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Characteristic study of fly-ash+quartz+illmenite composite coatings on copper substrates

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Fly ash produced from iron and steel industries contains rich amount of metal oxides, which has the potential of using it as a coating material on structural and engineering components. This demand leads to the development and characterizes various types of composite coatings of fly ash by using a robust technique, that is, plasma spraying. Plasma spray technology has the advantage of being able to process various low-grade minerals to obtain value-added products and also to deposit metals, ceramics and a combination of these, generating approximately homogeneous coatings with the desired microstructure. In the present investigation, coatings are developed on copper substrates using fly-ash+quartz+illmenite composite at various plasma torch input power levels ranging from 11 to 21 kW DC. Metallographic and chemical characterization of the produced composite coatings was performed with the aid of scanning electron microscopy and X-ray diffraction analysis. The adhesion strength was measured by using coating pull-out method. Maximum adhesion strength is found to be 6·32 MPa. Here, adhesion strength was higher than that of fly-ash+quatz and fly-ash+illmenite composite coating. It was found that the quality and properties of the composite coating are significantly affected by the operating power level of the plasma spray torch. This study identifies fly ash+quartz+illmenite as a potential coating material for structural and engineering applications.

1. Introduction

Fly ash is a finely formed powder generated as a solid waste in huge quantities in iron and steel industries. Only a small fraction of fly ash is used in the development of high-value products. New ways of utilizing fly ash are being explored in order to minimize the plant wastage and provide a safeguard to the environment. Fly ash is a finely divided powder, which can be used as a refractory in industry. Fly-ash composite has a number of useful applications, as given in reference.[1] It is well known that fly-ash composite coatings are used extensively for the protection of mild steel and copper substrates in various corrosion environments. However, the increasing and new technologically demanding applications have led to the development of new fly-ash composite coatings. Fly-ash composite coatings, such as fly-ash+jute-polymer,[2] fly-ash+Na-geopolymer,[3] fly-ash+redmud[4] and fly-ash+zinc coatings[5] have been extensively studied. According to recent investigations, composite fly-ash coatings can exhibit high corrosion resistance, in addition to increased wear resistance. Some of these recent reports concerning the development and surface properties of this type of fly-ash composite coatings are presented below.

Mishra and Padmanabhan,[6] first studied the behavior of fly-ash+aluminium composite coated on copper and stainless steel substrates. Considerable emphasis has been placed on the processing of low-grade ore minerals through thermal spray techniques. Fly ash has been found to be a cost-effective substitute for conventional extenders in high-performance industrial coatings.[7]

Again, Mishra and Das[8] performed experiments on the behavior of fly-ash+illmenite composite coated on metal substrates by

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means of plasma spraying techniques. These investigators found that the addition of illuminate powder within the fly-ash matrix led to a significant increase in the corrosion resistance of the mild steel substrate. In addition, they found that there is less deposition efficiency with respect to appropriate coating thickness and also the microhardness is less.

In 2009, Praharaj and Mishra[9] examined the plasma sprayed fly-ash+quartz composite coating on copper substrates. They observed that the morphology and structure of this composite coatings were significantly modified. In this investigation, the adhesion strength and deposition efficiency of the coating was not found to be very satisfactorily improved, but coating thickness significantly increased.

In the present experiment, plasma spray of fly-ash+quartz+illmenite composite coatings has been produced on copper substrates. The surface and cross-sectional morphology, crystal structure, surface roughness and microhardness of these coatings have been studied. In addition, the adhesion strength and coating deposition efficiency have been thoroughly examined. The results are compared with those of fly-ash+illmenite and fly-ash+quartz composite coatings. It should also be noted that this research investigation aims at expanding the technological applications of fly ash produced in industries. This research investigation aims at utilizing low-cost fly ash and expanding its technological applications in the important field of coatings technology. It is believed that fly ash might possibly replace other expensive commercial oxides in the production of composite-coating materials.

