D-gun Sprayed Alumina-Silicon Carbide Coating on Steel Substrate for Mechanical Applications

Ph.D. Thesis

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DISCIPLINE OF MECHANICAL ENGINEERING INDIAN INSTITUTE OF TECHNOLOGY INDORE

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by VISHAL SHARMA (Roll No. : 1401203008)



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INDIAN INSTITUTE OF TECHNOLOGY INDORE

CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled D-gun Sprayed Alumina-Silicon Carbide Coating on Steel Substrate for Mechanical Applications in the partial fulfillment of the requirements for the award of the degree of DOCTOR OF PHILOSOPHY and submitted in the Discipline of Mechanical Engineering, Indian Institute of Technology Indore, is an authentic record of my own work carried out during the time period from 29 December 2014 to 20 March 2020 under the supervision of Dr. Kazi Sabiruddin, Associate Professor, Indian Institute of Technology Indore.

The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other institute.

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-Vishal Sharma

Dedicated to my family for their love, care and blessings

ABSTRACT

Sand blasting is a popular method to prepare steel substrates prior to the thermal spray coating application to obtain good coating-substrate adhesion. Die-Sinking EDM is a non-conventional machining process which also produces rough surfaces. In this study, steel (EN 31) surfaces are prepared by both methods to obtain the same average roughness (Ra) of 3, 5 and 7 μ m. The prepared surfaces are studied and compared to investigate whether the rough EDMed surface is suitable for applying thermally sprayed Ni-5Al coating on it or not. XRD and SEM analysis of the samples are carried out. Nano-hardness behavior of the samples is also studied. Failing to obtain well-adhered D-Gun sprayed Ni-5Al coating on EDMed surface is due to the presence of hard cementite and austenite phases on the surface. It is concluded that for thermal spraying, adhesion of coating material on substrate cannot be achieved without proper metallurgical compatibility. Also, for thermally sprayed Ni-5Al coating application on steel substrate grit blasting method is the suitable process to adopt for substrate preparation.

Mechanically blended Al₂O₃-SiC feedstock powders with varying SiC content (0%, 3%, 5%, 7%) are deposited on AISI 1020 steel substrates by Detonation gun technique. All the coatings are successfully deposited on the substrate without decomposing SiC in the coating. The influence of SiC content on the mechanical properties of the coating is thoroughly studied. Through XRD analysis and scanning electron microscopy (SEM) the phases and microstructure of the coating are studied respectively. Quantitative phase analysis is performed by Rietveld refinement technique. Porosity of the coatings is estimated by image analysis technique. The wear behaviour of the coating is judged by ball-on-disc type tribometer. The micro-hardness and fracture toughness of the coatings are evaluated by using Vickers micro-hardness tester and scratch tester respectively. Among the four different coatings, Al₂O₃-3wt. %SiC coating is found to have the highest fracture toughness and microhardness values along with minimum porosity. Also, compared to the other three coatings Al₂O₃-3wt.% SiC has shown the highest wear resistant property. Adhesion induced spallation and brittle fracturing of lamellae are the two main wear mechanisms of the coatings. Phase stabilization of Al_2O_3 is found to happen while spraying with 3-5 wt. % of SiC.

Thermally sprayed coatings are often used to protect metallic components from high operating temperature. The oxidation of such components exposed to high temperature decreases their service lives and performance. In this study, the high temperature oxidation behaviour of bare AISI 1020 steel, Dgun sprayed pure Al₂O₃ coated steel and D-gun sprayed Al₂O₃-3wt.%SiC coated steel are studied. The study is carried out at 900 °C temperature for 50 cycles in a muffle furnace. The phase and microstructure of the oxidised samples are studied by XRD and SEM methods respectively. Both the coated samples show improved oxidation resistance properties compared to the same of bare AISI 1020 steel. Between the two coated samples Al₂O₃-3wt.%SiC is found to have higher resistance against oxidation. In order to obtain hardness and fracture toughness properties of the oxidised samples Vickers microhardness and scratch test are performed respectively. Al₂O₃-3wt.%SiC coated sample is found to retain maximum amount of mechanical properties at elevated temperature. The formation of large number of cracks within the oxidised pure alumina coating is the main reason for the decrease in its mechanical properties. On the other hand, due to the presence of 'SiC' in the Al₂O₃-3wt.%SiC coating the crack propagation is found to be minimum in such coatings. Through transformation toughening property 'SiC' is able to restrict the crack propagation.

Keywords: EDM, Sand blasting, Alumina, D-gun.

