

DEPOSITION OF SiC DERIVED FROM DESERT SAND AND WOOD CHARCOAL BY PLASMA PROCESSING

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE IN

Bachelor of Technology

in

Mechanical Engineering

By

RAKESH MOHANTY



**Department of Mechanical Engineering
National Institute of Technology Rourkela
2009**

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Under the Guidance of

Dr. Alok satapathy



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**NATIONAL INSTITUTE OF TECHNOLOGY
ROURKELA**

CERTIFICATE

This is to certify that the thesis entitled , “DEPOSITION OF SiC DERIVED FROM DESERT SAND AND WOOD CHARCOAL BY PLASMA PROCESSING ” submitted by Sri Rakesh Mohanty in partial fulfillment of the requirements for the award of Bachelor of Technology Degree in Mechanical Engineering at the NATIONAL INSTITUTE OF TECHNOLOGY, ROURKELA

(Deemed University) is an authentic work carried out by him under my supervision and guidance.

To the best of my knowledge ,the matter embodied in the thesis has not been submitted to any other University / Institute for the award of any Degree or Diploma .

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ACKNOWLEDGEMENT

I deem it a privilege to have been given such a project work as a part of our undergraduate course at this point of our student life. For this I am sincerely thankful to our **INSTITUTION NATIONAL INSTITUTE OF TECHNOLOGY, ROURKELA AND OUR MECHANICAL ENGINEERING DEPARTMENT .**

I would like to sincerely thank my project guide **Dr.Alok Satapathy** who has been a real source of inspiration, motivation to me and who at every point in the due course of my project guided me, helped me with his precious suggestions, and was ever willing to clear my doubts.

I would also like to sincerely thank Dr.K.P. Maity and Dr P. Rath who with their valuable comments and suggestions during the viva-voce helped me immensely. I would like to thank them because they were the ones who constantly evaluated me, corrected me and had been the guiding light for me.

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BRIEF ABSTRACT OF THE PROJECT

The basic aim of my project was to find a cheaper source of silicon carbide to use as coating on metal plates to increase their wear resistant properties.

Silicon carbide has very high wear resistant properties so is ideal for coating on metal surface using plasma processing.

The plasma process uses temperature of the order of 5000k and higher. So our target was to utilize this high temperature to fire a reaction between silica(SiO_2) and carbon to form silicon carbide.

For silica we used sand and for carbon we used wood charcoal. Though the reaction was theoretically possible but at such high temperature we couldn't be sure whether the chemical kinetics would follow the expected path. There was the risk of carbon behaving as reducing agent and converting alumina present in sand to aluminium.

So we decided to perform the experiment in Plasma Laboratory at the Laser and Plasma Technology Division, BARC so that the project does not just remain a theory.

CHAPTER 1

INTRODUCTION

BACKGROUND

The incessant quest for higher efficiency and productivity across the entire spectrum of manufacturing and engineering industries has ensured that most modern-day components are subjected to increasingly harsh environments during routine operation. Critical industrial components are, therefore, prone to more rapid degradation as the parts fail to withstand the rigors of aggressive operating conditions and this has been taking a heavy toll of industry's economy. In an overwhelmingly large number of cases, the accelerated deterioration of parts and their eventual failure has been traced to material damage brought about by hostile environments and also by high relative motion between mating surfaces, corrosive media, extreme temperatures and cyclic stresses. Simultaneously, research efforts focused on the development of new materials for fabrication are beginning to yield diminishing returns and it appears unlikely that any significant advances in terms of component performance and durability can be made only through development of new alloys.

As a result of the above, the concept of incorporating engineered surfaces capable of combating the accompanying degradation phenomena like wear, corrosion and fatigue to improve component performance, reliability and durability has gained increasing acceptance in recent years. The recognition that a vast majority of engineering components fail catastrophically in service through surface related phenomena has further fuelled this approach and led to the development of the broad interdisciplinary area of surface modifications. A protective coating deposited to act as a barrier between the surfaces of the component and the aggressive environment that it is exposed to during operation is now globally acknowledged to be an attractive means to significantly reduce/suppress damage to the actual component by acting as the first line of defense.

Surface modification is a generic term now applied to a large field of diverse technologies that can be gainfully harnessed to achieve increased reliability and enhanced performance of industrial components. The increasing utility and industrial adoption of surface engineering is a consequence of the significant recent advances in the field. Very rapid strides have been

made on all fronts of science, processing, control, modeling, application developments etc. and this has made it an invaluable tool that is now being increasingly considered to be an integral part of component design. Surface modification today is best defined as “the design of substrate and surface together as a system to give a cost effective performance enhancement, of which neither is capable on its own”. The development of a suitable high performance coating on a component fabricated using an appropriate high mechanical strength metal/alloy offers a promising method of meeting both the bulk and surface property requirements of virtually all imagined applications. The newer surfacing techniques, along with the traditional ones, are eminently suited to modify a wide range of engineering properties. The properties that can be modified by adopting the surface engineering approach include tribological, mechanical, thermo-mechanical, electrochemical, optical, electrical, electronic, magnetic/acoustic and biocompatible properties.

The development of surface engineering has been dynamic largely on account of the fact that it is a discipline of science and technology that is being increasingly relied upon to meet all the key modern day technological requirements: material savings, enhanced efficiencies, environmental friendliness etc. The overall utility of the surface engineering approach is further augmented by the fact that modifications to the component surface can be metallurgical, mechanical, chemical or physical. At the same time, the engineered surface can span at least five orders of magnitude in thickness and three orders of magnitude in hardness.

Driven by technological need and fuelled by exciting possibilities, novel methods for applying coatings, improvements in existing methods and new applications have proliferated in recent years. Surface modification technologies have grown rapidly, both in terms of finding better solutions and in the number of technology variants available, to offer a wide range of quality and cost. The significant increase in the availability of coating process of wide ranging complexity that are capable of depositing a plethora of coatings and handling components of diverse geometry today, ensures that components of all imaginable shape and size can be coated economically.

Existing surface treatment processes fall under three broad categories:

(a) Overlay Coatings: This category incorporates a very wide variety of coating processes wherein a material different from the bulk is deposited on the substrate. The coating is

distinct from the substrate in the as-coated condition and there exists a clear boundary at the substrate/coating interface. The adhesion of the coating to the substrate is a major issue.

(b) Diffusion Coatings: Chemical interaction of the coating-forming element(s) with the substrate by diffusion is involved in this category. New elements are diffused into the substrate surface, usually at elevated temperatures so that the composition and properties of outer layers are changed as compared to those of the bulk.

(c) Thermal or Mechanical Modifications of Surfaces: In this case, the existing metallurgy of the component surface is changed in the near-surface region either by thermal or mechanical means, usually to increase its hardness. The type of coating to be provided depends on the application. There are many techniques available, e.g. electroplating, vapour depositions, thermal spraying etc. Of all these techniques, thermal spraying is popular for its wide range of applicability, adhesion of coating with the substrate and durability. It has gradually emerged as the most industrially useful method of developing a variety of coatings, to enhance the quality of new components as well as to reclaim worn/wrongly machined parts.