2. Experimental procedure

Flay-ash, quartz and illmenite mixture was taken with their weight percentage ratio of 60:20:20 and mechanically milled in a FRITSCH-Planetary ball mill for 3 h to get a homogeneous mixture. This composite, used as the feed stock for plasma spraying, was sieved and particles in the range of 40–100 µm was separated out for plasma spraying. This powder composite is used as a coating material on copper substrates. The substrate materials have dimensions of 1-inch diameter and 3-mm thickness. The substrates were grit blasted at a pressure of 3 kg/cm^2 using alumina grit to make the surface roughness ~5·00 Ra. After grit blasting, the substrates were cleaned by acetone and immediately, plasma spraying was carried out. In plasma spraying, the powder composite is rapidly heated and accelerated to a very high velocity by the plasma flame. It impacts the surface of the substrate material in the form of molten or semimolten state and very quickly cools to form a high-quality coating.[10–13] The spraying process was carried out by using a 40-kW dc power supply plasma spray system at the Laser & Plasma Technology Division, BARC, Mumbai. The plasma input power level was varied from 11 to 21 kW. This is a typically atmospheric plasma spray process, which is working in the nontransferred arc mode. The injection of the powder from the torch nozzle was directed perpendicular to the plasma flow and parallel to the torch trajectory. The torch was operated using a mixture of argon (Ar) and nitrogen (N_2) plasma. The major subsystems of the set up include the power supply, powder feeder, plasma gas supply, plasma spray torch and substrate to torch distance controller, cooling water and spray booth. A water cooling system, consisting of a four-stage-closed loop centrifugal pump, regulated at a pressure of 10-kg/cm^2 supply, was used to cool the system. The operating parameters used for coating are summarized in Table 1. The flow rate of plasma gas (Ar) and secondary gas (N_2) are kept constant. Powder feed rate, powder size and torch to base distance are varied with respect to increase in power level. The coated samples were subjected to various analyzes. The thickness of the coatings was measured by a travelling microscope on a polished cross-section of the specimens. Surface and interface morphologies were studied using a scanning electron microscope (JEOL JSM-6480LV). The coating pull-out test was carried out on the specimen to evaluate the coating adhesion strength as per ASTM C633.[14] Phase identification study was done by X-ray diffraction (XRD) using a Phillips X-ray Diffractometer with Ni-filtered Cu K_α radiation.

3. Results and discussion

3.1 Scanning electron microscopy study of surface and interface

The composite-coating material and substrate interface play most important role in the adhesion of coatings.[15,16] The surface microstructure of composite coating is studied by using scanning electron microscopy (SEM). The SEM micrographs show the presence of different phases, typical examples of which are shown in Figure 1a and 1b. At 11-kW power level, some open pores are observed. These may have originated due to the inadequate flow of molten particles during their solidification.[17] However, at 21-kW power level, the composite particles are seen to be fully molten and uniformly spread on the surface. Here, there is no open pore, but

Operating parameters	Values
Plasma arc current (amp)	260–500
Arc voltage (volt)	40–44
Torch input power (kW)	11,15,18,21
Plasma gas (Ar) flow rate (IPM)	28
Secondary gas (N_2) flow rate (IPM)	3
Carrier gas (Ar) flow rate (IPM)	12
Powder feed rate (g/min)	15
TBD (mm)	100

TBD, torch to base distance.

Table 1. Operating parameters used during deposition of fly-ash+quartz+illmenite coatings.

there is some close pore present in between the splat layer. Close pores are generated due to much vaporization at higher torch input power.

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 were examined under SEM and are shown in Figure 2a and 2b. From the micrographs, it is evident that the coating, deposited at 11 kW, shown in Figure 2a has a lamellar structure with small number of cavitations at the interface between the lamellae. Here, splats are of small diameter. However, splats formed at 21-kW power level are larger in dimension and equiaxed type as shown in Figure 2b. 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 interdiffusion zones.

3.2 XRD analysis

Figures 3 and 4 represent XRD analyzes to examine the presence of various phases in the raw fly ash and in the resulting fly-ash+quartz+illmenite composite coatings, respectively. The XRD pattern for raw fly-ash particles (shown in Figure 3) exhibits distinct peaks that are assignable to the various metal oxide phases present, such as SiO_2, TiO_2, Ti_4O_7, $FeTiO_3$, Al_2O_3 and Al_2SiO_5. It is clear that this composite powder contains oxide elements. However, the XRD pattern of the composite coating suggests the presence of crystalline phases such as SiO_2, Ti_3O_5, and Al_2SiO_5 along with additional phases such as Fe_3O_4, $FeTiO_3$, Fe_2TiO_5 and Al_2SiO_5, Ti_4O_7. This suggests that, during plasma spraying at higher torch input power, some elements combine with other elements or transformed to its higher stable state.

