

Studies on Microstructure and Microhardness of plasma sprayed NiCrBSi/Flyash/TiO₂/Cr₂O₃/Mo composite coatings

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ABSTRACT

In a wide variety of applications, mechanical components are subjected to severe conditions, such as high load, speed or temperature and hostile chemical environment. Thus, their surface modification is necessary in order to protect them against various types of degradation. Thermal spraying has emerged as an important tool of increasingly sophisticated surface engineering technology. Plasma spraying is a rather simple process from a practical point of view. In the present investigation, NiCrBSi along flyash, Cr₂O₃, Mo and TiO₂ composite coating were obtained by atmospheric plasma spray process on Super Ni 76. The coating was characterized using scanning electron microscope to study the surface morphology and cross section to study the nature of coatings deposited. All the composite coatings had good bonding with substrate material and continuous interface without any porosity. The microhardness studies showed that the composite coatings had higher microhardness values than that of substrate material.

Key words: Flyash, Wear, Composite, Chromium, Plasma spraying

INTRODUCTION

Nickel based alloy coatings are widely used when the wear resistance combined with oxidation or high temperature corrosion resistance is required.¹ Currently, they are used in various mechanical components, such as piston rings, pump bushings, wearing plates, extruders, plungers, turbines, heat exchangers and coal fired boilers, and mud purging elements in cement factories. Nickel based alloy coatings feature advantages of covering large size components, such as earth working machines.² NiCrBSi alloys are modified from traditional Ni based alloys to gain certain properties. Chromium increases resistance to oxidation and high temperature corrosion and enhances the hardness of coatings by forming hard precipitates. Boron and silicon reduce the melting temperature, and boron facilitates the formation of the hard phases. Carbon produces carbides with high hardness levels that improve the wear resistance of coatings.¹ An advantage of Ni based alloy powders is that they can be used with hard ceramic particles, such as tungsten carbides, to achieve the desired coating hardness and wear resistance.³ Tungsten carbide alloys comprise WC particles of ultrahigh hardness and ductile metal binders (i.e. Co, Cr or Ni) that exhibit high hardness and acceptable ductility and thus show excellent mechanical properties.

In principle, any material that does not decompose as it is melted can be used as a thermal spray coating material. Depending on the thermal spray process, the coating material can be in wire or powder form. Choosing a coating material that is suitable for a specific application requires special knowledge about the service environment as well as knowledge about the materials. Apart from the physical characteristics, such as coefficient of expansion, density, heat conductivity and melting point, additional factors, such as particle shape, particle size distribution and manufacturing process of powder material (i.e., agglomerated, sintered, composited) will influence coating performance. As most spraying materials are available as alloys or blends, this leads to a nearly unlimited number of combination options, and only through many years of experience and broad know-how can a proper selection be made.

Coating Process	Typical Coating Thickness	Coating Material	Characteristics	Examples
PVD	1 – 5 μm (40 – 200 μin)	Ti(C,N)	Wear resistance	Machine tools
CVD	1 – 50 μm (40 – 2000 μin)	SiC	Wear resistance	Fiber coatings
Baked Polymers	1 – 10 μm (40 – 400 μin)	Polymers	Corrosion resistance, aesthetics	Automobile
Thermal Spray	0.04 – 3 mm (0.0015 – 0.12 in)	Ceramic and metallic alloys	Wear resistance, corrosion resistance	Bearings
Hard Chromium Plate	10 – 100 μm (40 – 4000 μin)	Chrome	Wear resistance	Rolls
Weld Overlay	0.5 – 5 mm (0.02 – 0.2 in)	Steel, Stellite	Wear resistance	Valves
Galvanize	1 – 5 μm (40 – 200 μin)	Zinc	Corrosion resistance	Steel sheet
Braze Overlay	10 – 100 μm (40 – 4000 μin)	Ni-Cr-B-Si alloys	Very hard, dense surface	Shafts