The type of thermal spraying depends on the type of heat source employed and consequently flame spraying (FS), high velocity oxy-fuel spraying (HVOF), plasma spraying (PS) etc. come under the umbrella of thermal spraying. Plasma spraying utilizes the exotic properties of the plasma medium to impart new functional properties to conventional and non-conventional materials and is considered as one highly versatile and technologically sophisticated thermal spraying technique. It is a very large industry with applications in corrosion, abrasion and temperature resistant coatings and the production of monolithic and near-net shapes [1]. The process can be applied to coat on variety of substrates of complicated shape and size using metallic, ceramic and /or polymeric consumables. The production rate of the process is very high and the coating adhesion is also adequate. Since the process is almost material independent, it has a very wide range of applicability, e.g., as thermal barrier coating, wear resistant coating etc. Thermal barrier coatings are provided to protect the base material, e.g., internal combustion engines, gas turbines etc. at elevated temperatures. Zirconia (ZrO_2) is a conventional thermal barrier coating material. As the name suggests, wear resistant coatings are used to combat wear especially in cylinder liners, pistons, valves, spindles, textile mill rollers etc. alumina (Al_2O_3), titania (TiO_2) and zirconia (ZrO_2) are the some of the conventional wear resistant coating materials [1].

One major limitation of the process is the relatively high price of the plasma sprayable consumables. Thus there is a need to explore the coatability of cheaper materials like desert sand, fly ash and other industrial wastes. 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 [2]. 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 [3]. Satapathy et al. reported the development of plasma spray coating of another industrial waste called red mud on various metal substrates [4]. The study revealed that the coatings of red mud pre-mixed with metal powder exhibit improved adhesion compared to the raw red mud coatings [5]. Ramakrishna et. al. [6] 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.

Against this background, the present study has been undertaken to produce and characterize plasma sprayed composite coatings of desert sand (Silica) premixed with carbon powder on metal substrates.

OBJECTIVE

The objectives of the present investigation can be outlined as :

- a. To explore the possibility of producing a SiC deposition by plasma spraying of desert sand+ carbon powder on metal substrates
- b. Micro-structural characterization to evaluate the soundness of the coatings.
- c. Mechanical characterization to evaluate the micro-hardness and interface bond strength of the coatings.

CHAPTER 2

LITERATURE REVIEW

INTRODUCTION

This chapter deals with the literature survey on various aspects of plasma spraying, the coating materials and their characteristics. At the end of the chapter a summary of the literature survey and the knowledge gap in the earlier investigations are presented.

THERMAL SPRAYING

It is the generic category of surface modification technique that apply consumables in the form of a finely divided molten or semi molten droplets to produce a coating onto the substrate kept in front of the impinging jet. The melting of the consumables may be accomplished in a number of ways, and the consumable can be introduced into the heat source in wire or powder form. Thermal spray consumables can be metallic, ceramic or polymeric substances. Any material can be sprayed as long as it can be melted by the heat source employed and does not undergo degradation during heating [7, 8]. An interesting aspect of thermal spraying is that the surface temperature seldom exceeds 200⁰ C. Hard metal or ceramic coating can be applied to thermosetting plastics. Stress related distortion problems are also not so significant. The spraying action is achieved by the rapid expansion of combustion gases (which transfer the momentum to the molten droplets) or by a separate supply of compressed air.

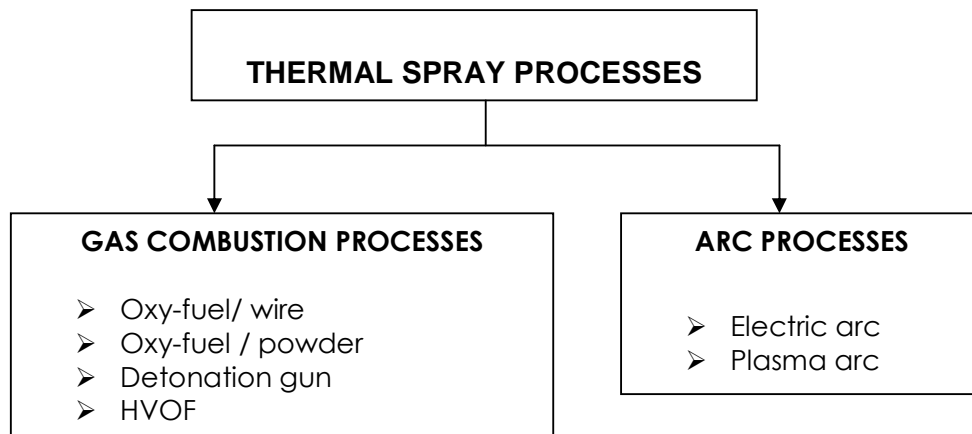


Fig. 2.1 Categorization of common thermal spray processes

Figure 2.1 shows the common thermal spray processes fitting into the above mentioned categories. The plasma spraying process is discussed briefly in the following.

Plasma Spraying

Plasma spraying is the most versatile thermal spraying process and the general arrangement is shown in Figure 2.2. 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 ionization in the high temperature environment resulting plasma. The ionization is achieved by collisions of electrons of the arc with the neutral molecules of the gas. The plasma protrudes out of the electrode encasement in the form of a flame. The consumable material, in the powdered form, is poured into the flame in metered quantity. The powders melt immediately and absorb the momentum of the expanding gas and rush towards the target to form a thin deposited layer. The next layer deposits onto the first immediately after, and thus the coating builds up layer by layer. The temperature in the plasma arc can be as high as $10,000^{\circ}\text{C}$ and it is capable of melting anything. Elaborate cooling arrangement is required to protect the plasmatron (i.e., the plasma generator) from excessive heating. The equipment consists of the following modules [9,10,11].

- The plasmatron : It is the device which houses the electrodes and in which the plasma reaction takes place. It has the shape of a gun and it is connected to the water cooled power supply cables, powder supply hose and gas supply hose.
- The power supply unit : Normally plasma arc works in a low voltage (40-70 volts) and high current (300-1000 Amperes), DC ambient. The available power (AC, 3 phase, 440 V) must be transformed and rectified to suit the reactor. This is taken care of by the power supply unit.
- The powder feeder : The powder is kept inside a hopper. A separate gas line directs the carrier gas which fluidizes the powder and carries it to the plasma arc. The flow rate of the powder can be controlled precisely.

- The coolant water supply unit : It circulates water into the plasmatron, the power supply unit, and the power cables. Units capable of supplying refrigerated water are also available.
- The control unit : Important functions (current control, gas flow rate control etc.) are performed by the control unit. It also consists of the relays and solenoid valves and other interlocking arrangements essential for safe running of the equipment. For example the arc can only be started if the coolant supply is on and water pressure and flow rate is adequate.

The Requirements for 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. The roughness obtained is determined by shot blasting parameters, i.e., shot size, shape and material, air pressure, standoff distance between nozzle and the job, angle of impact, substrate material etc.

Cleanliness of the substrates: 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 this purpose the substrate must be thoroughly cleaned (ultrasonically, if possible) with a solvent before spraying. Spraying must be conducted immediately after shot blasting and cleaning.

Cooling water : For cooling purpose distilled water should be used, whenever possible. Normally a small volume of distilled water is recirculated into the gun and. it is cooled by an external water supply from a large tank. Sometime water from a large external tank is pumped directly into the gun.

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. Deposition efficiency is the ratio of amount of powder deposited to the amount fed to the gun. An elaborate listing of these parameters and their effects are reported in the literature [12,13].

