PLASMA SPRAYED CERAMIC COATINGS ON METALLIC SUBSTRATES

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ABSTRACT

Plasma spraying stands out as one of the most versatile and technologically sophisticated thermal technique in the field of surface engineering. Plasma sprayed ceramic coated components are used as wear resistant and as thermal barrier materials.

The objective of the present work is to study the tribological and thermal behaviour of different types of ceramic coatings. Zircon and alumina-zircon coatings are tried out on mild steel substrates with (Ni-Al and high carbon iron) bond coat and also without bond coat. The coatings have been characterized by XRD, SEM, Wear, Grindability and Thermal Fatigue successfully. The presence of mullite in the top coat has been found to be reponsible for the superior high temperature properties of the coating.

INTRODUCTION

Surface coating techniques alter the surface of the material, but with localized heating. The substrate surface should not be damaged because of this heating and should retain its inherent properties. The objective of surface engineering is to upgrade their functional capabilities keeping the economic factors in mind [1]. Surface engineering is the name of the discipline - Surface modification is the philosophy behind it [2]. Thus through a surface modification process two (or more) materials are assembled by the appropriate method and are exploited the qualities of both [3].The following limitations should be kept in mind.

I) The technological value addition should justify the cost.

2) The choice of technique must be technologically appropriate.

THERMAL SPRAYING

It is the generic category of material processing technique that applies to consumables in the form of finely divided molten or semi molten droplets to produce a coating onto the substrate kept in a front of the impinging jet. The melting of the consumables may be accomplished in number of ways, and the consumables can be introduced into the heat source in wire or powder form. Thermal spray consumables can be metallic, ceramic or consumables. Another aspect of thermal spraying is that the surface temperature seldom exceeds 200 °C. There are two basic ways of generating the heat required for melting consumables [4].

i) Combustion of fuel gas
ii) High energy electric arc

Plasma Spraying

Plasma spraying is one of the most versatile thermal spraying process. The general arrangement of the set up is shown below.

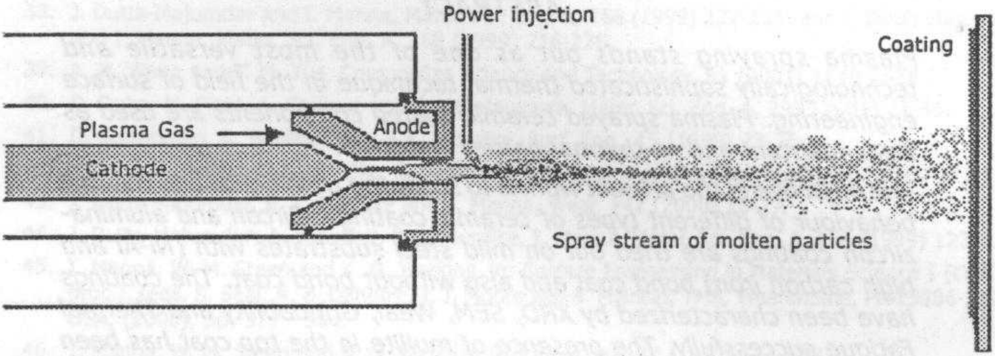


Fig. 1 : Plasma spraying

An arc is created between tungsten tipped copper cathode and an annular copper anode (both water cooled). Plasma generating gas is forced to pass through the annular space between the electrodes. While passing through the arc the gas undergoes ionisation in the high temperature environment resulting in plasma. The ionisation is achieved by collision of electrons of the arc with the neutral molecules of gas. The plasma protrudes out of the electrode encasement in the form of a flame. The consumable material in powdered form is poured intro the flame in tailored quantity. The powder melts immediately and absorbs the momentum of the expanding gas and rushes towards the target to form a thin deposited layer. The next layer deposits on the first immediately after and thus the coating builds up layer by layer.

The temperature in the plasma arc can be as high as 10000 deg C and is capable of melting anything. Electrode cooling arrangement is required to protect the plasmatron (i.e.plasma generator) from excessive heating.

Requirements of Plasma Spraying

Roughness Of The Substrate Surface : A rough surface provides a good coating adhesion. A rough surface provides enough room for anchorage of the splats facilitating bonding through mechanical interlocking. A rough surface is generally created by shot blasting technique.