Figure 1 Principal coating processes and characteristics

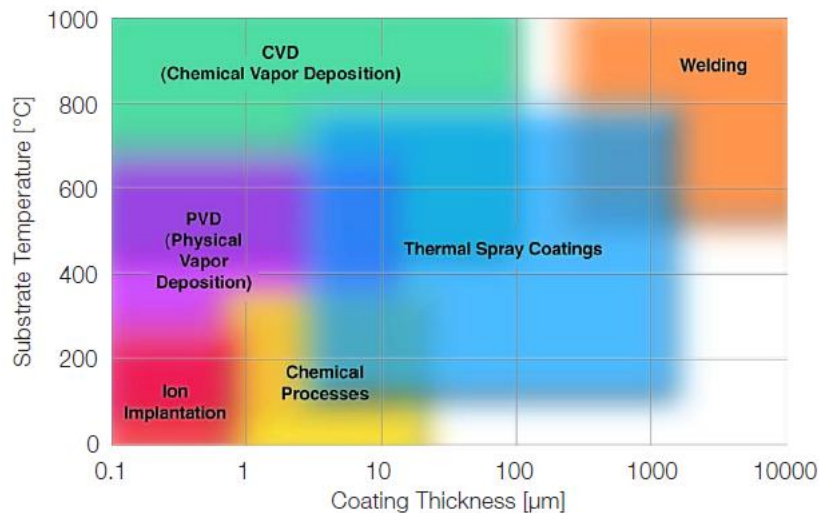


Figure 2 Coating process comparisons

Plasma spray process belongs to the family of thermal spray techniques. In this process, finely divided metallic and non-metallic materials are deposited in a molten or semi-molten state on the substrate by using thermal energy (Fauchais, 2001). A high energy spark produced between cathode and anode due to potential difference is the energy source for plasma spraying. The arc in DC plasma gun is sustained between a cylindrical tungsten cathode and radial concentric copper anode which also acts as the nozzle. The inert gases, usually argon (Ar), helium (He), or nitrogen (N₂) or mixtures of these, are introduced at the nozzle tip (Figure 1). Reactions between the electrons from the cathode source, and the gas molecules and/or atoms occurs, causing a dissociation or ionization of the gas, and thus, creating the plasma state. The gases are heated as they pass through the arc; they expand radially and axially, and accelerate through the nozzle exit with a flow rate of 3.5 Ltrs/min (Sidky and Hocking 1999). The temperature in the core region can reach values of more than 10000 K due to the heat released and radiation. The arc temperature is maintained in the range of 6,000-12,000°C at a distance of 1 cm from the nozzle and it decreases rapidly to 3000°C at a distance of 10 cm from the nozzle (Tucker, 1994).

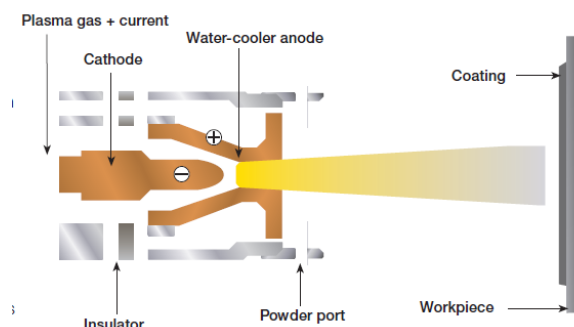


Figure 1 Schematic representation of plasma spray process (Tucker, 1994)

In the early fifties of twentieth century, the plasma torches were developed to test materials at high enthalpies for simulated re-entry vehicles. Then in late fifties and early sixties, the first serious attempts were reported on using plasma torches for spraying of primarily refractory materials. Almost any material can be plasma sprayed on almost any type of substrate. This flexibility is probably one of the major reasons for the rapid expansion of plasma spray technology (Pfender, 1988). The high temperatures enable the use of coating materials with very high melting points such as ceramics, cermets and refractory alloys. Materials can be processed as long as there is a temperature difference of at least 300K between the melting temperature and decomposition or evaporation temperature (Fauchais et al, 1991). Plasma techniques are capable of producing thick coatings films more than 100 μm at high production rates with no degradation of the mechanical properties of the alloy substrate (Yoshida, 1993). Probable problems that may be encountered are porosity and poor adhesion, especially in case of adhesion of ceramics to metals. Further, adhesion can be improved by the use of bond coat interlayer and /or powder of small particle size. Among other key features of plasma spraying are formation of microstructures with fine, noncolumnar and equiaxed grains, ability to produce homogeneous coatings that do not change in composition with thickness (length of deposition time), ability to process materials in virtually any environment (e.g., air, reduced-pressure inert gas, high pressure, under water).

