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A Brief Review on Fly Ash and Its Use in Surface Engineering

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Abstract: Fly ash is a by-product obtained from coal power plants. Over the past two decades, handling this industrial waste has been a great challenge for many developing countries. However, this menace can be used in many industrial applications viz., civil, automobile and aerospace applications. In civil industry, the fly ash has been used in concreate to enhance the porosity that increases the curing time of the concrete. The fly ash has been gaining importance these days as a feedstock material for many thermal spray processes. In automobile sector, the fly ash has been used as a thermal barrier coating in IC engines, whereas in aerospace industry, which demands lighter and stronger materials, the fly ash has been used as a reinforcement material. Hence, so far, fly ash has been used as an either single or a composite feed stock material in thermal spray processes. The fly ash with other materials like alumina, titania and red mud have been deposited using thermal spray processes. These coatings have exhibited higher wear, corrosion and erosion resistance as compared to the uncoated specimens. In this paper, a brief review on fly ash and its use, especially its use as a feed stock in thermal spray coating, is presented. Therefore, the use of fly ash has opened a new frontier of research in thermal spray coating area where economically viable coatings can be produced using industrial waste like fly ash.

INTRODUCTION

Fly ash is a by-product obtained from combustion of coal in power plants when the coal is burnt at sufficient temperature (1200-1700°C). In fly ash, as high as 316 individual minerals and around 188 mineral groups are identified [1]. It was disposed in the atmosphere as a pollutant. According to literature, for a few decades, nearly 500 million tonnes per annum of fly ash has been disposed to atmosphere [2]. With a growing civilization, consumption of energy is increasing day by day, and it intends to increase the resources for production of energy to fulfil the demands. This leads to an observation that the energy consumption rate might exceed the GDP, especially in developing countries like India [3]. According to reports in 2015, in fact, developing countries like India alone has used 107.77 MT of fly ash [4,5]. Generally, the fly as disposed in land fill sites. This conventional way of disposing fly ash can adversely affect the environment and the people residing in the nearby vicinity [6]. So, it is advisable to reuse the fly ash for some industrial applications. Recent researches have shown that the fly ash has a tremendous prospect in the field of surface engineering [7].

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Morphology of Fly Ash

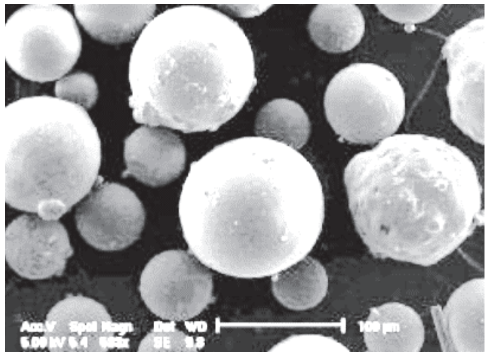

Figure 1: A high magnification scanning electron image of fly ash powder [8]

The morphology of fly ash particles depends on the combustion temperature and the subsequent cooling rate of coal. Figure 1 shows the Scanning electron microscopy (SEM) of fly ash powder. The fly ash powders are spherical in shape their size ranging 10 to 90µ [8]. Irregular shaped un burned carbon particles are also found along with the fly ash powder. The powder also contains mineral aggregates like corundum, quartz, and magnetite [9].

Generally, fly ash particles are heterogeneous in nature [10]. The finer particles produced by flue gas are collected in mechanical or electrostatic precipitators in coal combustion power plants at a temperature above 1482° C [11]. According to Loss on Ignition(LOI) test, major constituents of fly ash include SiO2, Al2O3, Fe2O3, CaO, MgO, K2O, Na2O and TiO2[12]. Non-organic matter which is present in the coal forms a molten droplet after quenching. (This sentence is not clear) This leads to formation of glassy spheres, which are either in solid or hollow form. The average particles size was around 8µm [13]. The density of these particles ranges from 1970.2 kg/m^3 to 2995.4 kg/m^3. Fly Ash is an amorphous powder containing mixture of Ferro-aluminosilicate minerals. However, the composition of fly Ash varies considerably depending on geographical location of coal mines, combustion conditions and the type of ash collection devices. The fly ash also contains other minor elements like Ti, Na, K, and S in the 0.5-3.5% range. A typical chemical composition & physical properties of fly ash are listed in Tables 1&2