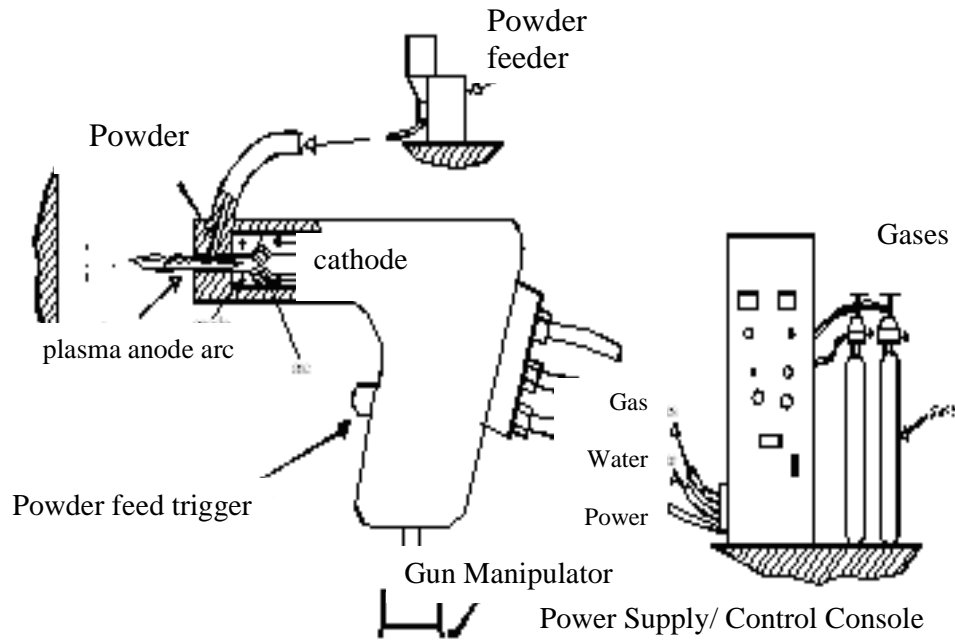


Fig. 2.2 Arrangement for the plasma spraying

Some important parameters and their roles are listed below:

Arc power : It is the electrical power drawn by the arc. The power is injected in to the plasma gas, which in turn heats the plasma stream. Part of the power is dissipated as radiation and also by the gun cooling water. 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 [14]. However, increasing power beyond a certain limit may not cause a significant improvement. On the contrary, once a complete particle melting is achieved, a higher gas temperature may prove to be harmful. In the case of steel, at some point vaporization may take place lowering the deposition efficiency.

Plasma gas: Normally nitrogen or argon doped with about 10% hydrogen or helium is used as a plasma gas. The major constituent of the gas mixture is known as primary gas and the minor is known as the secondary gas. The neutral molecules are subjected to the electron bombardment resulting in their ionization. Both temperature and enthalpy of the gas increase as it absorbs energy. Since nitrogen and hydrogen are diatomic gases, they first undergo dissociation followed by ionization. Thus they need higher energy input to enter the plasma

state. This extra energy increases the enthalpy of the plasma. On the other hand, the mono-atomic plasma gases, i.e. argon or helium, approach a much higher temperature in the normal enthalpy range. Good heating ability is expected from them for such high temperature. In addition, hydrogen followed by helium has a very high specific heat, and therefore is capable of acquiring very high enthalpy. When argon is doped with helium the spray cone becomes quite narrow which is especially useful for spraying on small targets.

Carrier gas: Normally the primary gas itself is used as a carrier gas. The flow rate of the 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 [15,16].

Mass flow rate of powder: Ideal mass flow rate for 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 buildup. On the other hand, a very high mass flow rate may give rise to an incomplete melting resulting in a high amount of porosity in the coating. The unmelted powders may bounce off from the substrate surface as well keeping the deposition efficiency low [17].

Torch to base distance : It is the distance between the tip of the gun and the substrate surface. A long distance may result in freezing of the melted particles before they reach the target, whereas a short standoff distance may not provide sufficient time for the particles in flight to melt [17]. The relationship between the coating properties and spray parameters in spraying alpha alumina has been studied in details [18]. It is found that the porosity increases and the thickness of the coating (hence deposition efficiency) decreases with an increase in standoff distance. The usual alpha-phase to gamma-phase transformation during plasma spraying of alumina has also been restricted by increasing this distance. A larger fraction of the unmelted particles go in the coating owing to an increase in torch to base distance.

Spraying angle: This 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°. 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. The influence of spraying angle on the cohesive strength of

chromia, zirconia 8-wt% yttria and molybdenum has been investigated, and it has been found that the spraying angle does not have much influence on the cohesive strength of the coatings.

COMMON CERAMIC COATINGS

Today a variety of materials, e.g., carbides, oxides etc., belonging to the above category are available commercially.

(i) Carbides: WC, TiC, SiC, ZrC, Cr₂C₃ etc.

(ii) Oxides: Al₂O₃, Cr₂O₃, TiO₂, ZrO₂ etc.

The choice of a material depends on the application. However, the ceramic coatings are very hard and hence on an average offer more abrasion resistance than their metallic counterparts.

Carbide Coatings

Amongst carbides, WC is very popular for wear and corrosion applications [19]. The WC powders are clad with a cobalt layer. During spraying the cobalt layer undergoes melting and upon solidification form a metallic matrix in which the hard WC particles remain embedded. Spraying of WC-Co involves a close control of the process parameters such that only the cobalt phase melts without degrading the WC particles. Such degradation may occur in two ways:

- Oxidation of WC leading to the formation of CoWO₄ and WC₂.
- Dissolution of WC in the cobalt matrix leading to a formation of brittle phases like CoW₃C which embrittles the coating.

An increase in the spraying distance and associated increase of time in flight lead to a loss of carbon and a pickup of oxygen. As a result the hardness of the coating decreases. An increase in plasma gas flow rate reduces the dwell time and hence can control the oxidation to some extent. However, it increases the possibility of cobalt dissolution in the matrix [20]. The other option to improve the quality of such coating is to conduct the spraying procedure in vacuum.

Often carbides like TiC, TaC and NbC are provided along with WC in the cermet to improve upon the oxidation resistance, hardness, and hot strength. Similarly the binder phase is also modified by adding chromium and nickel with cobalt. The wear mechanism of plasma sprayed WC-Co coatings depends on a number of factors, e.g., mechanical properties, cobalt content, experimental conditions, mating surfaces, etc. The wear mode can be abrasive, [21]

adhesive or surface fatigue. The coefficient of friction of WC-Co (in self mated condition) increases with increasing cobalt content. A WC-Co coating when tested at a temperature of 450°C exhibits signs of melting. The wear resistance of these coatings also depends on porosity. Pores can also act as source from where the cracks may grow. Thermal diffusivity of the coatings is another important factor. In narrow contact regions, an excessive heat generation may occur owing to rubbing. If the thermal diffusivity of the coating is low the heat cannot escape from a narrow region easily resulting a rise in temperature and thus failure occurs owing to thermal stress. The wear mechanism of WC-Co nano-composite coating on mild steel substrates has been studied in details [22, 23]. The wear rates of such coatings are found to be much greater than that of commercial WC-Co composite coating, presumably owing to an enhanced decomposition of nano-particles during spraying. Wear has been found to occur by subsurface cracking along the preferred crack paths provided by the binder phase or failure at the inter-splat boundary. Coatings of TiC or TiC+ TaC with a nickel cladding are alternative solutions for wear and corrosion problems. High temperature stability, low coefficient of thermal expansion, high hardness and low specific gravity of these coatings may outperform other materials, especially in steam environment. Instead of nickel, nickel chromium alloy can serve as the matrix material. The mode of wear can be adhesive, abrasive, surface fatigue or micro-fracture depending on operating conditions [24, 25].

Oxide Coatings

Metallic coatings and metal containing carbide coatings sometime are not suitable in high temperature environments in both wear and corrosion applications. Often they fail owing to oxidation or decarburization. In such case the material of choice can be an oxide ceramic coating, e.g., Al_2O_3 , Cr_2O_3 , TiO_2 , ZrO_2 or their combinations. However, a high wear resistance, and chemical and thermal stability of these materials are counterbalanced by the disadvantages of low values of thermal expansion coefficient, thermal conductivity, mechanical strength, fracture toughness and somewhat weaker adhesion to substrate material. The thickness of these coatings is also limited by the residual stress that grows with thickness. Therefore, to obtain a good quality coating it is essential to exercise proper choice of bond coat, spray parameters and reinforcing additives.