Applications for plasma spraying include corrosion, temperature and abrasion resistant coatings and production of monolithic and near net shape shapes, which at the same time take advantages of the rapid solidification process. Powder of glassy metals can be plasma sprayed without changing their amorphous characteristics. High temperature superconductive materials have also been deposited by the plasma spray process (Pfender, 1988). The plasma spray also finds application in reclamation of worn or corroded components, production of aerospace and nuclear power components. A new application of plasma spraying is in producing hydroxyapatite coatings onto the stems of orthopaedic endoprostheses (Batchelor et al, 2003).

However, atmospheric plasma sprayed coatings tend to have highly defective microstructures, with lamellar microcracks, unmolten particles, weak interfaces and voids between solidified splats [4,7]. The microstructure and consequently the mechanical properties of these coatings depend strongly on spraying conditions (voltage/secondary gas pressures, spraying distance) that affect the plasma temperature, on variables related to the injected powder (particle size, feeding rate, carrier gas) as well as on substrate mechanical properties [6–8]. For a long time, silica and alumino-silicate bricks have been preferred as refractory materials in many industrial applications due to their high wear resistance and high load bearing capacity at high temperatures. During the last decade, although a large number of investigations have been carried out for development of plasma spray ceramic coatings, not much effort has been made to use low-grade raw materials for plasma spray purposes [9]. Recently, attempts have been made to develop the plasma spray deposition of alumino-silicate composite coatings onto metal substrates using industrial waste, but the adherence of the coating was not satisfactory [10]. This investigation deals with the formulation of fly ash coatings on carbon steel by shrouded plasma spray process. The microstructure, porosity, microhardness of the coated steel has been investigated by the use of metallography, SEM/EDAX and X-ray diffraction (XRD) techniques.

Experimental Procedure

Substrate Material

Substrate is a material on which coating materials are sprayed in order to protect the surface from various types of degradation. Prior subjecting the substrate material to coating process, it is undergoes blasting operation to produce the rough surface, so it should consist of optimum hardness and adhesion strength to hold the coating to its surface. In the present investigation super Ni76 [ASTM equivalent – Hastelloy X] is selected as a substrate material. The primary reason behind selecting the Super Ni76 steel is because it is used in petrochemical process equipment and gas turbines in the hot combustor zone sections. It is also used for structural components in industrial furnace applications because of the excellent oxidation resistance. The material is purchased from MIDHANI, Hyderabad and the chemical composition is given in Table 2.1. The specimens of following dimensions 25mm x 25mm x 3mm, 25mm x 20mm x 3mm, and 12mm x 12mm x 3mm are used for coating experiments.

Type of substrate	ASTM code	Composition	C	Mn	Si	S	P	Cr	Mo	Fe	C	W	B	Ti	Ni
Super Ni 76	Hastelloy X	Nominal	0.08	-	2	-	-	18	-	Bal	-	-	-	0.4	11.5
		Actual	0.10	1.46	0.55	0.005	0.013	18.13	-	Bal	-	-	-	0.62	10.36

Table 2.1: Chemical composition (wt %) for various steels

Coating development and characterization

The chemical composition of coating material used in the present study is shown in Table 2.2. Here different composite coatings are obtained by mixing the NiCrBSi alloy powder with 40 wt% of flyash for 1st coating, 20 wt% of Mo/20 wt% of flyash for 2nd coating, 20 wt% of Cr₂O₃/20 wt% of flyash for 3rd coating and 20 wt% of TiO₂/20 wt% of flyash for last coating using ball mill technique. The particle size of each composite coating used in present study is also given in the Table 2.2. The cross section of coatings deposited on the substrate material is characterized using scanning electron microscopy (Make: Tescan Vega3). Here the SEM is used to study the coating thickness by observing the cross section and surface morphology of coating deposition. Vickers microhardness measurement was conducted by opting 200 gram load for a dwell time of 15 seconds over the cross section of coatings and substrate materials