Table.1 Chemical composition of fly ash [14]

SL.No.	Component	Wt%
1.	Silicon dioxide, SiO2	27.88-59.40
2.	Aluminum oxide, Al2O3	5.23-33.99
3.	Iron oxide, Fe2O3	1.21-29.63
4.	Calcium oxide, CaO	0.37-27.68
5.	Magnesium oxide, MgO	0.42-8.79
6.	Sulphur Trioxide, SO3	0.04-4.71
7.	Sodium carbonate, Na2O	0.20-6.90
8.	Potassium oxide, K2O	0.64-6.68
9.	Titanium dioxide, TiO2	0.24-1.73
10.	Other alkaline & unidentified	4.0-6.0
11.	LOI, (Loss-on-ignition) SO3	0.21-28.37

Classification of Fly Ash

According to ASTM C618, fly ash is typically classified in two categories depending on the way it is being produced: Class F and class C. The class F fly ash is produced when the older anthracite and bituminous coal burns sufficiently at high temperature ranging from 900-1000 °C and it possesses low cementing property. Since Class F contains low fraction of CaO and MgO constituents, this type of fly ash is typically employed in Civil construction [17]. However, Class C fly ash is produced from the burning of younger lignite or sub-bituminous coal. Class C possesses high cementing property. This type of fly ash contains some amount of moisture that can lead to increase in its strength and hardness during drying. Typically, this type of fly ash contains more than 20% lime (CaO) [16]. The CaO reacts with water and forms a paste, which can eventually lead to the nucleation of crack in concrete.

Table.2 Physical properties of fly ash [15]

SL.No.	Parameters	Fly Ash
1.	Density	2.17 g/cm^3
2.	Bulk density	1.26 g/cm^3
3.	Moisture content	2%
4.	Particle shape	Spherical/Irregular
5.	Colour	Grey
6.	Ph	6.0-10.0
7.	Specific gravity	1.66-2.55
8.	Grain size distribution	Sandy silt to silty loam
9.	Porosity	45%-55%
10.	Water holding capacity	45%-60%
11.	Electrical conductivity	0.15-0.45(dS/m)

PROBLEMS ASSOCIATED WITH FLY ASH PRODUCTION

Global Coal reserves are expected to last for another 200 years or so. India also has a vast coal reserve of 211 billion tones, making coal as one of the most extensively used fossil fuel for generating power in thermal power plants [18]. The coal fly ash produced from the power plants are either finer or coarser. These fly ashes are usually disposed in ash ponds. Disposal of fly ash requires large area of land which is a major concern associated with the power plants. For example, more than 175 million tons of fly ash was generated in the country by the year 2012. This would have demanded about 40000 hectares of land for the construction of ash ponds that leads to larger area for disposal as well as economic burden to a country [18]. To be specific, in India, the ministry of power estimated that the consumption of coal will be increased by 1800 million tons per year and 600 million tons of fly ash will be generated by 2031-2032 [18].

In order to manage the control and use of fly ash, In1994, In India, fly ash mission was established in association with department of science and technology and technology information, forecasting and assessment council (TIFAC) and many other government agencies [19]. The mission focuses on the demonstration of coal ash related technologies for infusing confidence and thus ensuring large scale adoption. Fly ash has been used in cement concrete as a reinforcement can not only for saving the cement cost but also it can add strength and durability. In order to achieve this, the fly ash content should typically lie in 30-75% range [20,21].

The fly ash can adversely affect the environment if it is not managed adequately. Typically, fly ash contains high amount of toxic and heavy metals like Pb, Cd, Cr, Cu, Zn, Fe and Mn.

In a recent study undertaken by department of environment has revealed the fact of presence of heavy elements like pb, Cd,Cr, Cu, Zn, Fe, Mn in the vicinity of ash ponds [22]. It has been alarmed that these elements contaminate the ground water in the locality. This adulteration of ground water can produce harmful medical implication on mankind [23]. Also, owing to the lack of ground water level, the growth of plants is hindered. This can eventually lead to uprooting the plants.