Chromia (Cr_2O_3) Coatings

These coatings are applied when corrosion resistance is required in addition to abrasion resistance. It adheres well to the substrate and shows an exceptionally high hardness 2300

HV 0.5 kg [26,27] Chromia coatings are also useful in ship and other diesel engines, water pumps, and printing rolls. A Cr_2O_3 - 40 wt% TiO_2 coating provides a very high coefficient of friction (0.8), and hence can be used as a brake liner. The wear mode of chromia coatings has been investigated under various conditions. Depending on experimental conditions, the wear mode can be abrasive, plastic deformation, microfracture or a conglomerate of all of these [28]. This material has also been tested under lubricated conditions, using inorganic salt solutions (NaCl , NaNO_3 , Na_3PO_4) as lubricants and also at a high temperature. The wear rate of self-mated chromia is found to increase considerably at 450°C , and plastic deformation and surface fatigue are the predominant wear mechanisms. Under lubricated condition, the coatings exhibit tribo-chemical wear]. It has also been tested for erosion resistance [29].

Zirconia (ZrO_2) Coatings

Zirconia is widely used as a thermal barrier coating. However, it is endowed with the essential qualities of a wear resistant material, i.e., hardness, chemical inertness, etc. and shows reasonably good wear behaviour. In the case of a hot pressed zirconia mated with high chromium containing iron (martensitic, austenitic, or pearlitic), it has been found that in course of rubbing the iron transfers on to the ceramic surface and the austenitic material adheres well to the ceramic as compared to their martensitic or pearlitic counterparts [30]. The thick film improves the heat transfer from the contact area keeping the contact temperature reasonably low; thus the transformation of ZrO_2 is prevented. On the other hand with the pearlitic or martensitic iron the material transfer is limited. The contact temperature is high enough to bring about a phase transformation and related volume change in ZrO_2 causing a stress induced spalling. In a similar experiment the wear behaviour of sintered, partially stabilized zirconia (PSZ) with 8 wt% yttria against PSZ and steels has been tested at 200°C . When metals are used as the mating surface, a transferred layer soon forms on the ceramic surface (coated or sintered). In ceramic-ceramic system the contact wear is abrasive in nature. However, similar worn particles remain entrapped between the contact surfaces and induce a polishing wear too. In the load range of 10 to 40 N, no transformation of ZrO_2 occurs. However, similar tests conducted at 800°C show a phase transformation from monoclinic ZrO_2 to tetragonal ZrO_2 . The wear debris of ZrO_2 sometimes gets compacted in repeated loading and gets attached to the worn surface forming a protective layer. During rubbing, pre-existing or newly formed cracks may grow rapidly and eventually interconnect with each other, leading to a spallation of the coating. Introduction of alumina as a dopant has been found to improve the wear performance of the ceramic significantly. Here plastic

deformation is the main wear mode. The wear performance of zirconia at 400°C and 600°C has been reported in the literature [31]. At these temperatures the adhesive mode of wear plays the major role.

Titania (TiO₂) Coating

Titania coating is known for its high hardness, density, and adhesion strength. It has been used to combat abrasive, erosive and fretting wear either in essentially pure form or in association with other compounds. The mechanism of wear of TiO₂ at 450°C under both lubricated and dry contact conditions has been studied [32, 33]. It has been found to undergo a plastic smearing under lubricated contact, where as it fails owing to the surface fatigue in dry condition. TiO₂-stainless steel couples in various speed load conditions have also been investigated in details [34]. At a relatively low load, the failure is owing to the surface fatigue and adhesive wear, whereas at a high load the failure is attributed to the abrasion and delamination associated with a back and forth movement. At a high speed, Fe₃O₄ forms instead of Fe₂O₃. The TiO₂ top layer also softens and melts owing to a steep rise in temperature, which helps in reducing the temperature subsequently. The performance of the plasma sprayed pure TiO₂ has been compared with those of Al₂O₃ – 40 wt% TiO₂ and pure Al₂O₃ under both dry and lubricated contact conditions [35]. TiO₂ shows the best results. TiO₂ owing to its relatively high porosity can provide good anchorage to the transferred film and also can hold the lubricants effectively.

Alumina (Al₂O₃) Coatings

Alumina is obtained from a mineral called bauxite, which exists in nature as a number of hydrated phases, e.g., boehmite (γ -Al₂O₃, H₂O), hydrargillate, diaspor (α -Al₂O₃, 3H₂O). It also exists in several other metastable forms like β , δ , θ , η , κ and X [36]. α -Al₂O₃ is known to be a stable phase and it is available in nature in the form of corundum. In addition, α -Al₂O₃ can be extracted from the raw materials by fusing them.

The phase transformation during freezing of the plasma sprayed alumina droplets has been studied in details [36, 37]. There are several advantages of alumina as a structural material, e.g., availability, hardness, high melting point, resistance to wear and tear etc. It bonds well with the metallic substrates when applied as a coating on them. Some of the applications of alumina are in bearings, valves, pump seals, plungers, engine components, rocket nozzles, shields for guided missiles, vacuum tube envelopes, integrated circuits, etc. Plasma sprayed alumina-coated railroad components are presently being used in Japan [38].

Properties of alumina can be further complemented by the particulate (TiO_2 , TiC) or whisker (SiC) reinforcement. TiC reinforcement limits the grain growth, improves strength and hardness, and also retards crack propagation through the alumina matrix. The sliding wear behaviour of both monolithic and SiC whisker reinforced alumina has been studied [39]. The whisker reinforced composite has been found to have good wear resistance. The monolithic alumina has a brittle response to sliding wear, whereas the worn surface of the composite reveals signs of plastic deformation along with fracture. The whiskers also undergo pullout or fracture.

TiO_2 is a commonly used additive in plasma sprayable alumina powder. TiO_2 , has a relatively low melting point and it effectively binds the alumina grains. However, a success of an Al_2O_3 - TiO_2 coating depends upon a judicious selection of the arc current, which can melt the powders effectively. This results in a good coating adhesion along with high wear resistance [40]. The wear performance of Al_2O_3 and Al_2O_3 -50 wt% TiO_2 has been reported in the literature [41]. In dry sand abrasion testing, alumina outperformed others presumably owing to its high hardness. In dry sliding at low velocity range, the tribocouple (ceramic and hardened stainless steel) exhibits stick-slip [42]. At relatively high speed range, the coefficient of friction drops owing to the thermal softening of the interface. The wear of alumina is found to increase appreciably beyond a critical speed and a critical load. Alumina has been found to fail by plastic deformation, shear and grain pullout. In dry and lubricated sliding as well, the mixed ceramic has been found to perform better than pure alumina. A coating of Al_2O_3 -50 wt% TiO_2 is quite porous and hence is quite capable of holding the transferred metallic layer which protects the surface. Wear performance of such coatings can further be improved by a sealing of the pores by polymeric substances. A low thermal diffusivity of the alumina coatings results in a high localized thermal stress on the surface. The mode of wear of alumina is mainly abrasive. The pore size and pore size distribution also play a vital role in determining the wear properties. The Al_2O_3 - TiO_2 coating has a high thermal diffusivity and hence it is less prone to wear.

As far as the field of ceramic coating is concerned, during last decade, although a large number of investigations have been carried-out on processing of variety of plasma spray ceramic coatings, not much effort has been made to use low-grade and cheaply and abundantly available materials for this purpose. Desert sand being rich in silica, has 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.

