraying.

INTRODUCTION

With rapid industrialization, it is but natural that in coming years, the power generation will keep increasing. At present, about 70% of total power generation in India is through thermal power plants where sub-bituminous coal and/or lignite are burnt in huge amount and consequently there is an estimated generation of about 80-90 million tons of fly ash per annum as the major solid waste[1]. Fly ash is a finely divided powder generated as a solid waste, in huge quantities during power generation in coal based power plants. In India, less than half of this is used as a raw material for concrete manufacturing and construction; the remaining is directly dumped on land side as land fill or simply piled up. Only a small fraction of it is used in development of high valued product. Due to environmental regulations, new ways of utilizing fly ash are being explored in order to safeguard the environment and provide useful ways for its utilization and disposal.

The disposal and utilization fly ash will continue to be an important area of global concern due to dependence of countries like India on coal based thermal power generation. Although fly ash management has seen considerable improvement over the past few years, still its utilization level is very low. Some areas of fly ash utilization wherein technology demonstration projects have been completed or are under way include mine filling, road constructions, embankments, hydraulic structures, manufacturing of several building components like bricks, blocks, and tiles etc. Due to increasing environmental concern and growing magnitude of the problem it has become imperative to manage fly ash.

As already mentioned, fly ash is a finely divided powder with the particle size ranging from 150 nm–120 μm. It is abrasive and refractory in nature. It is essentially a mixture of ceramic materials such as: SiO_2, Fe_2O_3, Al_2O_3 and TiO_2 etc. An empirical formula for fly ash based on the dominance of certain key elements has been proposed[2] as:

$$Si_{1.0}\,Al_{0.45}\,Ca_{0.51}\,Na_{0.047}Fe_{0.039}\,Mg_{0.020}K_{0.013}Ti_{0.011} \qquad (1)$$

Presence of arsenic, mercury and antimony has also been reported and the mineralogical structure of the ash is a key variable determining reactivity. Qualitative analysis of chemical composition of power station fly ash shows the presence of SiO_2 (52–66%), Fe_2O_3 (6-8%), Al_2O_3 (21-27%), Ca (6%) and Ti, P, Mg, Na, S, K (< 1%).

Fly ash has a number of useful applications that serve to utilize some of the large amounts being produced. It is used extensively worldwide as an extender in cement in concrete[3]. Other outlets for fly ash include the treatment of acid mine drainage[4,5], production of zeolites[6-8] as a supplementary feedstock for cement production[9,10], application as bricks (both clay-fired and refractories)[11] and as a filler in paint[12]. Besides, glasses and glass ceramics are obtained by mixing up to 50% of Italian coal fly ash with glass cullet and float dolomite[13]. With a small addition of fly ash and without dolomite, very stable glassy materials are obtained[13]. Fly ash used in the preparation of ceramic tableware and art ware is found to improve the mechanical strength as compared to original products[14,15]. Fly ash is also being used in the preparation of ceramic filters suitable for hot gas cleaning[16]. The use of fly ash in plastic composites has shown promise[17-19], as has application in metal composites, in particular aluminium[20-22]. Fly ash filled aluminium alloy composites made by stir casting exhibited similar or higher hardness and elastic modulii, and improved abrasive wear resistance and are considered potential materials for components like pulleys, oil pans, intake manifolds and valve covers[22]. Fly ash can be used to reduce the density of metal composites, with the cenospheres within the ash providing added buoyancy, better insulation properties, reduced shrinkage and warp age values[23].

Fly ash has also been used as a liner material in waste disposal sites to augment the containment capability of the existing soil and also it has been tried for improving the performance of clay liners to contain toxic and hazardous waste materials[24,25]. Waste oil and gas sludge in a semi liquid state with solids content greater than 30% could be solidified using cement and fly ash mixtures[26]. A greenhouse study showed that lime and fly ash significantly increased the soil pH, above ground plant biomass and root biomass[27]. Fly ash has been utilized as a base for construction of research field plots for growing corn[28]. The incorporation of fly ash on soil properties and growth yield of wheat, mustard, rice and maize is reported[29,30]. Fly ash with high calcium reduces the release of soil phosphorus to outer surfaces of the soil[31]. Fly ash has been shown to increase the water holding capacity of soils[32]. The addition of 5% fly ash to soil is also found to significantly increase the growth of tomato plants and reduced the amount of galling on the roots caused by root-knot nematode[33]. Studies reveal that tons of fly ash are produced from power stations annually in countries like UK, USA, Australia and India, out of which, as is reported, only 10-30% is reclaimed, with almost all going to the construction industry[34].