Cleanliness Of The Substrate Surface : The substrate to be sprayed on must be free from any dirt or grease or any other material that might prevent intimate contact of the splat and the substrate. For that the substrate must be thoroughly cleaned (ultrasonically) with a solvent before spraying. Spraying must be immediately done after shot blasting and cleaning. Otherwise on the nascent surfaces, oxide layers tend to grow quickly and moisture may also affect the surface. These factors deteriorate the coating quality drastically.

Bond Coat : Materials like ceramics may not be sprayed directly onto the metals owing to the large difference between their thermal expansion coefficients. Ceramics have much lower value of and hence undergoes much less shrinkage as compared to the metallic base to form a surface in compression. If the compressive stress exceeds a particular limit, the coating tends to peel off. To alleviate this problem a suitable material, usually metallic of intermediate value, is plasma sprayed onto the substrate and is followed by plasma spraying of the ceramics. The choice of the bond coats depend on the type of application,e.g. in wear and thermal barrier applications Ni-Al [5] bond coat is popular when the top coat is a ceramic.

Process Parameters in Plasma Spraying : In plasma spraying one has to deal with a lot of process parameters which determine the degree of particle melting, adhesion strength, and deposition efficiency of the powder.[6] Some parameters are listed below:

- Arc Power :

Arc power determines the mass flow rate of a given powder that can be effectively melted by the arc. Deposition efficiency improves to a certain extent with an increase in arc power since it is associated with an enhanced particle melting. [7]

- Plasma Gas :

Normally nitrogen or argon doped with about 10% hydrogen or helium is used as plasma gas. The major constituent of the gas mixture is known as primary gas and the minor one is known as secondary gas.

- Carrier Gas :

Normally the primary gas itself is used as carrier gas. The flow rate of carrier gas is an important factor. A very low flow rate cannot convey the powder effectively to the plasma jet and if the flow rate is very high then the powders might escape the hottest region of the jet. There is an optimum flow rate for each powder at which the fraction of unmelted powder is minimum, and hence the deposition efficiency is maximum [6].

- Mass Flow Rate Of Powder :

Ideal mass flow rate of each powder has to be determined. Spraying with a lower mass flow rate keeping all other conditions constant results in under utilization and slow coating build up. On the other hand a very high mass flow rate may give rise to an incomplete melting resulting in high amount of porosity in the coating.

- Stand Off Distance :

It is the distance between the tip of the gun and the substrate surface. A long distance may result in the freezing of the melted particles before they reach the target, whereas a short standoff distance may not provide sufficient time for the particles in the flight to melt [7]. It is found that porosity of the coating increases and the thickness of the coating (hence deposition efficiency) decreases with an increase in the standoff distance.

- Spraying Angle :

The parameter is varied to accommodate the shape of the substrate. In coating alumina on, mild steel substrate, the coating porosity is found to increase as the spraying angle is increased from 30° to 60°[7]. Beyond 60° the porosity level remains unaffected by a further increase in spraying angle. The spraying angle also affects the adhesive strength of the coating.

- Substrate Cooling :

During continuous spraying the substrate might get heated up and may develop thermal stress related distortion accompanied by the coating peel off. This is especially true in situations where thick deposits are to be applied. To harness the surface temperature, it is kept cool by an auxiliary air supply system.

EXPERIMENTAL DETAILS

Ball Milling

As received zircon sand (procured from RRL Bhubeneshwar) could not be used directly for plasma spraying because of the size of the particle was too large for effective spraying. So the zircon powders were subjected to ball milling in a planetary ball mill. The ball milling parameters are listed below (Table 1).

Table 1 : Ball Milling Parameters :

Grinding balls	Agate
Milling medium	Toluene
Milling time	3 hrs
Milling speed	300 rpm
Ball to powder weight ratio	10 : 1
No. of balls	25
Ball diameter	10 mm
Volume of vial	250 cc

Sieving

Sieving is carried out because the powder size required for plasma spraying should be as uniform as possible to get uniform coating characteristics. The particles in the size range 45 μm to100 μm are taken for spraying. The finer particles and the particles above 100 μm are rejected.