Table 2: Chemical composition and Size of coating powder

Coating powder	Chemical composition(wt %)	Particle Size
NiCrBSi/Fly ash	60%(Ni/15.3Cr/3.1B/4.8Si /4.2Fe/0.6C)/ 40%Fly ash	-45 to 10µm
NiCrBSi/Fly ash/Cr ₂ O ₃	60%(Ni/15.3Cr/3.1B/4.8Si /4.2Fe/0.6C)/ 20%Fly ash/20%Cr ₂ O ₃	-45 to 10µm
NiCrBSi/Fly ash/TiO ₂	60%(Ni/15.3Cr/3.1B/4.8Si /4.2Fe/0.6C)/ 20%Fly ash/20%TiO ₂	-45 to 10µm
NiCrBSi/Fly ash/Mo	60%(Ni/15.3Cr/3.1B/4.8Si /4.2Fe/0.6C)/ 20%Fly ash/20%Mo	-45 to 10µm

RESULTS AND DISCUSSION

SEM micrograph showing the surface morphology of NiCrBSi/40 wt% of flyash coatings fabricated by plasma spray technique is shown in Fig. 4. It can be observed from the micrographs that both the coating have partially melted and unmelted composite powder particles. The top surface of the composite coating showed the interlocked particles of both NiCrBSi with flyash and showed dense packing with high cohesion.

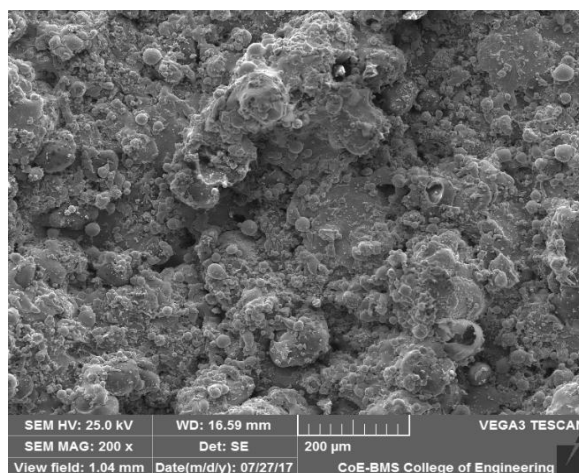
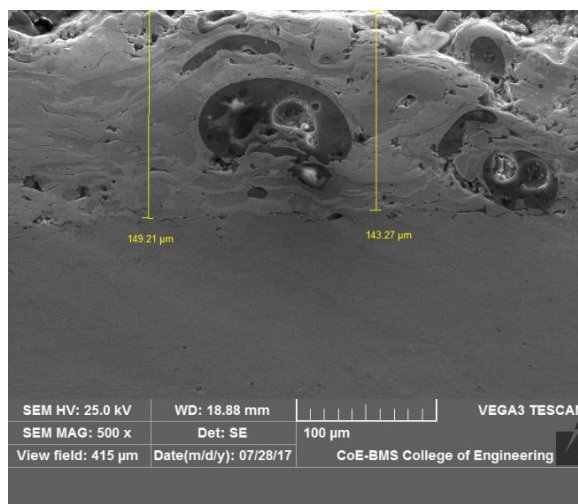
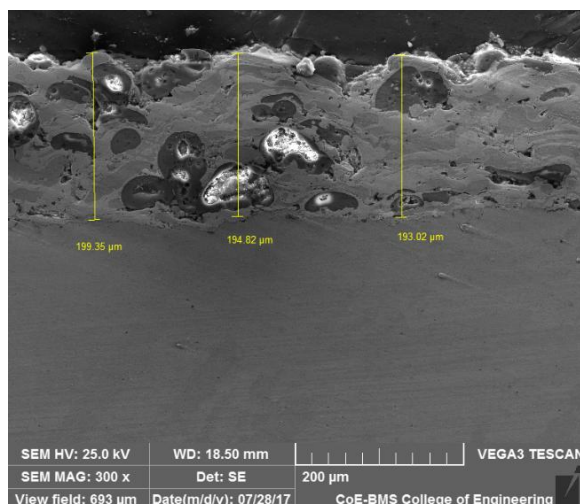