Recently, while considerable emphasis has been placed on the processing of low-grade ore minerals through thermal spray techniques[34], fly ash can be a cost effective substitute for conventional extenders in high performance industrial coatings[35]. Over the past few decades thermal plasmas have been used for processing of various types of materials some of which would not have been possible by conventional techniques[36]. The development of plasma technology, especially plasma processing has been commercially successful mostly in the field of spray coating. Today plasma spray coatings find wide applications not only in R&D

area but also in the industrial work places ranging from textile industries to even medical applications. In the automotive industries of many industrially advanced countries, plasma sprayed coatings are used to improve the wear resistance, thermal resistance and resistance to corrosion of machine components. Ceramic coatings on relatively ductile metal alloy substrates behave in complex ways under a mechanical load and/or when temperature change occurs, which contribute to poor interfacial mechanical properties and hence restrict the choice for raw materials in plasma spray purposes. Again, the mismatch between the thermal expansion coefficients of ceramics and metals leads to the development of excessive stresses at the interface which is the main cause of problems in metal-ceramic joining[34]. Recent studies, however, have shown improvement of coating properties with pre-mixed metal-ceramic powders[35]. Attempts have been made to develop the plasma spray deposition of alumino-silicate composite coatings onto metal substrates using industrial waste, although the adherence of the coating has not been found to be very satisfactory[34].

In thermal plasma, it is possible to spray all metallic and non metallic materials such as metal oxides, carbides, nitrides, silicides etc[37-39]. The oxides of iron, aluminum and silicon are known to have high hardness, high wear resistance and good corrosion resistance, which are desirable properties for protective coatings. Chemical analysis of fly ash shows silicon oxide (SiO_2), aluminum oxide (Al_2O_3), iron oxide (Fe_2O_3), titanium oxide (TiO_2), etc., as its major constituents. Thus, the chemical composition of fly ash indicates its coating potential. Moreover, during recent years, although a large number of investigations have been carried-out on production of ceramic coatings using these metal oxides, not much effort has been made to do plasma processing of low grade materials and industrial wastes for this purpose. Mishra and Ananthapadmanabhan, in 1998, made the first successful attempt to spray coat raw fly-ash on copper and stainless steel substrates through plasma processing[34]. They further repeated the plasma spraying of fly-ash mixed with ilmenite, graphite and alumina powder respectively in different proportions leading to development of protective coatings of high effectiveness[40]. Satapathy et al. reported the development of plasma spray coating of another industrial waste called red mud on various metal substrates[41]. The study revealed that the coatings of red mud pre-mixed with metal powder exhibit improved adhesion compared to the raw red mud coatings[42]. Ramakrishna et. al.[43] reported the coatability of fly ash on steel substrates by detonation spraying. Still, research/study on development of thermal spray coatings using low grade mineral and/or industrial waste is meager. Industrial wastes like fly ash, being rich in metal oxides, have tremendous potential to be used as coating materials and this aspect needs to be explored. More so because many of the conventional coating materials are relatively expensive, to the extent that cost of spray grade powders alone can account for even 50-60% of the cost of operating a plasma spray unit. On the contrary, an industrial waste like fly ash is not only free of cost but also is abundantly available. Against this background, the present study has been undertaken to produce and characterize plasma sprayed composite coatings of fly ash premixed with aluminum powder on metal substrates.