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NOMENCLATURE

- A Area of conical indenter
- *D* Mean diagonal of Vickers indentation
- H_{ν} Vickers microhardness
- *P* Applied load in Vickers indentation
- R_a Average surface roughness
- α Angle between opposite faces of the Vickers diamond indenter
- θ Semi angle of Berkovich indenter
- λ Wavelength of the X-ray radiation
- h_T Average depth of wear track
- \emptyset Half-apex angle of conical indenter
- ω_d Specific wear rate
- *P* Applied load in Vickers indentation
- *p* Perimeter of conical indenter

Chapter 1 Introduction

In early 1980's, the need arouse to save various types of engineering components due to their degradation while in service by surface related issues such as wear, fatigue and corrosion. This led to speedy evolution of surface engineering. The field of surface engineering consists of some conventional and innovative coating techniques to apply a protective layer of some other material or by forming a composite material layer on the surface of such engineering components to have much better properties on the surface. There are various methods to coat a surface which differ from each other in terms of the coating materials, deposited coating thickness, bonding of coating with the substrate and the process parameters. The factors to be considered while selecting a coating deposition process are as follows:

• The bulk properties of the substrate material should remain unaffected due to the effect of coating material. Also, the surface coating should not alter the properties of the bulk material otherwise there will be no point of applying a coating for the protection of the bulk material.

• The process of deposition should be capable enough to coat the whole component i.e. it is able to cover the whole shape and size of the component. For example, PVD (physical vapour deposition) is a line of sight process and to coat on all the surfaces of a material the component requires motion.

• The process to be used for surface treatment must be economical; it should consume less time for coating deposition and also improve the quality of the product.

One successful surface modification technology is thermal spray process which is popular for its ability to deposit variety of coating materials on various types of substrates. This technology allows depositing thick coating material on almost any size and shape of the substrate. The Detonation gun (D-gun) spraying process is one of such thermal spray techniques which is being used in some industries due to its flexibility, and ability of producing dense coatings.

The coatings of advanced materials such as ceramics (Al₂O₃ and SiC etc.) are in demand now-a-days as they are much harder and are more wear resistant compared to intermetallic or other types of thermally sprayed coatings. These advanced materials tend to melt and dissociate while spraying by plasma spray technique. High flame temperature and residence time in flame favour the dissociation. Dissociation of such coating materials is less in case of spraying by HVOF/D-gun technique as those offer comparatively less flame temperature and lesser residence time. Deposition of 'SiC' is very difficult due to its nature to decompose at high temperature. Thermally sprayed Al₂O₃ contains metastable phases in it. Stabilization of Al₂O₃ by addition of 'SiC' can be an interesting topic to study. However, spraying 'SiC' by thermal spray technique without decomposition is challenging in nature.

Prior to thermally sprayed coating application preparation of substrate is a mandatory step to follow as it imparts proper roughness to the substrate. The roughness of the substrate helps to achieve good coating-substrate adhesion through mechanical anchorage. Sand blasting is the commonly used technique for cleaning and roughening the substrate prior to the coating application. In sand/grit blasting, alumina grits of suitable size are thrown on to the substrate at high speed and pressure to create roughness on the workpiece by abrasion. Sometimes, few grit particles are stuck on the relatively soft substrate surface and cause contamination.

Roughening of the metallic substrate to a desired value is also possible by Electro-discharge machining (EDM) process. In EDM, electrical energy is used to form spark in a pulsed mode to melt and evaporate the work surface in a controlled manner. The nature of material removal is such that the process leads to production of a surface with high roughness. This range of roughness (R_a) value is suitable for good mechanical anchorage with thermally sprayed coatings which improves the coating adhesion. The suitability of EDM as a substrate preparation process for thermal spraying must be checked. Therefore, a comparison of EDM processed steel surface with sand blasted

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steel substrate on the basis of thermally sprayed coating application would be an interesting study.

This thesis aims to check whether the die-sinking EDM process can be a potential method for the preparation of steel substrates before the application of thermal spray coating or not. Also, the thesis is focussed on D-gun sprayed Al_2O_3 -SiC coatings sprayed on suitably prepared steel substrate. It will give an in depth analysis of D-gun sprayed Al_2O_3 -SiC coatings prepared by spraying Al_2O_3 -SiC powder mixture with different ratios to develop an overlay coating with good wear and oxidation properties for steel substrates.

The thesis consists of several different chapters. The previous research work on the above mentioned subjects are presented in chapter 2. This chapter gives a detailed literature review of surface engineering concentrating mainly on materials sprayed by D-gun thermal spray process. Most of the research work associated with D-gun sprayed or any other type of thermally sprayed Al_2O_3 based coatings are kept in this chapter. Moreover, comprehensive review is done on the pre-treatment of the substrate surface by sand blasting process before application of D-gun coatings and the effect of EDM on the surface morphology and metallurgy of steel workpiece. In the end, the objectives of this research work are formulated by finding some new research gaps through this literature review.

Chapter 3 consists of a detailed description of all the materials and methods used for this research work.

Chapter 4 represents a fundamental study on steel substrates prepared by sand blasting and EDM technique. This chapter is based on the comparison between sand blasted and EDM processed samples with same surface roughness values to check the possibility to use EDM as a roughening process prior to the application of thermally sprayed coatings on steel substrates. The surfaces produced by both the processes are thoroughly studied by XRD and FE-SEM analyses. The hardness behavior of the samples is investigated by using Nanoindentation technique. A suitable substrate preparation technique is adopted for the next level of research work.