Against this background, the present research work has been undertaken, with an objective to explore the possibility of developing a SiC coating from a mixture of desert sand and carbon on metals. Sand does not belong to the so called plasma sprayable category and is cheap.

The future possesses challenges to the scientists, technologists and engineers towards sound exploration of cheaper and less expensive coating materials like sand. It will continue to be an important area of concern in coming years. The present investigation is a step in this direction.

CHAPTER 3

MATERIALS AND METHODS

This chapter deals with the details of the experimental procedures followed in this study. The coating process itself requires some basic preparations that include powder sieving, shot blasting on the substrate surface, cleaning etc. After plasma spraying, the coated materials are subjected to a series of tests, e.g., micro-structural characterization, micro-hardness measurement, X - ray diffraction, adhesion test etc. The details of each process are described here.

DEVELOPMENT OF THE COATINGS

Powders for Coating

In this study, desert sand (Silica) and coal dust (Carbon) are used as raw materials for coating deposition on aluminum substrates. The as-received silica sand is sieved to obtain particles in the desired size range i.e. 80 - 100 micron. Desert sand (Silica) and coal dust (Carbon) powders are thoroughly mixed in 5:1 ratio by weight.

Preparation of Substrates

Commercially available aluminium is chosen as the substrate material. The specimens are rectangular in shape having a dimension 50 mm x 25 mm x 2 mm and are grit blasted at a pressure of 3 kg/cm² using alumina grits having a grit size of 60. The standoff distance in shot blasting is kept between 120-150 mm. The average roughness of the substrates is 6.8 μm . The grit blasted specimens are cleaned with acetone. Spraying is carried out immediately after cleaning.

Plasma Spraying

The spraying is done at the Thermal Plasma Laboratory at the Laser and Plasma Technology Division, BARC. A conventional atmospheric plasma spraying (APS) set up is used. The plasma input power is varied from 8 to 24 kW by controlling the gas flow rate, voltage and the arc current. The powder feed rate is kept constant at 10 gm/min, using a turntable type volumetric powder feeder.

The general arrangement of the plasma spraying equipment and schematic diagram of the plasma spraying process are shown in figures 3.1 and 3.2 respectively. The equipment consists of the following units:

1. Plasma spraying gun
2. Control console
3. Powder feeder
4. Power supply
5. Torch cooling system (water)
6. Hoses, cables, gas cylinders and accessories

Argon is used as the plasmagen gas. The powders are deposited at spraying angle of 90° . The powder feeding is external to the gun. The other operating parameters during coating deposition process are listed in Table 3.1.

Operating Parameters	Values
Plasma Arc Current (amp)	200, 250, 320, 400
Arc Voltage (volt)	40, 48, 50, 60
Torch Input Power (kW)	8, 12, 15, 20, 24
Plasma Gas (Argon) Flow Rate (lpm)	20
Carrier Gas (Argon) Flow Rate (lpm)	7
Powder Feed Rate (gm/min)	10
Torch to Base Distance TBD (mm)	100

Table 3.1 Operating parameters during coating deposition

CHARACTERIZATION OF COATINGS

Coating Thickness Measurement

Thickness of the coatings on different substrates are measured on the polished cross-sections of the samples, using an optical microscope. Five readings are taken on each specimen and the average value is reported as the mean coating thickness.

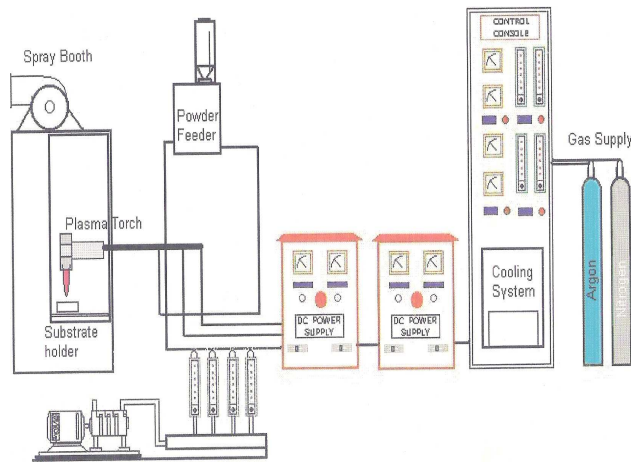


Fig. 3.1 General arrangement of the plasma spraying equipment

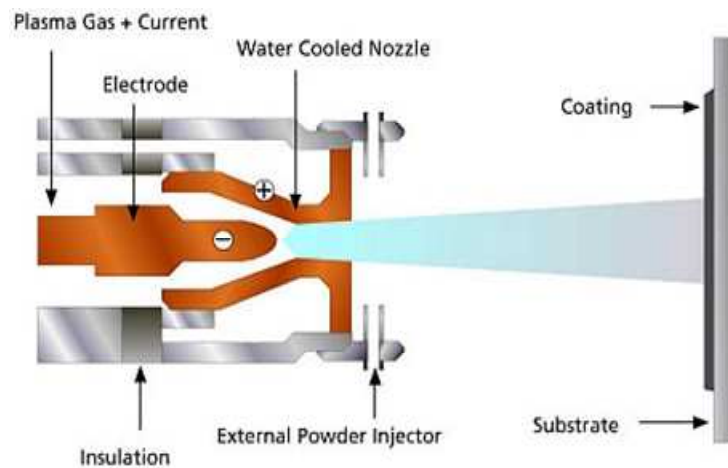


Fig. 3.2 Schematic diagram of the plasma spraying process

Evaluation of Coating Adhesion Strength

To evaluate the coating adhesion strength, a special type jig is fabricated. Cylindrical mild steel dummy samples (length 25 mm, top and bottom diameter 9.5 mm) are prepared. The surfaces of the dummies are roughened by punching. These dummies are then fixed on top of the coating with the help of a polymeric adhesive (epoxy 900-C) and pulled with tension after being mounted on the jig (fig. 3.3). The coating pullout test is carried out using the set up Instron 1195 (fig. 3.5) at a crosshead speed of 10 m/minute. The moment coating gets torn off from the specimen, the reading (of the load), which corresponds to the adhesive strength of the coating, is recorded. A typical test set up (during testing) is shown in figure 3.4. The test is performed as per ASTM C-633.



Fig. 3.3 Jig used for the test



Fig. 3.4 Specimen under tension



Fig. 3.5 Adhesion test set up Instron 1195

X-Ray Diffraction Studies

The coatings are examined for the identification of the (crystalline) phases with a Philips X Ray Diffractometer. The X ray diffractograms are taken using Cu K α radiation.

Scanning Electron Microscopic Studies

Specimens of size 10 mm x 13 mm x 2 mm are sliced from the coated samples for SEM observation. The coating surfaces and interfaces (cross section of specimens) are observed in scanning electron microscope Jeol T 330 mostly using the secondary electron imaging.

Porosity Measurement

Measurement of porosity is done using the image analysis technique. The polished top coats are kept under a microscope (Neomate) equipped with a CCD camera (JVC, TK 870E). This system is used to obtain a digitized image of the object. The digitized image is transmitted to a computer equipped with VOIS image analysis software. The total area captured by the

objective of the microscope or a fraction thereof can be accurately measured by the software. Hence the total area and the area covered by the pores are separately measured and the porosity of the surface under examination is determined.

Microhardness Measurement

Microhardness measurement is made using Leitz Microhardness Tester equipped with a monitor and a microprocessor based controller, with a load of 0.493N and a loading time of 20 seconds. About five readings are taken on each sample and the average value is reported as the data point. A diamond indenter, in the form of a right pyramid with a square base and an angle 136° between opposite faces, is forced into the material under a load F. The two diagonals X and Y of the indentation left on the surface of the material after removal of the load are measured and their arithmetic mean L is calculated. In the present study, the load considered F = 0.493N and Vickers hardness number is calculated using the following equation.

$$H_v = 0.1889 \frac{F}{L^2} \quad \text{and} \quad L = \frac{X + Y}{2}$$

Where F is the applied load (N), L is the diagonal of square impression (mm), X is the horizontal length (mm) and Y is the vertical length (mm).