EXPERIMENTAL DETAILS

The fly ash used in the present work is of cenosphere type and has been collected from the Captive Power Plant of National Aluminium Co. (NALCO) located at Angul in India. The as-received fly ash is screened through sieves so as to obtain particles in the size range of 75-93 microns. Six compositions are made by premixing fly ash with 5, 10, 15, 20, 25 and 30 wt.% of aluminum powder (average particle size 75 micron), procured from NICE Ltd. The raw materials are mixed thoroughly prior to spraying. The substrates (aluminum plates of dimension 50mm x 50mm x 3 mm) are made ready for coating deposition by sand blasting to produce a surface roughness of about 4.0 - 5.0 Ra. Plasma spray coatings are deposited with a non-transferred arc plasma torch operating at various power levels ranging from 9 to 18 kW DC. The powder is fed at a rate of about 12 gm/min using argon as the carrier gas flowing at a rate of 10 litres/min. The torch-to-base distance is fixed at 100 mm. The coated samples are subjected to various analyses. The thickness of the coatings is measured by a travelling microscope averaging over a length of 10 mm on a polished cross-section of the specimens. Surface and interface morphologies are studied using a scanning electron microscope JEOL JSM-6480LV. The coating pull-out test is carried out on all specimens to evaluate the coating adhesion strength as per ASTM 633C.

RESULTS AND DISCUSSION

The variation of coating thickness with input power level is shown in Figure (1). It is evident that with increase in torch input power the thickness of the coating increases, such a trend is generally being observed with plasma spray coatings[39]. From the figure it is observed that the coating thickness is largely affected by the torch input power and also by the aluminum content. The thickness of the coating varied between 180 and 360 micron with change in operating power from 9 to 18 kW. The feed material with 30 wt% Al powder resulted in a greater coating thickness, with a maximum of 360 m at the 18 kW power level. This may be because of melting of the aluminium powders during the in-flight traverse through the plasma and the resulting better inter-particle bonding of the ceramic powders and molten/semi-solid particles impacting on the substrate, giving rise to a higher rate of deposition.

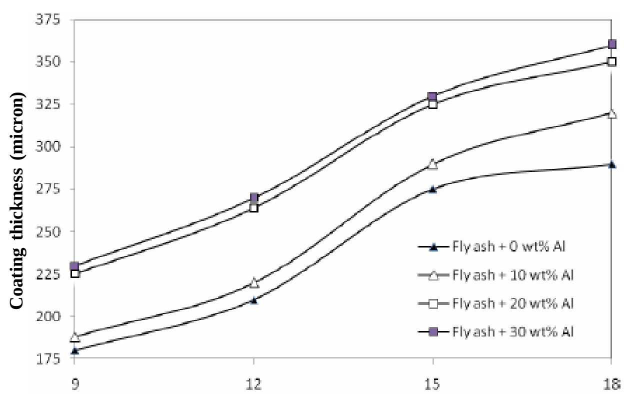


Figure 1 : Variation of coating thickness with plasma torch input power

The interface bond strength of the coating is evaluated by the coating pull-out method. It is seen that in all cases fracture occurred at the coating-substrate interface. Coating adherence tests have been carried out by many investigators with various coatings. However, it has been stated that[35] the fracture mode is adhesive if it takes place at the coating-substrate interface and that the measured adhesion value is the value of practical adhesion, which later is strictly an interface property, depending exclusively on the surface characteristics of the adhering phase and the substrate surface conditions. The variation of coating-substrate interface adhesion strength is shown in Figures (2) and (3), where the increase in adhesion strength with increase in the weight proportion of aluminium powder in the feed material is evident. The strength has increased with power level up to 12 kW and a maximum value of 34.54 MPa is recorded with raw material having 15 wt% Al powder. Further increase in the operating power level exhibited a detrimental effect on the interface strength.

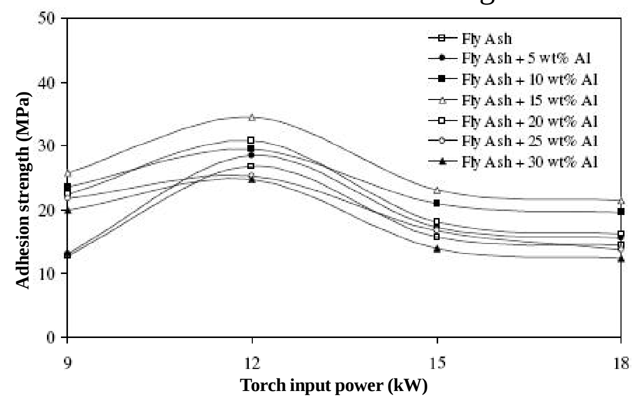


Figure 2 : Variation in coating adhesion strength with plasma torch input power level