Further, according to another recent study by the center for science and environment (CSE), around 50% of the total fly ash produced has been unused for industrial applications. In fact, approximately 173 million tonnes of fly ash was produced across India in 2013-14[24]. The unused fly ash dumped into poorly designed ash ponds. As per estimates, about a billion tonnes of this toxic ash lie dumped in these ponds, polluting land, air and water. By 2021-22, it has been forecasted that the rate of production fly ash is going to exceed 300 million tonnes per year. This increasing trend of growth rate of fly ash is going to be a major concern for the country.

USABILITY OF FLY ASH

Fly ash could be employed in wide range of applications, including civil construction. According to literature, addition of fly ash in various weight percentage in the ordinary Portland cement (OPC) can improve the pore volume. This leads to increase in the curing time of concrete [25]. Normally, cement concrete has high compressive strength, but weak in tension. With an addition high compressive strength is an important factor for any civil construction. This was achieved by adding 30 wt% fly ash has resulted in 30% improvement in compressive strength of the concrete [26]. Some recent studies show that even though natural sand can also be replaced by fly ash. Because of its low specific gravity, leads to decreases in the density of mortars and concretes. Addition of fly ash can considerably improve the permeable pore space of mortars and concretes. Owing to this porosity effect, in countries like China, the fly ash was used as an additive material for concrete and cement. This has led to an extensive use of fly ash as high as 68% of the total fly ash has been employed in industrial applications for value addition [27]. For any civil construction, curing time of concrete is an important aspect. The curing time can be extended by adding fly ash which leads to an increase in porosity of the structures [28]. Therefore, in this way the durability of concrete increases [29].

Fly ash has also been used as a reinforcement in metal matrix composites to enhance the wear and mechanical properties. According to the literature, mere addition of a few weight fraction of fly ash in aluminum A356 can improve various properties of the composite as explained below:

- A 6-volume percentage of fly ash in A356 Al alloy has resulted in increased wear resistance at low loads namely, at10 N and 20 N [30].
- A 12-volume percent of fly ash reinforced composites has shown lower wear rates as compared to the unreinforced alloy in the load range 20–80 N [31].
- With the same fraction fly ash in composite, proof stress, tensile and compressive stresses have decreased for 12 wt.% [31]. This was attributed to the formation of second phase particles at matrix. The second phase was formed due to a few constituents of fly ash like silica and iron tend to migrate into alumina phase. This phase augments the mechanical properties of the coating [32]
- Fly ash can even provide cushioning effect to the 6061 Al composite [33]. Addition of fly ash can induce voids in the composite, resulting in increased damping coefficient.
- A 9 vol% of fly ash has improved the pitting corrosion resistance of aluminium composite by 28% as compared to the unreinforced counterpart [34].

Use of Fly Ash in Surface Engineering.

Surface engineering is a branch of science that deals with imparting the superior properties to the base material which it lacks [35-37]. for example, a thin alumina coating on WC-Co tool can prolong its tool life substantially [38].

Many surface modification techniques are available in the literature. like strain hardening, surface hardening, thermos-chemical treatments, electro/electroless plating, chemical vapor deposition, physical vapor deposition, pulsed laser deposition and thermal spray coatings. Among these surface treating techniques, thermal spray is one of the popular, versatile and commercial technique to improve surface properties of the base material (substrate).

In thermal spray process, molten or semi molten particles are accelerated towards the substrate. Upon impact, these particles flatten and solidify to form splats. Layer by layer deposition of these splats yield a coating of desired thickness [39-41].

Very few reports are available to explain the role of fly ash as a feed stock material in thermal spray coating. It has been demonstrated that the fly ash can be used as a coating on steel substrate to enhance its hardness and wear resistance and corrosion resistance of substrates.