3.3 Adhesion strength and deposition efficiency of composite coating

The interface bond strength of the coating is evaluated by the coating pull-out method. It is seen that, in all cases, fracture occurs at the coating-substrate interface. However, it has been stated by Lima and Trevisan that the fracture mode is adhesive if it takes place at the coating-substrate interface and the measured adhesion value is the value of practical adhesion, depending exclusively on the surface characteristics of the adhering phase and the substrate surface conditions.[7] Adhesion strength increased with power level up to 18 kW and attained a maximum value of 6·18 MPa, and further

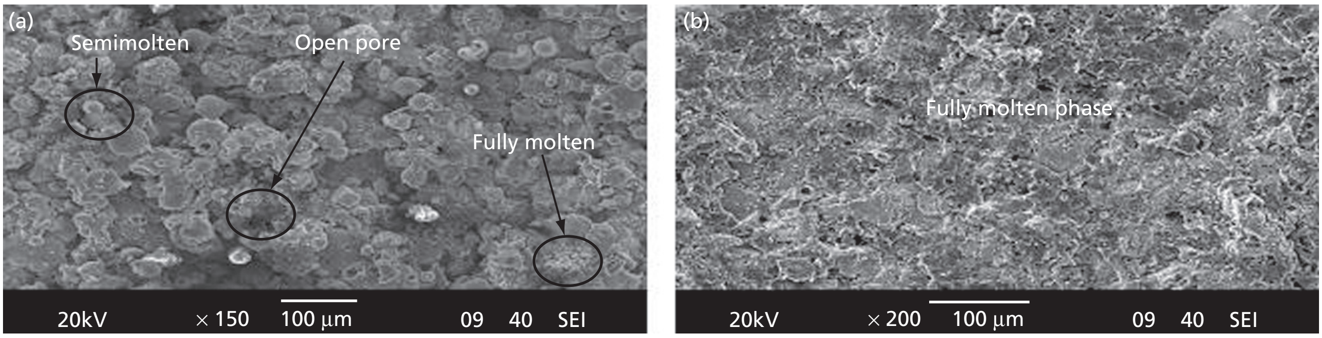

Figure 1. SEM surface morphology of Fly-ash+quartz+illmenite composite coated at (a) 11 kW and (b) at 21 kW. SEM, scanning electron microscopy.

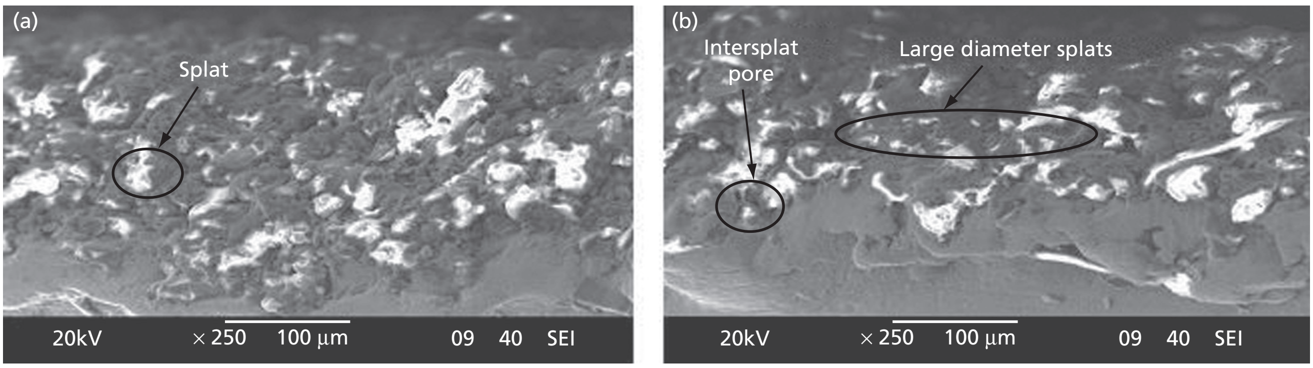

Figure 2. SEM interface morphology of Fly-ash+quartz+illmenite composite, coated at (a) 11 kW and (b) at 21 kW. SEM, scanning electron microscopy.