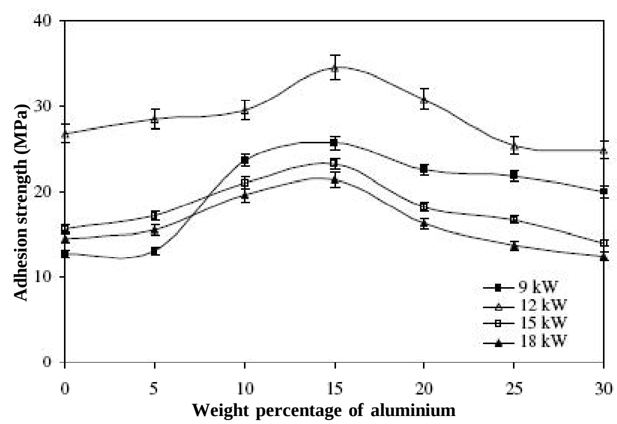


Figure 3 : Variation in coating adhesion strength with aluiminum content in the feed stock

Initially, when the operating power level is increased from 9 to 12 kW, the melting fraction and velocity of the particles also increase. Therefore there is better splashing and mechanical inter-locking of molten particles on the substrate surface leading to increase in adhesion strength. But, at much higher power levels (beyond 12 kW), the amount of fragmentation and vaporization of the particles are likely to 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.

The presence of a suitable proportion of molten species, i.e., aluminium, is also found to have helped in inter-particle bonding as well as interface bonding. This could be one of the reasons for the greater adhesion strength with 15 wt% Al powder in the raw material. Similar investigations have been carried out to study the effect of metallic bond coating and coating with pre-mixed metal powder on the interface strength of thermal barrier coatings[35], where the adherence strength was found to be greater with certain optimum proportion of the metal powder in the pre-mixed feed stock. Thus in the present study, the observation of maximum adhesion strength with 15 wt% Al powder content in the mix is not surprising. However, the decline in the value of adhesion strength with metal content beyond 15 wt% in the feedstock needs to be investigated.

Deposition efficiency is defined as the ratio of the mass of coating deposited on the substrate to the mass of the expended feedstock. Weighing method is accepted widely to measure this. In this investigation, the deposition efficiency presents a sigmoid-type evolution with the torch input power (Figure 4). As the power level increases, the net available energy in the plasma

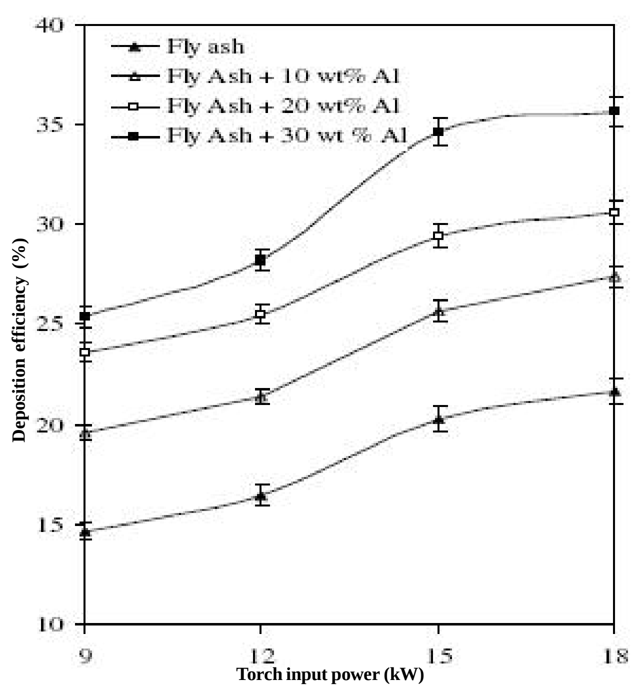


Figure 4 : Coating deposition efficiency of metal-ceramic mixture at different power levels

jet increases leading to a better in-flight particle molten state and hence to higher probability for particles to flatten. The deposition efficiency reaches a plateau for the highest current levels due to the plasma jet temperature increasing which in turn increases both the particle vaporization ratio and the plasma jet viscosity.