Evaluation of Coating Deposition Efficiency

Deposition efficiency is defined as the ratio of the weight of coating deposited on the substrate to the weight of the expended feedstock. Weighing method is accepted widely to measure this. Each specimen is weighed before and after coating deposition. The difference is the weight (G_c) of coating deposited on the substrate. From the powder feed rate and time of deposition the weight of expended feed stock (G_p) is determined. The deposition efficiency (η) is then calculated using the following equation.

$$\eta = \left(\frac{G_c}{G_p} \times 100 \right) \%$$

Weighing of samples is done using a precision electronic balance with + 0.1 mg accuracy.

CHAPTER 4

RESULTS AND DISCUSSION

Plasma sprayed sand and charcoal powder coatings are developed on two different substrates (aluminium, mild steel) using a 40 kW atmospheric plasma spray system supplied by M/s Ion Arc Machines (India) Pvt. Ltd. at the Thermal Plasma Laboratory in the Laser and Plasma Technology Division, BARC. Spraying is done at five different input power level to the dc plasma torch in the range from 8 kW to 24 kW. Characterization of the coatings is done with respect to their quality. The results of various tests are presented and discussed in this chapter.

COATING ADHESION STRENGTH

From the microscopic point of view, adhesion is due to physico-chemical surface forces (Vander-walls, Covalent, ionic...), which can be established at the coating-substrate interface and corresponds to the work of adhesion. From the mechanical point of view, adherence can be estimated by the force corresponding interfacial fracture and is macroscopic in nature. Coating adherence tests have been carried out by many investigators with various coatings. It has been stated that 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 condition.

In this work, evaluation of coating interface bond strengths is done using coating pullout method, conforming to ASTM C-633 standard. It is found that in all the samples fracture occurred at the coating-substrate interface. The results obtained for coatings are shown as the variation of coating-substrate interface adhesion strength with operating power level of the plasma torch are presented in Figures 4.1. Maximum adhesion strength of about 23 MPa is recorded on aluminium substrate at 16 kW.

The influence of torch input power on coating adhesion is evident from all these graphs. In case of pure fly ash coating on aluminium substrate, the strength has increased with increase in operating power from 6 kW to 9 kW. Coating deposited beyond 9 kW operating power exhibited a detrimental effect on interface bond strength. It is noted that invariably in all cases the interface bond strength increases with the input power of the torch up to a certain power level and then shows a decreasing trend in coating adhesion. Initially, when the

operating power level is increased, the melting fraction and velocity of the particles also increases. Therefore there is better splashing and mechanical inter-locking of molten particles on the substrate surface leading to increase in adhesion strength. But, at a much higher power level, the amount of fragmentation and vaporization of the particles 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.

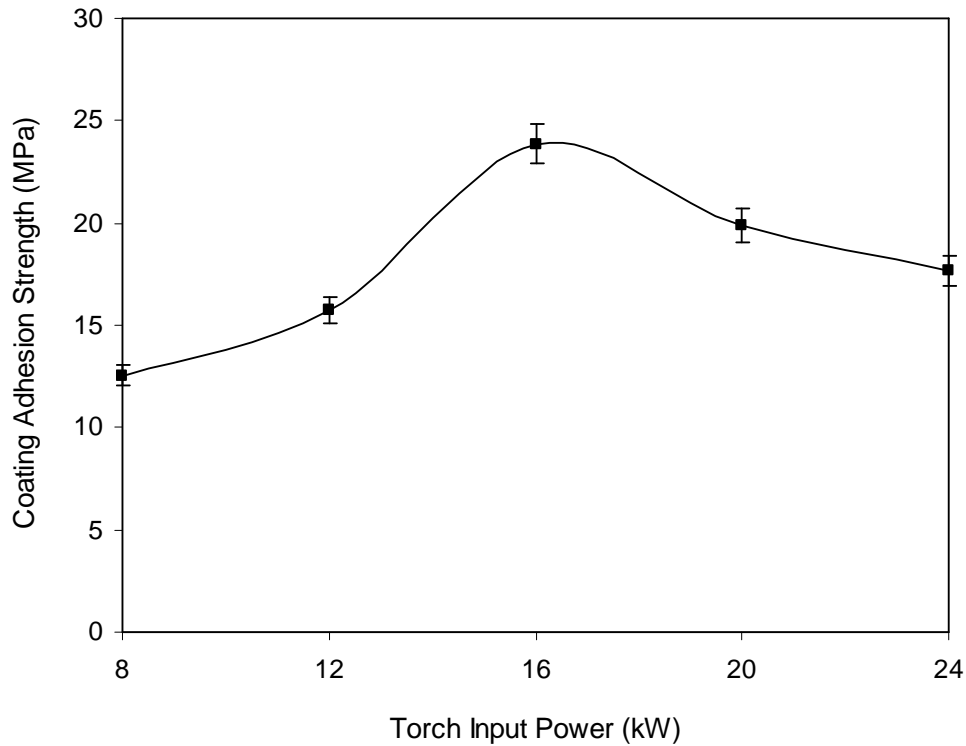


Fig. 4.1 Coating Adhesion strength of Silica-Carbon Coatings made at different power level

It is noted that the interface bond strength increases with increase in aluminium content in the sand and wood charcoal powder + aluminium composite coatings. This improvement in interface adhesion with addition of aluminium may be due to formation of alumina which might have helped in increasing the inter-particle bonding.

COATING HARDNESS

Micro-hardness measurement is done on these coatings with Leitz Micro-Hardness Tester using 50Pa (0.493N) on all samples. The results are summarized in table 4.1. The results show that these coatings bear high hardness, varying from 918 to 1058 Hv. Premixing of carbon powder to silica sand is also found to enhance hardness values. This may be due to

the formation of SiC during the in-flight traverse within the high temperature plasma jet and the formation of some inter-oxide compounds.

Torch Input Power (kW)	Maximum Coating Hardness (Hv)
8	918
12	1058
16	965
20	968
24	959

Table 4.1 Micro-hardness of Coatings deposited at different operating power level

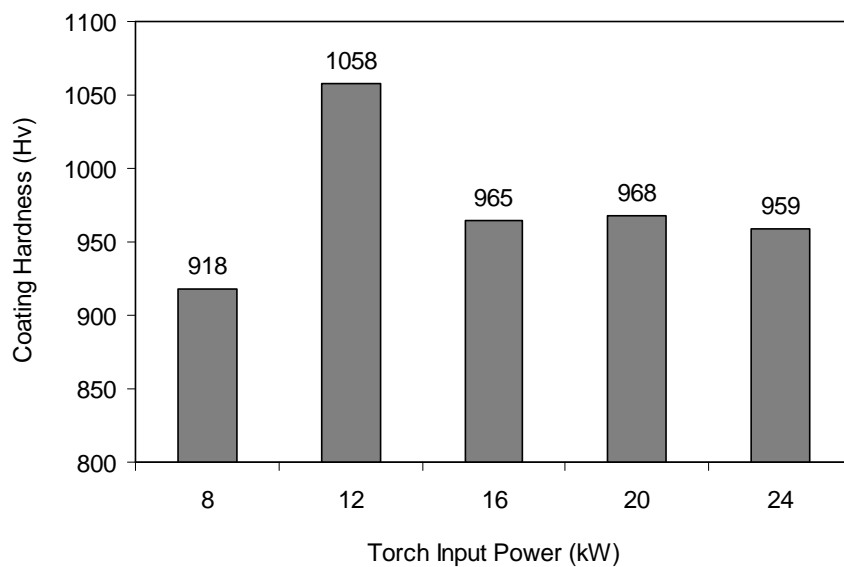


Figure 4.2 Micro-hardness of Coatings deposited at different operating power level

XRD PHASE COMPOSITION ANALYSIS

To ascertain the phases present and phase changes / transformation taking place during plasma spraying, the X-ray diffractograms are taken on the raw material and on the coatings using a Philips X Ray Diffractometer. The XRD results are shown in Figures 4.3 and 4.4. From the diffractograms it is seen that the major constituent present in the raw material (desert sand) is quartz (SiO_2) with little amount of cristoballite (SiO_2) and alumina (Al_2O_3).