USE OF FLY ASH AS A FEED STOCK MATERIAL FOR THERMAL SPRAY COATING

To our knowledge, Krishna et al. [42] was fly ash as a feedstock material for thermal spray. They have deposited fly ash (some word missing here.) on mild steel substrate using detonation spraying technique. Before proceeding to coating, samples were grit blasted and degreased using acetone in an ultrasonic cleaner [42]. After pre-processing, coating of thickness 275µm was deposited [41]. Coating hardness was examined by using Vicker's hardness test. It was observed that the fly ash coated samples have shown improvement in their hardness. This was attributed to large fraction of silica present in fly ash. The tribo tests were conducted in accordance with ASTM G99 manual. Wear rate was estimated in terms of mass loss using pin on disc apparatus. WC-10.5%Co coated steel disc steel was used as counter body. The sliding velocity, Nominal applied stress and sliding distance has been set as 3.4m/s, 0.7 MPa and 3km, respectively. The improvement in the wear resistance was attributed to hard mullite phase present in the coating [34]. Wear resistance improvement was also attributed to decrease in coefficient of friction owing to the formation of brittle, glassy phase in the coating.

The fly ash as an alone as a feed stock material has exhibited the following drawbacks.

- Poor wear resistance
- Less harder coating
- Adequate adhesion strength

Table. 3 Use of fly ash as a feedstock material for thermal spray coating

Sl.No	Author	Feedstock material composition	Powder-Preparation method	Major findings	Deposition technique
1	Mishra.S.C et al. (2000)	Fly ash mixed with 5 & 15wt%.	Manual mixing	Maximum adherence strength	Plasma spray
2	S.P.Sahu et al. (2010)	Fly ash with 5,10,15,20,25 & wt.%.	Manual mixing	Maximum adherence strength and solid particle erosion	Plasma spray
3	Sutar H et al. (2015)	Red mud 90 + fly ash 10 wt.%. Red mud 80 + fly ash 20 wt.%. Red mud 50 + fly ash 50 wt.%.	V-shaped drum mixer.	High Wear resistance	Plasma spray
4	Sutar H et al. (2016)	Red mud 90 wt.% + Fly Ash 5 wt.% + Alumina 5 wt.%	Manual mixing	High Wear resistance	Plasma spray

Fly Ash with Other Additives in Composite Coating

To improve the properties of the fly ash coatings, some additive materials like alumina, red mud, titania and polypyrrole have been added [43].

Mishra et al. [45] have reported that fly ash with additive like alumina was coat able. Because alumina is well known for its superior wear resistance properties [44]. Alumina was manually mixed with fly ash, and the resulting powder was coated on grit blasted stainless steel substrate. Plasma spray process was used to deposit a coating of 520 µm thickness [45]. A pull-out method was used to determine the adhesion strength of coating. Adhesion strength of 52 MN/m^2 for 15 wt.% of alumina was recorded [45]. The report showed that the adhesion strength was dependent on thermal conductivity of substrate. Heating the substrate slows the solidification rate of splats. This leads to an increase in splat size that intern enhances the adhesion strength of the coating [46]. Not only the composition of feedstock material but also the heating power used to melt the powder can greatly influence the mechanical properties of the coatings [45].

Sahu et al. [47] have investigated fly ash/ alumina composite deposited using plasma spray technique. The alumina was varied in 5-25 wt. % range. At plasma power 18 kW, another sample thickness of 360 µm was deposited. In this coating alumina content was set as 30 wt.%. authors have used Taguchi technique to optimize the few operating parameters to maximize deposition efficiency and adhesion strength. The parameters list includes impact velocity, aluminum content and impingement angle. In addition, the author has investigated the role of addition of alumina in the composite coating to improve deposition efficiency and adhesion strength of coating [47]. The researchers have also conducted erosion wear test on the coating. The apparatus consists of an air compressor, an air particle mixing chamber and accelerating chamber. A mixture of compressed and abrasive particles is accelerated to collide with the surface of the coating and wear rate was recorded. During study, the effect of impact velocity, stand-off distance, erodent size, impingement angle and aluminum content were analyzed. It was observed that erodent size, standoff distance, alumina content were the most influencing factors of wear [47].

Fly ash is also effectively used in automobile industries to reduce the heat transfer rate of the coatings. MohamedMusthafa et al. [48] have plasma sprayed fly ash on the parts of diesel engine such as cylinder head, cylinder liner, piston crown, exhaust and inlet valves of the diesel engine to provide thermal barrier coating of 200 thickness [48]. A coated single cylinder, 4S, constant speed, water cooled direction injection diesel engine was used to assess the effectiveness of thermal barrier coating. During test, parameters like fuel consumption, exhaust gas temperature and exhaust emissions such as NOx, CO, HC, CO_2 and smoke were measured.