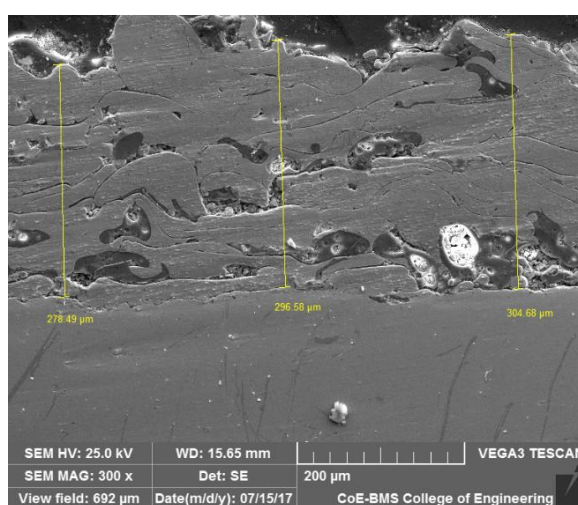
Figure 4 SEM micrograph showing the surface morphology of NiCrBSi/40 wt% of flyash



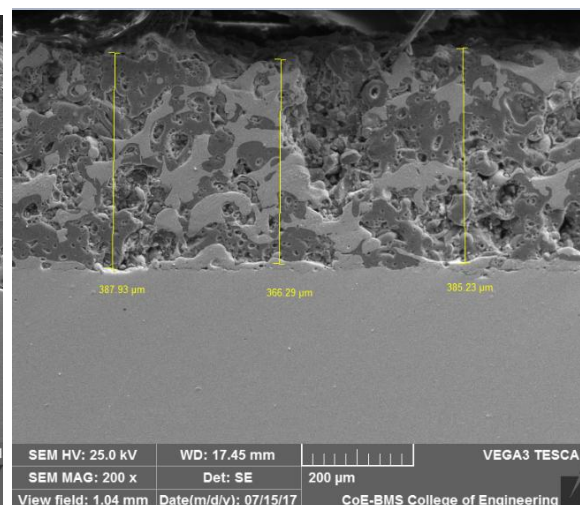
NiCrBSi+Flyash+TiO₂



NiCrBSi+Flyash+Mo



NiCrBSi+Flyash+Cr₂O₃



NiCrBSi+Flyash

Figure 5 SEM micrograph showing cross section of all the coatings

Fig. 5 shows the SEM micrographs of cross sections of all composite coatings with the coating thickness depicting in the micrographs. It can be observed that the NiCrBSi/flyash/TiO₂ and NiCrBSi/flyash/Mo coating thickness were in the range of 140 to 200 μm while that of NiCrBSi/flyash/Cr₂O₃ and NiCrBSi/flyash coating thickness were in the range of 270 to 390 μm. From micrographs it is quite clear that all the coatings having NiCrBSi had strong bonding with the flyash particles. Overall the coating had good bonding with substrate material and continuous interface without any porosity is observed.

Microhardness

The microhardness data for all composite coatings on substrate material are shown in Table 3. In all the cases the microhardness of the substrate material is found to lower than that of composite coatings. Highest microhardness was observed for composite coating NiCrBSi/flyash combination while lowest was observed for NiCrBSi/flyash/Mo. The improved microhardness value in case of composite coatings is attributed to the high density, low porosity and high cohesive strength between individual splats of both the constituents NiCrBSi and flyash.

Table 3 hardness values for different coatings

Sl No	Sample identification		Hardness values measured in HV0.02			
			1 st Value	2 nd Value	3 rd Value	4 th Value
1	NiCrBS+FA+Mo					
		Substrate	210	215	218	220
		Coating	561	574	601	620
2	NiCrBSi+FA+Cr ₂ O ₃	Substrate	194	198	202	200
		Coating	445	460	650	700
3	NiCrBSi+FA+TiO ₂	Substrate	220	225	228	230
		Coating	565	574	683	702
4	NiCrBSi+FA	Substrate	236	346	326	340
		Coating	453	624	865	890

Conclusion

The conclusions drawn from the current work are as follows,

- Successful fabrication of different composite coatings consisting of NiCrBSi, flyash and other materials like TiO₂, Cr₂O₃ and Mo using plasma spray technique.
- The cross section SEM images of all the composite coatings showed excellent cohesion strength with minimal porosity which is attributed to plasma spray process in which particles are impinged on substrate at appropriate velocity and temperature.
- In all the cases the composite coatings had higher microhardness than that of substrate materials.
- The improved microhardness of composite coatings is attributed to the high density, low porosity and high cohesive strength between individual splats.

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