Blending And Mixing

The alumina-zircon weight percent is decided as per the ternary diagram of alumina-zirconia-silica from the literature .To obtain mullite toughened zirconia Al_2O_3 / SiO_2 ratio should be 3 : 2 (mol %) as per the stoichiometry

In the plasma gas 1 mole of $ZrSiO_4$ will, be dissociated into 1 mol of ZrO_2 and 1 mol of SiO_2. So we can say $ZrSiO_4$: Al_2O_3 ratio equals 2 : 3 mol %. So the final composition arrived at was zircon = 55 weight % and alumina = 45 weight %. The blending was carried out in planetary ball mill in dry condition for 25 minutes.

Preparation Of Substrates

Low carbon steel (0.2% C) has been chosen as the substrate material. The specimens are rectangular having the dimensions 160 mm x 13 mm x 5 mm. The specimens are grit blasted at a pressure of about 60 psi using alumina grits. The grit blasted specimens are cleaned in an ultrasonic cleaning machine. Spraying is immediately carried out after cleaning.

Plasma Spraying

Nitrogen is used as a primary gas and hydrogen as the secondary gas. The powder feeding is external to the gun and an impingement angle of 90° is usually used. The properties of the coating are intimately associated with the spray process parameters and the parameters are listed below (Table 2 & 3).

Table 2 : Bond Coat Spraying Parameters

Parameter	Unit	Ni-Al bond coat	High carbon iron (HCI) bond coat
Primary gas pressure	psi	50	50
Secondary gas pressure	psi	50	50
Primary gas flow rate	cuft/hr	150	10
Secondary gas flow rate	cuft/hr	150	10
Carrier gas flow rate	cuft/hr	40	40
Powder flow rate	gm/min	70	60
Current	amperes	500	500
Voltage	volts	70-80	60-74
Standoff distance	mm	100-175	75-125

Table 3 : Top Coat Spraying Parameters

Parameter	Unit	Zircon top coat	Alumina – zircon top coat
Primary gas pressure	psi	50	50
Secondary gas pressure	psi	50	50
Primary gas flow rate	cuft/hr	100	75
Secondary gas flow rate	cuft/hr	10	15
Carrier gas flow rate	cuft/hr	40	40
Powder flow rate	gm/min	45	50
Current	amperes	520	500
Voltage	volts	65-70	68-74
Standoff distance	mm	50-100	50-100

RESULTS AND DISCUSSIONS

X–Ray Diffraction

X-Ray diffraction pattern of coated zircon-alumina is shown in the Figure 2. It consists of various phases of alumina along with monoclinic zirconia, cubic zirconia and mullite. The high temperature cubic zirconia is retained because of the splat cooling associated with the plasma process. Zircon dissociates into ZrO_2 and SiO_2 at 1676°C.

However at this temperature zircon remains in the solid state and therefore the kinetics of dissociation process is quite slow. If the zircon particles are heated above their melting point followed by rapid quenching, a near total phase seperation between ZrO_2 and SiO_2 is possible owing to a high difference in melting point of these two oxides (about 1000°C). Since the reaction takes place in liquid phase, the dissociation process is quite fast. Thermal plasma with a temperature as high as 15000°C is suitable for this dissociation. One or two mullite peaks are also obtained because at around 1500°C alumina combines with silica of zircon to form mullite, which gives superior thermal shock resistance to the coatings.

No sharp and separate SiO_2 peaks are present in the XRD pattern owing to the fact that SiO_2 exists in the amorphous state due to the rapid cooling associated with the plasma spraying. An amorphous solid has a structure characterized by an almost complete lack of periodicity and a tendency to order, only in the sense that the atoms are fairly tightly packed together and show a statistical preference for a particular interatomic distance; the result is an x-ray scattering curve showing nothing more than one or two broad maxima.