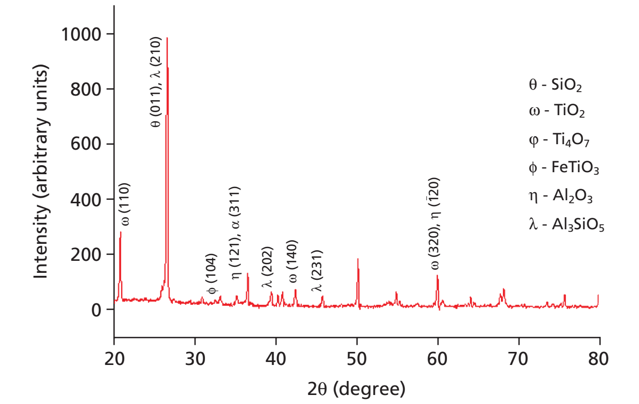

Figure 3. X-ray diffractogram of the raw fly-ash composite.

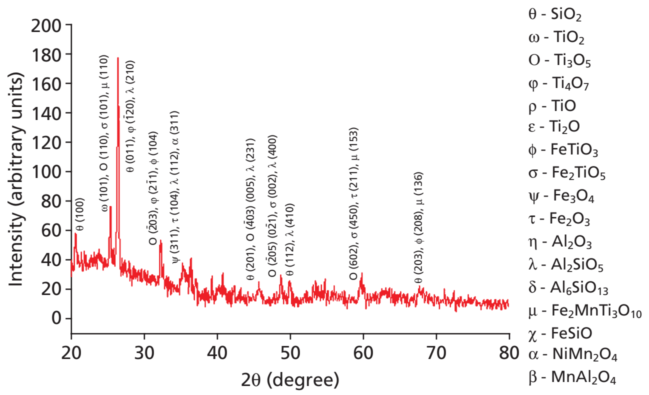

Figure 4. X-ray diffractogram of the composite coating on copper substrate.

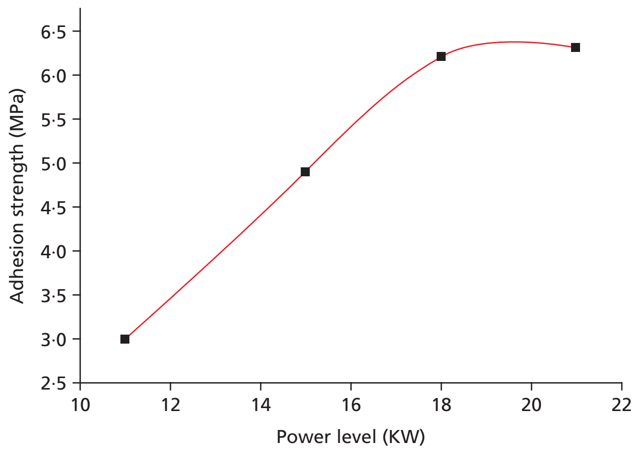

Figure 5. Adhesion strength between composite-coating material (fly-ash+quartz+illmenite) and the copper substrate with increase in power level.

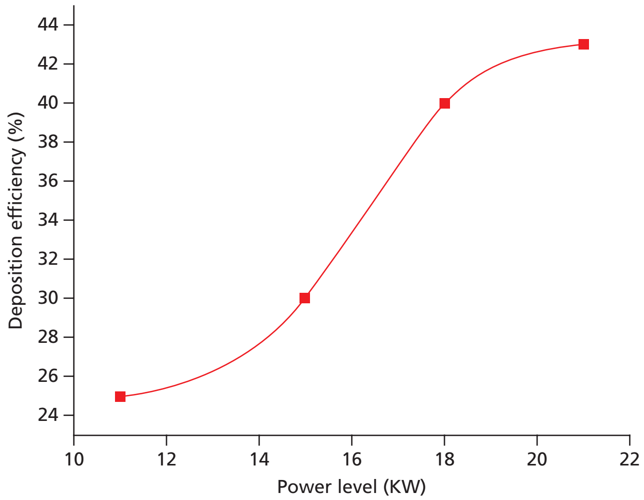

Figure 6. Deposition efficiency of composite-coating material (fly-ash+quartz+illmenite) on copper substrate with increase in power level.