In chapter 5, the general features of D-gun coated pure Al_2O_3 and Al_2O_3 -SiC coatings are studied. The phase and micro-structure of the coatings are investigated. Also, the phases of Al_2O_3 present in the coatings are quantified by Rietveld refinement method. Finally, the effect of 'SiC' addition on the stable α -Al_2O₃ phase formation in the coating is studied.

In chapter 6, the porosity, hardness, toughness and wear behaviour of the Al_2O_3 based coatings are studied in detail.

In chapter 7, the oxidation behaviour of D-gun sprayed pure Al_2O_3 , Al_2O_3 -3wt.%SiC and steel substrate is studied and compared by cyclic oxidation tests. The phases and micro-structure of the oxidized coated samples are studied by XRD analysis and scanning electron microscopy (SEM) methods respectively. The hardness and toughness properties of the oxidized samples are estimated and studied.

The general conclusions from the work are made in chapter 8. Also, the future scope of research work along with the contribution of the work to science is outlined.

Chapter 2 Literature Review

2.1 Surface Engineering

Surface engineering is a branch of study which deals with the enhancement of functional capabilities of the engineering components by modifying their surface properties with the help of various methods which in turn increases the life of such components even in extreme operating conditions (1, 2). For example, the components used in aircraft, boiler and petroleum industries during their service are subjected to high temperature and wear conditions. Such operating conditions can affect the surface properties of the materials of a component which in turn can change the shape and size of that component and make it unsuitable to use. In another case, a cutting tool insert used for metal cutting in machining operations gets damaged due to wear, which increases with increasing cutting temperature. The damage due to corrosion is another problem for industrial components. For example, in electrical industries, the devices and equipment are generally exposed to corroding environments (3-5). Surface engineering provides solution to these problems and enhances the service life of the components.

The surface of any component not only defines the outer limit of that component but also is expected to perform diverse engineering functions. Depending on the function and working environment a surface should have some specific properties. Following surface properties are commonly desired for mechanical components.

- High wear resistance
- Less frictional loss
- High hardness and toughness
- Ability to provide good thermal insulation
- High corrosion resistance
- Aesthetically good

The desired properties of a surface can be obtained by modifying the surface with the help of a suitable technology. The commonly used surface modification technologies are shown in figure 2.1. Among the different technologies thermal spray is a popular method to deposit a thick coating (metal, non-metal, and polymer) on almost any substrate material for mechanical applications. In the next segment different thermal spray coating processes are described with an emphasis on D-gun spray technique.



Figure 2.1: Various types of surface modification technologies (6)

2.2 Thermal Spraying

Max Ulrich Schoop is known as the "father" of thermal spray techniques who developed the first thermal spraying technique which was wire flame spray process (also known as metallizing) during early 1900s in Zurich, Switzerland. In this process, initially metal in wire form was melted, and then the molten metal was sprayed on to a substrate surface by using a compressed air jet with a very high velocity. The technique started to catch attention and by 1920, almost 15 countries started to use this metal spray technique. Gradually different thermal spray techniques were invented and widely accepted by the industries. Thermal spray techniques are able to melt and deposit any type of material as a coating. In the last five decades the demand of coating new types of materials on variety of substrate materials has increased. Hence, a lot of research and development work is needed in this

field. Also, many attempts have been made to improve the properties of the deposited coatings like hardness, toughness and to reduce the porosity content by spraying a mixture of two or more powders as feedstock material. Powders are mixed with different proportions to study the effects on the properties of coatings. Sometimes even small quantity of one material in a powder mixture can lead to significant improvement in the properties of the deposited coatings. For example, rare earth elements are added with thermal spray coating materials such as NiCrAlY coatings to improve the performance of these coatings at high temperature operating conditions (7). Similarly, TiO_2 , Cr₂O₃, ZrO₂ etc. are added to Al₂O₃ feedstock material to get coatings with improved wear resistance (8-11). Such addition of materials and their effects on thermally sprayed coatings are described in the later part of this literature survey. Currently, seven types of thermal spray coating processes are used for industrial applications: Plasma spray, electric arc spray, flame spray, D-gun, warm spray, HVOF, and HVAF (12). The detailed discussion on these processes is as follows:

2.2.1 Wire spray

It is the oldest among all thermal spray technologies and is still used by many industries to provide metallic coatings on various types of surfaces at minimal production cost. A wire in a diameter range of 3-5 mm is fed towards the middle of a multi-jet flame as shown in figure 2.2 with the help of a motor or air based turbine. The tip of the wire gets melted and a compressed air jet strips-off this molten material from the tip of wire and accelerates it towards the substrate at a particle velocity of around 100 m/s. Acetylene gas is generally used as a fuel; hydrogen or propane is sometimes preferred over acetylene for some metals like copper as it reacts with acetylene. The wire spray equipment is portable and it can be easily used for onsite applications. For reliable and best results it is suggested to control the movement of the gun by using some manipulator.

The process is capable to deposit various types of ferrous and non-ferrous materials shown in table 2.1. The wire feeding rate can be as high as 20 kg/hr to cover an area of around 20 m² with 0.1 mm of coating thickness in case of copper deposition. The modification of this technique known as 'Rockkide

process' is used to spray non-metallic materials like alumina and chromia on different types of substrate materials (13). Cermet coatings can also be deposited by this process by melting metallic wires containing ceramic particles in it, for example aluminium wire containing particles of SiC or alumina.