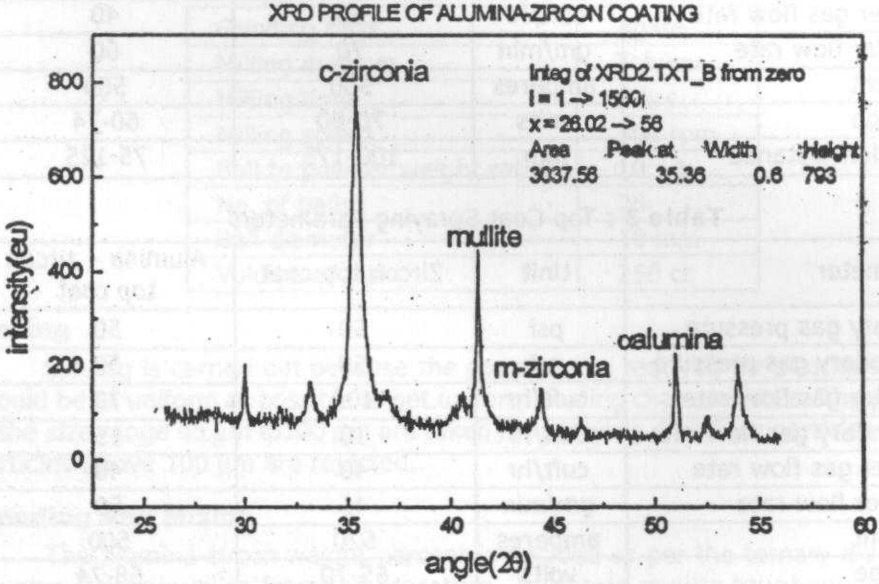
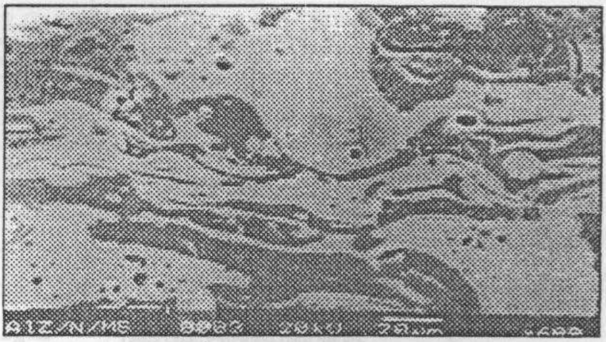


Fig. 2 : XRD Profile Of Alumina-Zircon Coating

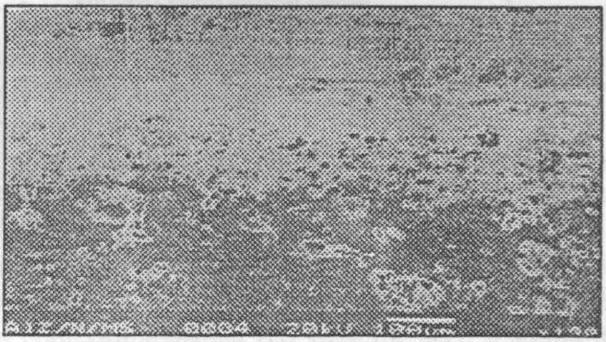
Scanning Electron Microscopy

The SEM micrographs for the cross section (Fig. 3) reveal that the substrate/ bond coat and the bond coat/top coat interfaces are continuous and without any trace of cracks. The coating seems to be very much adherent to the bond coat.

The SEM photograph of the polished top surface shows a uniformly distributed multi phase mixture of alumina, mullite and zirconia. The distribution of the phases is quite homogenous and no cracks are seen on the surface.



zircon-alumina top surface



zircon-alumina interface

Fig. 3 : SEM Photograph Of Top Surface(Above) And Coating Interface

Thermal Fatigue

The final failure of the coatings may occur owing to the oxidation of the bond coat. The ceramic coatings, in general have interconnected porosities and therefore the bond coat becomes oxidized after a finite number of cycles owing to the diffusion of oxygen through the interconnected pores of the top coat to the bond coat. This problem gets exacerbated by thermal fluctuation. Formation of these oxides is accompanied by an increase in volume resulting in the spallation of the coating.

Wear

The main objective of this project apart from producing a thermal barrier coating is to produce a wear resistant coating. Wear is expressed in terms of a cumulative weight loss as a function of time. In the present work, Zircon – alumina coating shows (Fig. 4) better wear resistance than zircon coating as is revealed by the graph. It shows that alumina-zircon top coat with Ni-Al bond coat shows better wear resistance than the one with high carbon iron bond coat. But both of them far outweigh zircon top coat. This may be due to the fact that alumina present in the coating strengthens the wear properties of the coating.