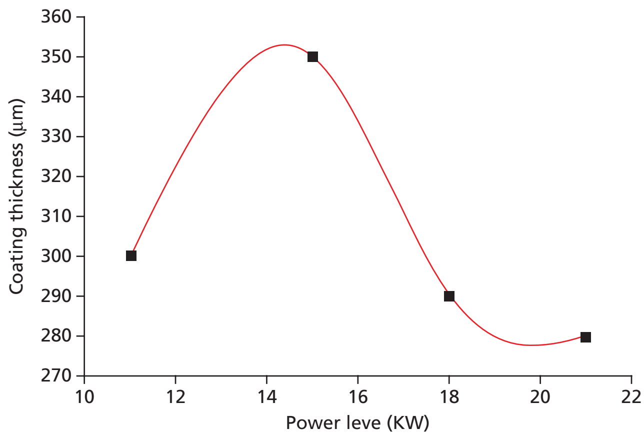

Figure 7. Variation of coating thickness of composite (fly ash+quartz+illmenite) on copper substrate with respect to power level.

increase in the operating power level exhibited a detrimental effect on the interface strength (shown in Figure 5). Initially, when the operating power level is increased from 11 to 18 kW, the melting fraction and velocity of the particles also increase. Therefore, there is better splashing and mechanical interlocking of molten particles on the substrate surface leading to an increase in adhesion strength. However, at much higher power levels (beyond 18 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. During in-flight traverse through the plasma, a fly-ash particle would melt either partially or fully depending on the temperature and the flame residence time of that particular particle.

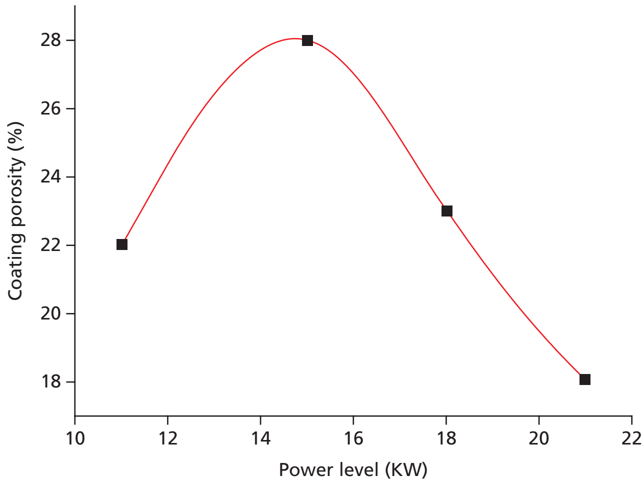

Figure 8. Variation of coating porosity of composite (fly-ash+quartz+illmenite) on copper substrate with respect to power level.

Figure 6 shows deposition efficiency of fly-ash+quartz+illmenite composite on copper substrate as a function of power level. The deposition efficiency can be 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 parameter. In this investigation, the deposition efficiency exhibits a sigmoid-type evolution with the torch input power. As the power level increases, the net available energy in the plasma 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 increasing plasma jet temperature which, in turn, increases both the particle vaporization ratio and the plasma jet viscosity. It is found that the maximum deposition efficiency is 48% at 21-kW power level.

3.4 Interdependency of composite-coating parameters

The variation of coating thickness with input power level is shown in Figure 7. It indicates that, with increase in torch input power, the thickness of the coating increases up to a certain point. On further increase in power level, there is a decrease in coating thickness, because by gaining higher energy, the composite powder becomes fully molten and spreads on the surface. The thickness of the coating varied between 280 and 350 μm with change in operating power from 11 to 21 kW. At 15-kW power level, a higher coating thickness of 350 μm was obtained. Here, there is an increase in coating thickness with increase in coefficient of thermal conductivity by decreasing thermal gradient between coating and substrate. Therefore, the adhesion strength increases.[18] It is known that for higher hardness, lower porosity and lower surface roughness can be obtained at lower coating thickness.[19–21]

Figure 8 shows the fly-ash+quartz+illmenite composite–coating porosity dependence on power level. It is known that, lower is the porosity better is the product. At 15-kW power level, there is a higher porosity. Porosity increases with respect to coating thickness as there is an inadequate amount of energy gain by the composite material to form fully molten material and is deposited with more amount of intergranular pore.

4. Conclusions

Fly-ash composites can be gainfully used as a potential cost-effective material for deposition of plasma spray coatings on metallic substrates. Premixing of quartz and illmenite powder with fly ash can produce metal-ceramic composite coatings of improved interfacial adhesion. Maximum adhesion strength of about 6·18 MPa was recorded. The adherence strength was significantly affected by the plasma torch input power level. The operating power level of the plasma torch also affects the coating deposition efficiency and morphology of the coatings.

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