The coating surface micro-structures studied using scanning electron microscopy show the presence of different phases, typical examples of which are shown in Figures (5a - 5d). The morphology of the coating reveals regions of fully molten ceramic particles and fully molten metallic particles. In case of ceramic particles where the particle wetting was higher, micro-cracks are observed. The micro-cracks seem to relieve thermal stresses during coating formation. Aluminium particles seem to bridge the ceramic phases. No sizable cracks are noted on the coating surface, however, some cavities are observed in the coating.

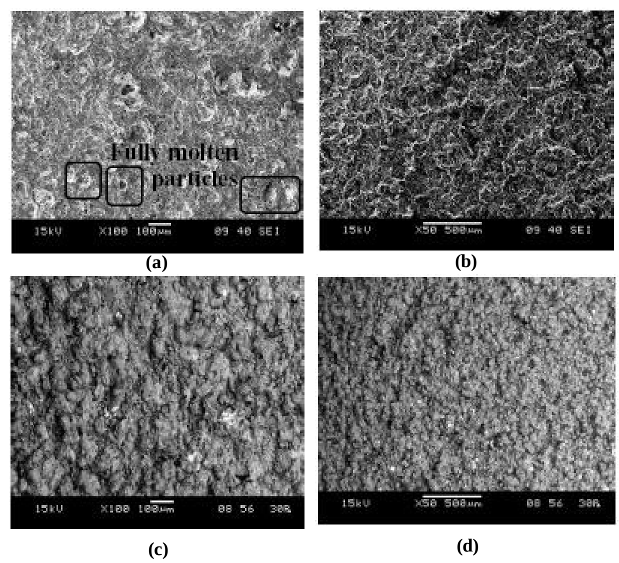
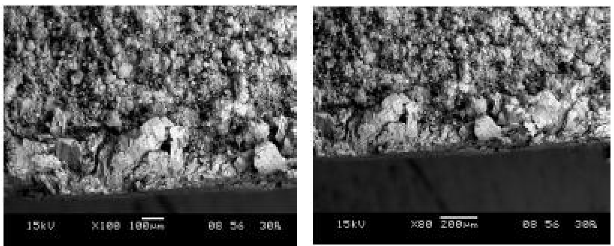


Figure 5 : SEM images showing the surface morphology of Fly Ash + 10 % al coating

The coating substrate interface plays the most important role in the adhesion of coatings. The surface morphology of the coatings cannot predict the interior (layer deposition) structures and their importance / acceptability. Thus, the polished cross sections of the samples are examined under SEM and are shown in Figure (6). From the micrographs, it is evident for the coating deposited at 12kW (Figure 6a) shows a lamellar structure with some amount of cavitations at the interface between the lamellae. Presence of some open pores is seen. Some spheroidal particles are also observed at some places. Splats formed are globular, larger in dimension and equi-axed type (Figure 6b). Other than the mechanical interlocking of the sprayed coating with the metal substrate, some metallurgical bonding might have occurred at the interface which is evident from the presence of some inter-diffusion zones.



(a) (b)

Figure 6 : SEM images showing the interface morphology of Fly Ash + 10 % al coating

CONCLUSIONS

This study shows that fly ash pre-mixed with aluminium powder can be used to produce plasma spray metal-ceramic composite coatings on metal substrates with improved interfacial adhesion. Maximum adhesion strength of 34.54 MPa is recorded in such coatings with 15 wt% of aluminium content in the fly ash-aluminum mix. The adherence strength is noticed to be greatly affected by the plasma torch input power level. The operating power level of the plasma torch also affects the coating deposition, morphology and mechanical properties of the coating. With more than 80 million tonnes of fly ash produced annually only in India, its use as a surface coating material for structural and engineering components in industries will help in a big way in its bulk utilization. In future, this study can be extended to polymer matrix composites using other waste materials.

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