Figure 2.2: Schematic diagram of wire spray technique (6)

Table 2.1: List of materials	which are deposited	by wire spray	technique (13)
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Material	Application
Mild Steel	Reclamation and machine element work
Carbon and alloys steel	Reclamation, corrosion resistance and medium
	wear resistance
NiCr (80/20)	Corrosion and high temperature oxidation
	resistance
NiCrFe	High temperature corrosion resistance
NiAl	Intermediate layer used to improve the adhesion of
	ceramic coatings
Al	Resistant to atmospheric and marine corrosion,
	resistant to oxidation after heat treatment
Zn	Atmospheric and marine corrosion
2.2.2 Electric arc spraying

This process utilizes two wires which are given opposite electrical polarity and are fed through an angled electrode holder to connect the tips of these two wires and create an electric arc. The arc possesses a temperature of around 6000 K due to which the wires get melted. This molten metal is atomised with the help of a compressed air jet and a spray stream is formed as shown in figure 2.3. A 3-phase transformer is used to supply power to the arc torches and the arc characteristics are controlled to melt different materials with different properties. Generally, low voltage (20-40 V) and high current (200-300 A) are used to operate the process.



Figure 2.3: Schematic diagram of Electric arc spray technique (6)

This process is capable of depositing material up to 50 Kg/hr. It is also possible to deflect the stream of spray up to an angle of 90° by flowing a secondary gas through an attachment which makes this technique more versatile. Also, this process has capability to apply 'pseudo-alloy' coatings by melting wires of two dissimilar metals. The size of the molten droplets present in the spray stream depends on the voltage applied, atomization pressure, and the diameter of the wire. With an increase in voltage and the wire diameter it is found that the size of droplets increases whereas with an increase in atomization pressure the size of droplets decreases (9). It is also reported that this process can deposit oxide free coatings as it remains stable even in low-pressure conditions. Hence, sensitive metals can also be deposited and high density coatings can be achieved.

2.2.3 Plasma spray technique

In plasma spray process, very high voltage is applied between a water-cooled nozzle which acts as an anode (generally made of Cu) and a cathode (generally made of tungsten) to create an arc. A mixture of gases like Argon (Ar), Helium (He), Nitrogen (N₂), and hydrogen (H₂) are fed through that arc to get dissociated and ionized (figure 2.4).



Figure 2.4: Schematic of Plasma spray gun (6)

The flame temperature generated in this process is very high (6000 K-15000 K) which is the main advantage of this process. The coating powder is injected outside/inside the gun nozzle and in the flame it is accelerated with a velocity of around 200 m/s towards the substrate surface. The molten volume with high impact velocity spreads well on the substrate surface. A very high deposition rates can be achieved by this process compared to other thermal spray processes. The rate of spray depends on various parameters like design of gun, powder injecting technique, material to be sprayed, powder particle characteristics, and plasma gases (15). The process is capable of spraying metal, alloys, ceramics, composites, cermets, and even some plastic materials. The most important requirement for applying coating is the existence of

material in liquid state, for example SiC, and Si_3N_4 are difficult to spray by thermal spray process as they get decomposed while spraying. The flexibility of this process is a big reason for rapid development of this process. Some features of the coatings produced by this process are homogenous, equiaxed, non-columnar and fine grain microstructure, with high coating thickness. The process is mainly used to apply corrosion, abrasion, temperature and erosion resistant coatings. It is also possible to spray super conducting and glassy metals without altering their amorphous traits. In recent years, hydroxyapatite coating applications on dental implants and stems of orthopaedic endoprostheses are also done by this process (16).

The conventional plasma spray process is generally known as atmospheric or air plasma spray (APS). In this technique, an inert gas mixture of gases is/are usually superheated by using DC arc to create plasma. The commercial guns used in this process generally operate between a power range of 20 to 200 kW. Another variant of this technique is vacuum plasma spray (VPS) which is also known as low pressure plasma spray (LPPS), which uses plasma spray with modified torch in a low pressure chamber (<0.1 mbar). VPS offers coatings with improved adhesion, high coating density, greater control on coating thickness and higher deposition rates (17). The size of plasma becomes large in low chamber pressure and the gas speed is increased by using convergent-divergent nozzles. The capability of this process to operate with higher substrate temperatures gives dense and adherent coatings with very less oxide formation (18).

The most important application of VPS technology is the application of MCrAIY ('M' stands for any metal like Ni, Co, Fe etc.) coatings on turbine blades in aerospace industries. The main function of such coatings is to protect the turbine blades from hot corrosion in order to improve their lives. The VPS sprayed MCrAIY coatings are homogenous, dense, free from oxides, and have large diffusion zones (19). Also, these coatings are used as bond coats before applying ceramic coatings on steel substrates.

A lot of efforts have been made to expand the limits of this process to spray some reactive elements like tantalum and titanium. Although the coatings of

such reactive materials are not usable for thermal barrier applications but those can be used for bio-medical applications. One more additional application of this process is the development of diamond coatings and alloying with substrate surface.