It was observed that the heat transfer rate via the combustion chamber parts was decreased due to the fly ash coating, resulting an increase in cylinder gas and wall temperature. Consequently, combustion was improved and thereby contributed to improve the thermal efficiency. Increase in wall temperature was also attributed to the formation of heat insulation in coated condition, resulting in decreasing of specific fuel consumption [48].

In addition to alumina and titania, fly ash was also mixed with red mud, another industrial by-product to investigate the wear resistance of the coatings. Sutar et al. [49] have used fly ash powder particles ranging their size from 85 to 100µm. subsequently, red mud was added to this powder. The concentration of red mud has been 10, 20 and 50 wt.% [49]. The homogeneous mixture was prepared with the help of V-shaped drum mixer. The average thickness of 721.65µm coating was realized by plasma spry process. The properties of fly ash composite coating were compared with that of red mud coatings. It was observed that fly ash composite coating has shown the improvement in the hardness 496 to 658 HV [49]. Also, fly ash has been effective in increasing the density of coating, there by an improvement in hardness of coating was recorded. During wear test, at higher sliding distance, a significant wear rate of the coating has been observed. This was observed for all weight fractions of fly ash [49].

Aluminum alloys have been extensively used in aerospace applications due to their high strength to weight ratio [50]. Initially, Fly ash was mixed with titania with different fractions. This composite powder was coated using plasma spray technique on 6061Al substrate. The improvement in bond strength and hardness of the coatings has been observed [51].

In another report by Sutar et al. [52] have shown that the mixing of fly ash with red mud can also improve the wear resistance. Author has concluded that reinforcing fly ash in red mud gives better result than using red mud alone in the coating [52]. It has observed that cumulative mass loss was approximately 5300 mg for red mud alone coating. It was relatively high as comparing with fly ash/red mud composite coating of mass loss 2800mg [52].

In a sequel paper, Sutar et al. [53] have deposited composite coating of alumina, red mud and fly ash using plasma spray technique. Homogeneous mixture prepared by manual mixing of same particle size in 80-100µm range [53]. After coating, sliding wear test was performed using pin on disc test apparatus. The composite coated cylindrical substrates tested against a disc made of hardened ground steel. Normal load of 10 N and sliding speed of 60 rpm were set. Wear rate was calculated in terms of mass loss. It was concluded that the additives like fly ash and aluminum can improve the surface properties of mild steel by modifying the physical and interfacial characteristics [53].

In another study by Naveena et al. [54] have studied the slurry erosion wear behavior of plasma sprayed alumina/fly ash coating. The composite powder of fly ash and alumina wt.% was prepared by manual mixing method and subsequently, coated on to a Al6061 substrate. A 50 µm Ni-Cr bond coat was deposited on substrate before the top coat [54]. After coating, slurry erosion test was performed by varying different parameters like speed, slurry concentration and slurry particle size. In wear test, the coated specimens outperformed the uncoated specimens. Owing to higher cooling rate, the α phase transforms into γ-Al_2O_3 phase. The improvement in wear resistance was attributed the presence of other phases in the coating, namely, quartz, mullite, hematite, $CaCO_3$ and alumino-silicates [54]. also confirms the presence of mixture of hard oxides like quartz, mullite, hematite, $CaCO_3$ and Alumino Silicates.

CONCLUSION

Fly ash is an amorphous powder of ferro-alumino silicate minerals. Though fly ash is an industrial waste, it could be economically used in potential applications like civil, automobile and aerospace industries. In civil construction, fly ash has been useful to improve the properties of concrete. Especially, composite coatings deposited by thermal spray coating are gaining importance these days. This powder can be used for depositing coatings by many thermal spray techniques viz., atmospheric plasma spray and detonation gun. In automobile industry, it was mainly used to retard the heat transfer rate. Fly ash has been effective in aerospace applications as well. In this domain, fly ash as a reinforcement with other hard powders like alumina have been found coatable and was provide reasonably good wear, erosion, and corrosion properties to the coatings. Further investigation in this field is required to explore the possibility of different combinations of composites to produce coatings of sound erosion, corrosion and wear resistance properties.

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