It can be visualized that after plasma processing, silica present in the sand has reacted with the carbon particles at high temperature leading to formation of large amount of Silicon Carbide (SiC). Besides, there is also evidence of formation of inter-oxide phases like Mullite

($2\text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2$) and Alumino-silicate (Al_2SiO_5), are formed. This may probably be due to the enhancement of reaction kinetics during spraying.

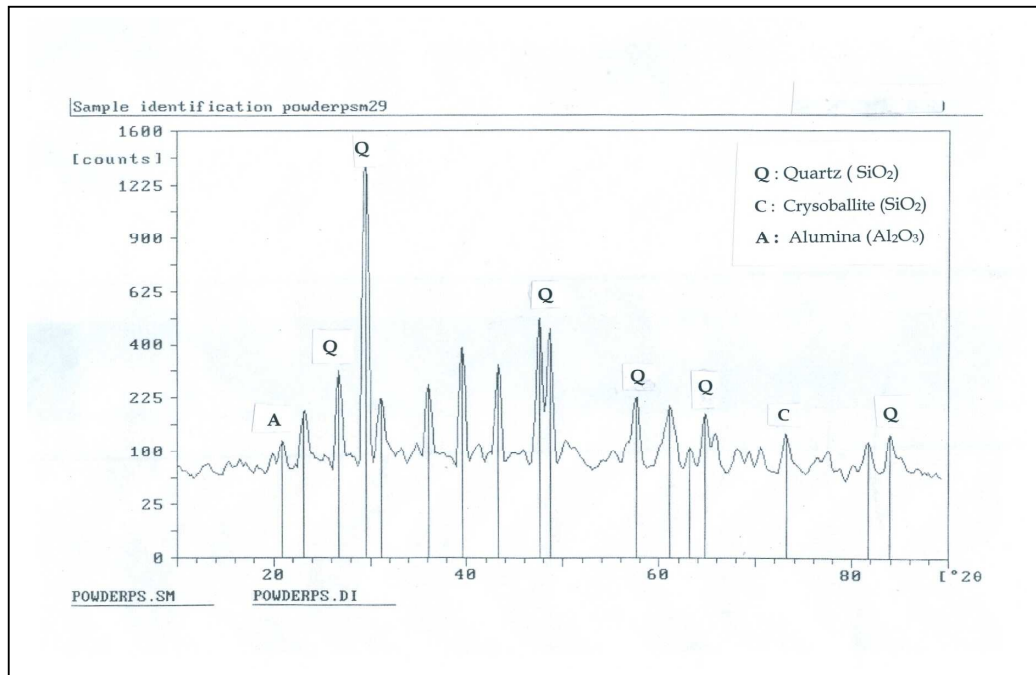


Fig. 4.3 X Ray Diffractogram of Raw Silica-Carbon Mixture (Feed Material)

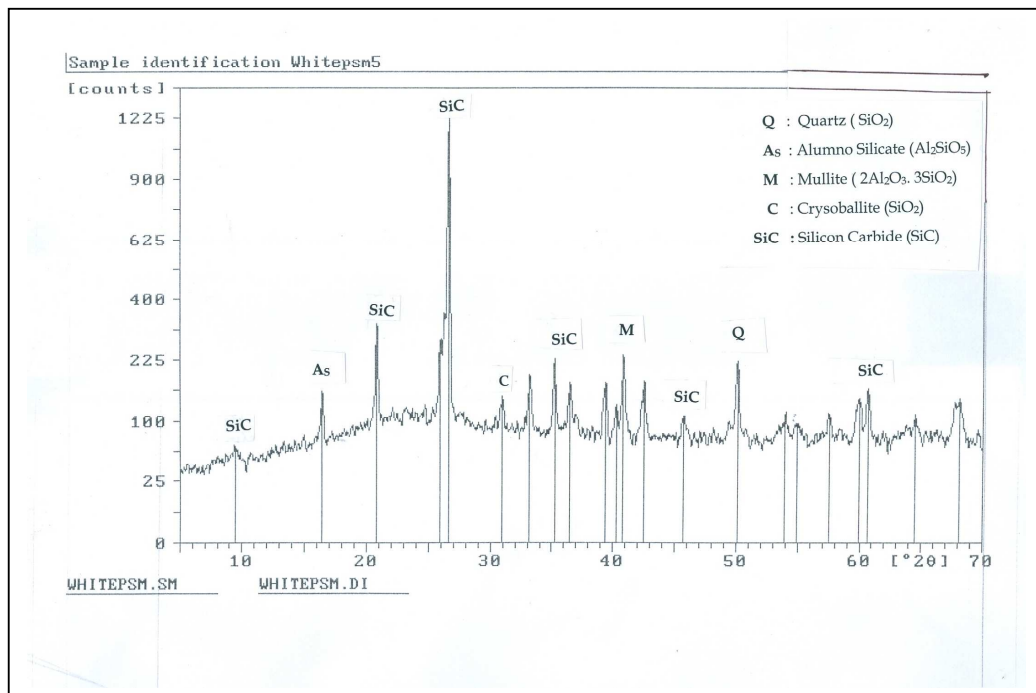


Fig. 4.4 X-Ray Diffractogram of Silica-Carbon Coating deposited at 12 kW power level

COATING DEPOSITION EFFICIENCY

The deposition efficiency presents a sigmoid-type evolution with the torch input power (fig. 5.3 to fig. 5.6). As the power level increases, the total and the net available energies increase (the arc current intensity increases from 200A to 400A for operating power increasing from 6 kW to 16 kW). This leads 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.

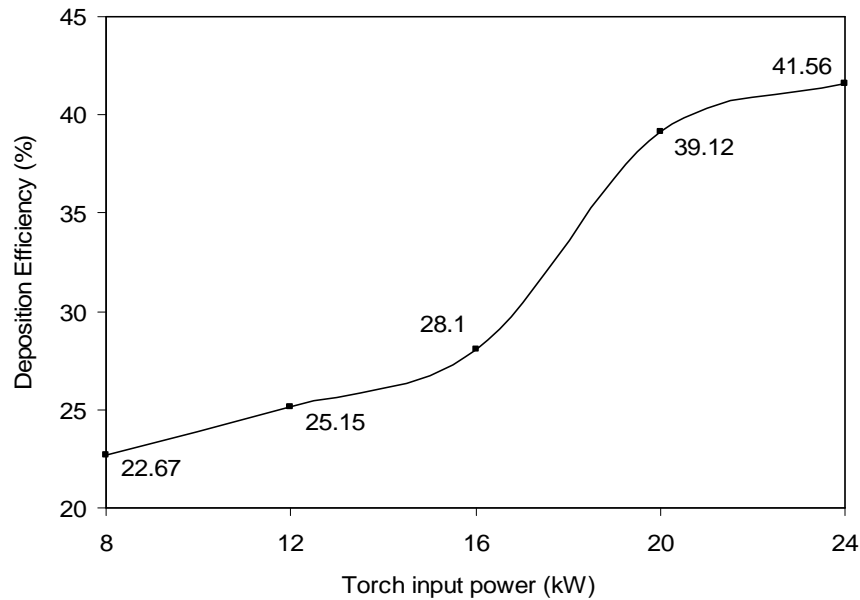


Fig. 4.5 Deposition efficiency of silica-sand+carbon coatings on metal substrates

Functional coatings have to fulfill various requirements. The deposition efficiency is one the main requirements of the coatings developed by plasma spraying. It represents the effectiveness of the deposition process as well as the coatability of the powders under study. In order to achieve certain values of deposition efficiency accurately and repeatedly, the influence parameters of the process have to be controlled accordingly. Since the number of such parameters in plasma spraying is too large and the parameter-property correlations are not always known, statistical methods can be employed for precise identification of significant control parameters for optimization.