2.2.4 Flame spraying technique

Figure 2.5 shows another type of thermal spray technique known as flame thermal spray torch. In this technique, it is observed that the nozzle is designed in such a way that the combustion of the gases takes place in an area which is around central position of the powder injector. In this system, the coating powder is supplied in a gas stream with the help of gravity; the powder can be fed in a much better way by utilizing some specially designed powder feeder units. The melted/semi-melted/unmelted powder particles are pushed forward towards the substrate at a high velocity (around 100 m/s). Sometimes, compressed air is also used to increase the kinetic energy of the powder particles to reduce the deposition time.



Figure 2.5: Schematic diagram of powder flame spray technique (6)

This process provides coatings with good integrity, but the deposition efficiency gets reduced drastically in case of ceramics as re-solidified and unmelted particles bounce back after hitting the substrate instead of adhering to the substrate. The process is capable of melting most of the materials as a flame temperature of around 3000 K can be obtained by burning the oxyacetylene gas and is a useful technique to process materials which are available in powder form.

Material	Application
Low carbon steel	Reclamation and machine element work
Martensitic stainless	Corrosion and wear resistance
steel	
Austenitic steel	Corrosion resistance and machinability
NiAl	Wear resistance and intermediate layer used to
	improve the adhesion of ceramics
NiCrAl	High temperature resistance and bonding
NiCr (80/20)	Corrosion and high temperature oxidation
	resistance
NiCrFe	Corrosion and high temperature oxidation
	resistance
WC	High wear resistance
Cr ₂ O ₃	Wear and corrosion resistance
Al_2O_3	Electrical and wear resistance
Al ₂ O ₃ /TiO ₂	Wear resistance

 Table 2.2: Materials sprayable by powder flame spray technique (20)

Different types of materials such as metals, oxides and carbides can be sprayed by this technique as shown in table 2.2. Plastic coatings can also be deposited on large components by using this process. Self-fluxing alloys which fuse after deposition to produce dense coatings are also deposited at a lower spray rate of 1-2 Kg/hr by this process. The deposition rate can further be increased with specially designed torch. Coatings can be produced on the internal surfaces of the components in the same way as it is done by wire spraying process.

2.2.5 High velocity oxy-fuel (HVOF) process

This technique is a successor or we can say a newer version of conventional oxy-fuel thermal spray technique (figure 2.6). The coating deposition by this process started in 1980's and it is still an outstanding thermal spray process used by many industries (21). This process is generally used for depositing cemented carbide coatings, and produces dense and adhesive coatings with

good phase stability. The roughness of the deposited coatings can be decreased by various machining operations in order to get a smoother surface. Such types of coatings have been utilized for either production of a new part or repairing worn out parts (22).



Figure 2.6: Schematic diagram of HVOF technique (6)

2.2.6 Detonation gun (D-gun) process

D-gun process was developed by Union Carbide Corporation in 1950's from the experiments which involved controlling of the detonation occurred due to the burning of gases (oxy-acetylene mixture). It consists of a 1-1.5 m long barrel with an internal diameter of 20-30 mm, in which a mixture of oxygen and acetylene (fuel gas) is injected and burned by igniting a spark by using spark plug (figure 2.7). The burning of the oxy-acetylene mixture creates a shock wave or detonation. This shock wave travels at a speed of approximately 3000 m/s, and at a temperature of around 3300 °C. The coating powder particles are carried in the barrel by nitrogen gas before the ignition of the oxy-acetylene gas mixture. The detonation wave comes in contact with the suspended powder particles which get heated and then accelerated at a supersonic velocity of 800-1200 m/s towards the substrate surface. The higher kinetic energy attained by the powder particles helps those to collide with the substrate to produce a coating with high bond strength and density.

The frequency of detonations can be varied between 3-10 shots/s and an average of 6 μ m thickness of the coating can be achieved from one shot. In this process, Nitrogen gas is used firstly to carry the coating material to the barrel and secondly to purge the barrel after completion of every detonation cycle. This process produces very loud noise (approximately 150 dB) which

is one of its major dis-advantages. Therefore, an acoustically insulated room is required to keep this whole D-gun unit. It is proven to be a successful process to deposit oxides, carbides, high temperature alloys and cermets (23). However, like most of the thermal spray processes this technique deposits coatings with tensile residual stress which results in reduced fatigue strength of the coatings. This problem again can be countered by applying bond coat material in between the top coat and the substrate material.



Figure 2.7: Schematic diagram of D-gun process (6)

2.3 Features of thermally sprayed coatings

The coating developed by thermal spray process in open air atmosphere is a mixture of the coating material, porosity and the oxide inclusions (24, 25). The molten powder particles during their flight come in physical and chemical contact with the surrounding atmosphere. These coatings consist of lamellar splats whose boundaries remain parallel to the substrate surface. During solidification process, within each lamellar splat fine-grained equiaxed crystal formation takes place. As the spray nozzle proceeds over the substrate surface around 5-15 lamellae get formed in the first layer of coating. The columnar orientation of the grains decreases gradually with an increase in the thickness of the coating. This change from columnar to random grain morphology happens due to the decrease in cooling rate by which the grains get enough time to re-crystallize or reform. The formation of some structural defects like vacancy, dislocation and coagulation takes place due to the rapid solidification of thermal spray coatings. The microstructure of the coatings depends a lot on the quenching rate. Figure 2.8 shows a perfect splat formation on the surface of the substrate.