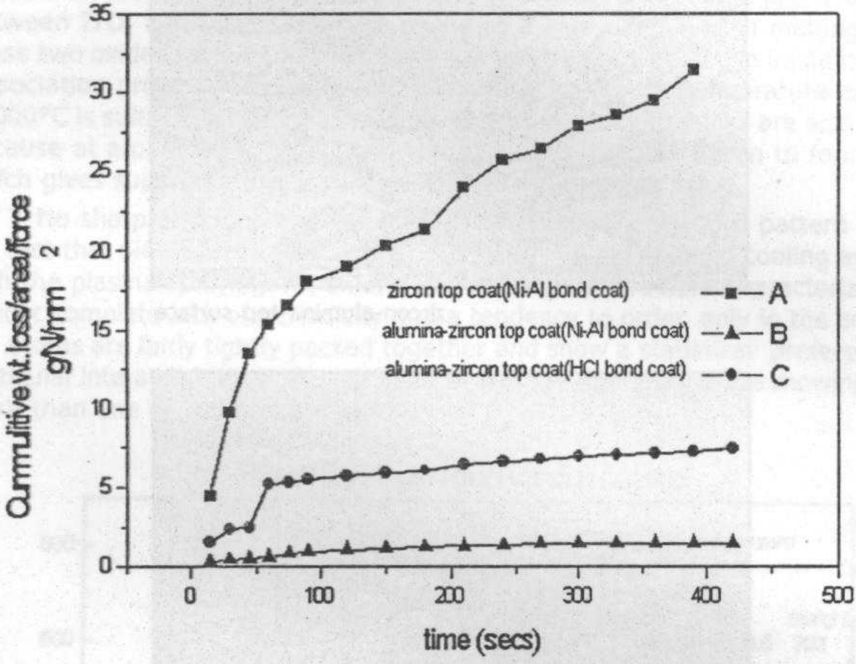


Fig. 4 : Wear Test Results

Grindability Of Plasma Sprayed Ceramic Coatings

The normal and tangential forces (Table 4) during grinding of plasma sprayed ceramic coating are obtained for different infeeds. It was observed that for an infeed of 25 microns, the tangential force comes to the range of 2-3 N whereas the normal force is between 3-4 N. When infeed is increased to 50 microns, no appreciable change in tangential force was observed. However the normal force increases and now varies from 7 to 13 N. The ratio of Fn to Ft also increased to about 3.3.

For an infeed of 75 microns, both the tangential and normal forces increased. The tangential force varied from 4-6 N while the normal force varied from 13 to 17 N. the ratio of Fn to Ft comes to around 2.5.

The ratio of tangential to normal forces was within acceptable limits given the fact that ceramics are very hard.

Table 4 : Grinding Forces, Grinding Specific Energy And Surface Finish

Infeed (µm)	Grinding forces (N)			Specific energy (J/mm3)	Surface roughness (R_a) µm
	Ft	Fn	Ft/Fn		
25	2.2	3.2	0.68	9.24	
	2.3	3.4	0.67	9.66	4.49
	2.0	3.0	0.67	8.40	
50	2.2	13.4	0.16	4.62	
	1.7	11.2	0.15	3.57	4.01
	2.2	7.0	0.31	4.62	
75	4.3	13.2	0.32	6.02	
	6.2	17.3	0.36	8.68	3.34
	6.4	15.2	0.42	8.96	

Cutting velocity, Vc=750.84 m/min., Work piece velocity, Vw=550m/min., Width of cut = 13 mm.

CONCLUSION

– The XRD results show the formation of mullite phase which exhibits excellent thermal shock resistance along with a good wear resistance.

– Wear behaviour of alumina-zircon top coat with Ni-Al bond coat is better than zircon top coat

– Thermal fatigue resistance obtained is also promising, the failure of the coating is due to the peel off from the oxidized layer of substrate and the bond coat and not due to the bond coat–top coat peel off.

– The grindability study reveals that the ratio of grinding forces are within an acceptable range, thus suggesting that the coatings have a good grindability.

– The SEM photographs show a continuous and a sound interface with no cracks in both the, cross section and the polished top surface.

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