MICROSTRUCTURAL INVESTIGATION OF THE COATINGS

Surface Morphology

SEM micrographs of silica-sand + carbon coating surfaces are shown in Fig 4.8. The coating deposited at 8 kW power level (Fig. 4.6a), shows a uniform distribution of molten/semi molten particles, which have been agglomerated. Coating made at 12 kW (Fig. 4.6b) bears a different morphology. Some spheroidal splats are found, indicative of complete melting of particles during coating deposition. Deep pores are found but the amount of cavitations is less. Some (open) large pores are found on the inter particle boundaries and triple particle/grain junctions. These may have originated due to the inadequate flow of molten particles during their solidification.

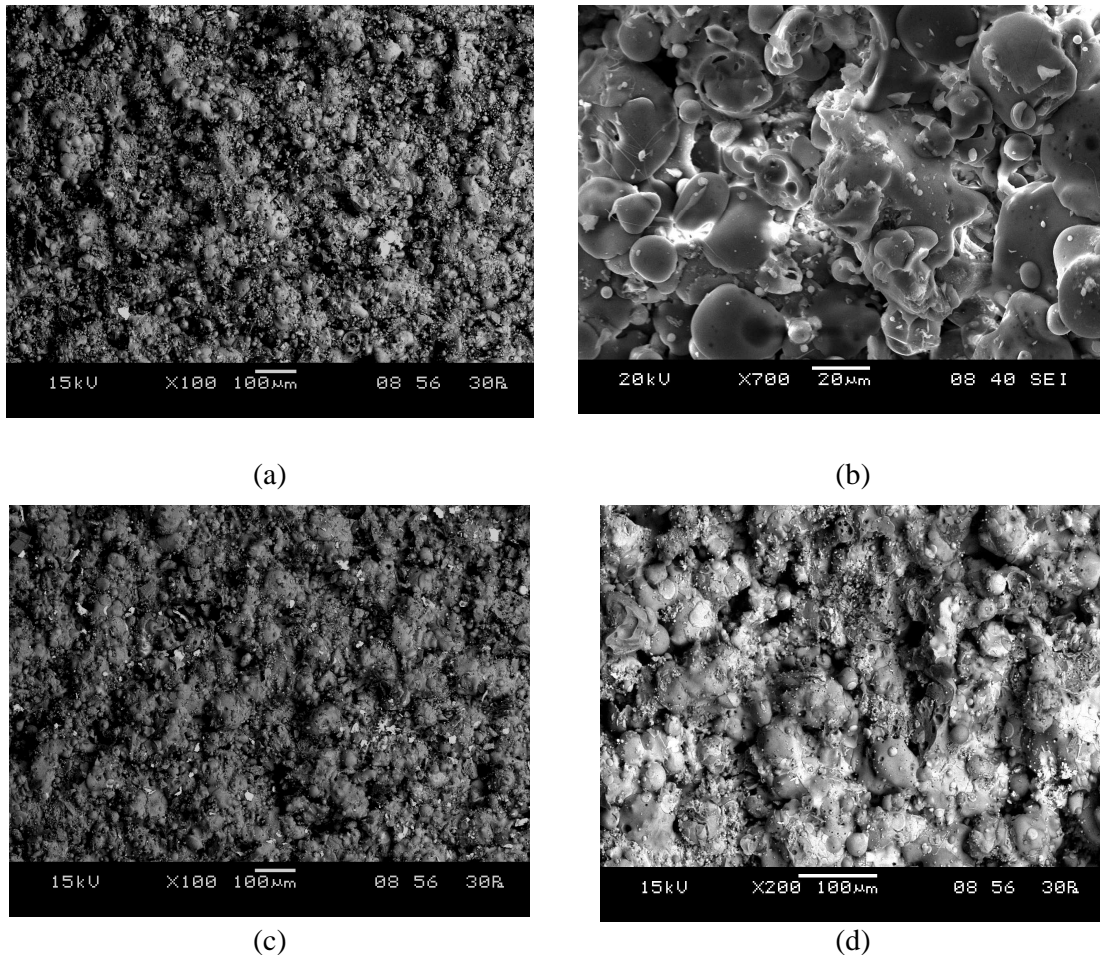


Figure 4.6 Surface Morphology of silica-sand + carbon coatings deposited at different power level i.e. (a) 8 kW (b) 12 kW(c) 16 kW (d) 20 kW

In case of coatings made at 16 kW (Fig.4.6c), the particles carry more thermal energy. So during solidification from molten state, they agglomerate to form splats in the form of flattened regions. Less cavitation is observed at inter-granular boundaries. This may be the reason for better interface adhesion of the coating onto the substrate leading to increase of adhesion strength.

At still higher power level i.e. 20 kW (Fig.4.6d), much smaller particles are found formed by breaking / fragmentation of bigger particles during their in-flight traverse through the plasma jet and then solidified in the form of spheres due to fast rate of quenching and are fused together in lumps to form flattened regions. The amount of porosity appears to have increased. This might be the cause for the improper inter-particle bonding and poor stacking to the substrate, which have resulted in lowering the interface bond strength.

CHAPTER 5

SUMMARY AND CONCLUSIONS

Summary

The phase composition of the coatings, as ascertained by X-ray diffraction, shows that it consists of largely silicon carbide, alumino-silicate and mullite (the inter-oxide of silica and alumina). A detailed analysis of the diffractograms reveals that the proportion of silicon carbide phase is more in the case of the coatings made from the mixture of raw desert sand and carbon. The formation of SiC and other such hard phases is the reason for the enhanced coating hardness.

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 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. In the present investigation, the variation of interface adherence strength shows that the maximum strength is recorded at an intermediate power level of 16 kW and this influence of torch input power on coating adhesion is evident from the graph. It is noted that the interface bond strength increases with the input power of the torch up to a certain power level (16 kW) and then shows a decreasing trend. This may be attributed to the following:

Initially, when the operating power level is increased, the melting fraction and velocity of the particles also increases. Therefore there is better splashing and mechanical inter-locking of molten particles on the substrate surface leading to increase in adhesion strength. But, at a much higher power level, the amount of fragmentation and vaporization of the particles 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.

Conclusions

From this study it has been found that desert sand with carbon powder additions can be used to provide plasma spray ceramic coating of silicon carbide based composite on metal substrates. It is evident that silica in the sand reacts with carbon at high temperature during the in-flight travel through plasma jet leading to formation of silicon carbide and small amounts of inter-oxide compounds such as mullite and alumino-silicate. Maximum adherence strength of 23 MPa is recorded in such coatings. The operating power level of the plasma torch affects the coating deposition and the morphology and mechanical properties of the coating.

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