Figure 2.8: Splat formation on a substrate (26)

2.3.1 Composition of sprayed coatings

The composition of thermally sprayed coatings differs from the composition of the starting powder due to the interaction of molten particles with the atmospheric gases. The extent of interaction of this molten material with the atmospheric gases is important to determine the properties obtained in the final coating. It is reported that the consequences of oxidation of the assprayed aluminium and bronze coatings are detrimental for the compressive strength of the coatings. Although, discontinuous oxide particles present in the as-sprayed coatings provide strength to the coating and also improve its wear resistant property (27). Spraying tungsten carbide often results in loss of carbon content in the final coating due to oxidation (28). The oxidation of metallic coating also takes place during deposition due to which oxide scales form on the particle and increases the impurity content of the coating. The extent of reaction taking place between the molten particles and the atmosphere can be controlled by controlling the process parameters. Due to rapid solidification of molten volume metastable phase formation also takes place. In the as-sprayed alumina coatings, the quantity of alpha phase gets reduced due to the formation of gamma, theta and delta phases by rapid cooling of high temperature splats deposited on highly conductive substrates.

2.3.2 Residual stress generation

In thermally sprayed coatings, residual stress generates as a result of rapid cooling of the molten particles when they are sprayed as a splat on a cold substrate. Normally the cooling rate of super hot splats is very high. In

contact with metallic substrate and open atmosphere splats undergo quenching. This quenching may help to improve the mechanical interlocking between the splat and the surface asperities. However, if the variation in coefficient of thermal expansions (CTE) of the coating and substrate material is more then spallation of coating may occur resulting from shear along the splat-substrate interface. In such coating-substrate combination application of bond coat is found to be beneficial. These two effects, quenching and differential thermal expansion play major roles in inducing residual stress in the coating. There is another reason of inducing residual stress namely 'peening stress', which occurs owing to the high-velocity impingement of powder particles on the substrate (or the previously deposited coating layers).

The amount of stress generated depends on the spraying parameters, rate of deposition, the properties of the substrate and coating material, and the type of auxiliary cooling used (29). The residual stress generation is also dependent on the size of the powder particles used for deposition. The smaller size particle leads to more stress generation and vice-versa. In the case of thick coatings, it is reported that the value of stress increases linearly with an increase in coating thickness. The increased stress can further cause cracking and spalling in the developed coating. The tensile residual stress is the main cause of cracks generated in the coating microstructure (30). Using the following methods this residual stress can be reduced:

- Pre-heating the substrate before applying thermal spray coating
- Proper selection of coating material (material with minimum shrinkage should be preferred)
- Use of low expansion material to develop the components
- Annealing of the deposited coatings

2.3.3 Coating-substrate adhesion

In thermal spray coatings, the diffusion between the coating and substrate material is very limited due to rapid cooling effect. The bond formation in such coatings is majorly physical in nature instead of chemical or metallurgical bond. The molten particles get deformed on reaching the roughened substrate and on cooling they get mechanically interlocked with

the substrate surface. The roughening of the surface is done by grit blasting process which activates the surface. The resultant shear force action of sand blasting damages and cleans the oxide layer already present on the surface, hence giving a proper metal to metal contact on coating deposition. In some cases the deposited coating itself cleans the oxide layer present on the substrate surface as it happens while depositing aluminium coatings on mild steel substrates (31). The bond strength of the thermally sprayed coatings is generally measured by standard pull-off tests (ASTM C633). The bonding characteristics of the coatings depends a lot on the substrate material on which coating is to be produced and the parameters used for the coating.

A cooler substrate affects the flattening of splats (melted and deformed particles) on the substrate and can alter the physical and mechanical properties of the thermally sprayed coatings. The splat formation is an important phenomenon in thermal spraying process as it elucidates the characteristics of sprayed thickness of the coating. Many models on molten particle impingement on rough flat surface have been proposed (32).

It is reported that the flattening ratio or the rate at which a material spreads on the substrate surface decreases with an increase in surface roughness. Splats of many coating material are attached to the substrate due to the force resulted from liquid particle shrinkage muffled around the surface irregularities. The degree of adhesion at the contact area of the splat and the substrate depends on the physical and metallurgical interaction between the two. Following are some pre-requisite conditions need to be performed to achieve better substrate-coating interaction:

- Proper cleaning of the surface is required
- Surface should be activated or should be in high energy state (e.g. plastic deformation by blasting the surface).
- The contact should be closed (this happens automatically as the lamella is in liquid state).

There are two main mechanisms of fusion bond formation; diffusion and chemical reaction between the splat and the substrate. In some cases (coating material), formation of fusion bond by local welding is reported (32).

2.3.4 Anisotropy of the sprayed coatings

Successive deposition of the coating material on the already deposited material leads the particles to acquire the similar splat shape as of the already deposited splats. This results in the formation of the coatings with a lamellar structure (anisotropic) which is parallel to the surface of the substrate. This type of structure formation together with directional solidification results in anisotropic property generation in such type of coatings. This type of anisotropic behaviour is more pronounced for metallic and cermet coatings.

2.3.5 Stabilization of the thermally sprayed coatings

Thermally sprayed coatings are generally composed of different phases of same material (e.g. Al₂O₃ coatings). α -Al₂O₃ phase is generally used as the feedstock material for the deposition of Al₂O₃ coatings. Metastable phases like γ , δ , and θ gets formed in the thermally sprayed Al₂O₃ coatings along with the α -Al₂O₃. The main reason behind the formation of such phases is the complexity of the process and the cooling rate of the splats. It is believed that the mechanical properties of the metastable phases are inferior to that of the α -Al₂O₃ phase (34). Hence, the presence of metastable phases in the as-sprayed coating is considered to be harmful for the life of the coatings used for mechanical applications. It is very important to develop Al₂O₃ coatings with more amount of stable α -Al₂O₃ phase in the final coating.

- Annealing the as-sprayed coating at a temperature of 1100 °C helps to convert γ -Al₂O₃ to α -Al₂O₃. Due to the chance of damaging the substrate by this high temperature heat treatment technique, this method is not considered as a good choice for α -Al₂O₃ conversion (35).
- Retention of more unmelted/semi-melted particles in the as-sprayed coatings also helps to increase the α -Al₂O₃ content in the final coating (36, 37).
- α -Al₂O₃ phase stabilization can also be done by adding Cr₂O₃, TiO₂, and CeO₂ etc. oxides in the α -Al₂O₃ feedstock powder (38-42).

In a study, it is reported that by annealing the as-sprayed Al₂O₃ coating above 1100 °C temperature, coating with mostly α -Al₂O₃ phase can be achieved (39). In another work it is observed that heat treatment of plasma sprayed alumina-chromia coating at a temperature of 1200 °C and 1550 °C can produce only α -Al₂O₃ in the resulting coating. However, this practice is not widely accepted due to the exposure of metal substrate to the high temperature during heat treatment (40). 100% α -Al₂O₃ can be obtained in the coating during deposition by moving the deposition spray gun/torch at a very slow rate and increase the average substrate temperature. Hence, the α -Al₂O₃ to γ -Al₂O₃ transformation can be suppressed by steady cooling of the deposited splats (37).

Another way of stabilizing α -Al₂O₃ is to deposit Al₂O₃ along with some other materials like Cr₂O₃, TiO₂, and CeO₂ (34). Co-deposition of these materials is achieved either by spraying pre-alloyed powder or by spraying powder mixture prepared by mechanical blending. Addition of TiO₂ to Al₂O₃ enhances the mechanical performance of alumina coatings. Still, TiO₂ is not much effective in stabilizing the Al₂O₃ phases. Materials like Cr₂O₃ and CeO₂ are also added to the Al₂O₃ feedstock to study the effect on phase stabilization.

Rietveld refinement technique is a useful tool to estimate the quantity of phases present in the thermally sprayed coatings (36, 41). This method utilizes least square method to fit an experimentally obtained XRD profile with theoretically created XRD profile. The theoretical profile is created with the help of ICSD data of the known phases found from the X-ray diffraction data. Further, with the help of profile fitting function and varying its different parameters the calculated profile is fitted with the measured full range XRD pattern to achieve minimum difference between the profiles. This technique also gives detailed information about the crystallographic structure, crystal size, and micro strain etc. of the measured sample (43). Rietveld refinement performed on Al_2O_3 -ZrO₂ composite coating is also reported (44). This technique is used to estimate the quantity of amorphous phases present in the plasma sprayed Al_2O_3 coating.

To estimate the different Al₂O₃ phases present in the Al₂O₃ based coatings Rietveld refinement method is important to apply. No such work of applying Reitveld refinement method for phase study of D-Gun sprayed alumina based coatings is noticed in the available literature.

2.4 The D-gun process

In a D-gun process fuel gases are mixed with proper proportion and burned to create a detonation. The sudden high energy released by the detonation is responsible for melting and accelerating the coating particles. Hydrogen fuel gases like propane, acetylene etc. are burned with oxygen and the maximum temperature attained by this process depends on the type of fuel gas and the oxy-fuel ratio. The D-gun cycle starts with filling the gun barrel with fresh mixture of combustion gases and coating powder. This fresh charge of the combustible gases is subjected to an impulse burn-out. The burn-out of this gaseous mixture creates a detonation in the barrel and the powder particles come in contact with the detonation of this combustible mixture. The powder particles get melted and are accelerated towards the substrate surface. While travelling the composition of the powder particles changes due to the oxidation of the molten particles. The fully melted particles deposit on the substrate surface as splats whereas unmelted/dried up powder particles bounce back from the substrate surface. Layer by layer the coating deposits and the thickness of the coating keeps on increasing after each detonation cycle. The quality of the coatings produced by D-gun process depends on three main stages of this process (45):

- (a) First stage is comprised of:
- The process parameters like the composition of mixture, size of powder particles, concentration and position of powder cloud in the gun barrel during the initiation of the detonation process (0.25 g is the optimum amount of powder quantity), degree of filling of gun barrel, and the stand-off distance between the nozzle and the substrate.
- The design factors of the spraying body include the shape and size of the gun barrel, the point where the gas mixture is ignited, the distance

between the location of powder cloud and the ignition point of the gas mixture, and the firing rate.

(b) Second stage includes

The temperature and velocity of the gas mixture and the powder particles, gas pressure and density, and the time during which powder particles are in the high temperature zone (a two-phase flow does not exist for more than 0.005s).

(c) Third stage includes

The chemical and physical processes involved between the two contacting materials and the time duration, which control the bond formation between the coating and substrate materials or between the new and old splats deposited.

D-gun is an intermittent process (with a frequency from few Hz to 100 Hz), which enables the substrate to remain at low temperature (around 100 °C). The frequency of a D-gun process can be defined as $1/t_c$, where t_c is the duration of the cycle which generally consists of six distinct time intervals (46): Time required to fill the barrel by fresh mixture of gas (Δt_{gfl}), time required for feeding the coating powder (Δt_{pfl}), purging time (Δt_{pr}), time required for initiation of detonation (Δt_{in}), detonation traverse time through the gun barrel (Δt_{tr}), time required to exhaust the detonation products (Δt_{ex}), i.e.

$$t_{c} = \Delta t_{gfl} + \Delta t_{pfl} + \Delta t_{pr} + \Delta t_{in} + \Delta t_{tr} + \Delta t_{ex} \qquad \dots \dots (1)$$

The dynamic filling of gas and purging/exhaust processes consume most of the cycle time which can be reduced by using high dynamic pressure during operation. However, filling losses should be considered while selecting high dynamic pressure values. The size of the barrel (length and volume) and the velocity of filling the gas determine the time required to fill the barrel by fresh gas (Δt_{gfl}) as the mass flows in the transverse direction of the barrel length. The rate of filling is suppressed when the injected gas velocity reaches Mach 0.5 due to the occurrence of compressibility effects. For a 1 m long barrel with an operating pressure of 0.1 MPa, 100 Hz of cycle frequency can be attained. This frequency can be varied by using multiple injections at various locations (47).

The diameter of the barrel depends on the heat lost to the tube walls and is commonly of 15-20 mm for most materials and gas mixtures used in this process. A barrel with an internal diameter of 15 mm is adequate to spray WC coatings with acetylene as fuel gas, and a gun barrel of 40 mm internal diameter is required when propane is used as fuel gas (48). It is reported that by varying the cross-sectional area of the barrel along the length uniform filling can be achieved. The performance of the D-gun process can be improved by using a nozzle at the end of the barrel. D-gun nozzle operates at unsteady state conditions, hence proper design and optimization of the process parameters should be considered. The main purpose of attaching a nozzle at the end of the gun barrel is to ease the expansion of the gases and to decrease the rate of pressure drop inside the barrel. However, it increases the barrel length and decreases the frequency of operation.

The average roughness of the channel wall surface is approximately 20 μ m. The surface roughness modifies the turbulence of the hot gas and in turn promotes the heat loss to the walls and also causes more uniform mixing of combustion products and the powder. Roughness can be attained by forming threads of various profiles along the length of the barrel, or may be in section. When the threaded grooves are formed on the inlet section of the barrel, then the pre-detonation distance is to be reduced. But, if the grooves are located at the outlet of the barrel then it improves the mixing of powder and also boosts the heat exchange. For safe detonation, it is not recommended to use premixed fuels and oxidizers. As the cycle of D-gun process is transient and a very short period of time is available for the mixing, the mixing enhancement is a critical issue in this field (49).

A new method of detonation spraying has been proposed and patented in recent times. It offers improved homogeneity of detonation mixture. This new method differs from the conventional method by uninterrupted feeding of combustible gas mixtures inside the combustion chamber. The mixture of combustible gases is kept away from the products of detonation by periodic

feeding of any neutral gas like nitrogen/argon between the ignition point of the gas mixture and the powder supply point. The pressure of the neutral gas is kept 2.5-3.0 times more than the pressure of combustion gases. Hence, it is able to prevent the mixture of combustible gases to enter the detonation area and the backfiring can be avoided. An excellent quality of coating can be deposited by this new D-gun method (49).

The consumption of combustible gases per unit mass of the coating material in D-gun process is four to eight times lesser compared to the same of HVOF process (45). D-gun process generates high noise of about 145 dB which makes this set-up to be used only in acoustical enclosures. According to Zeldowicz-Von Neuman-Doering (ZND) theory, the detonation wave is comprised of the shock wave zone, the chemical reaction zone and detonation products zone. A detonation wave can be imagined to propagate as a stationary distribution of temperature, pressure, density, and velocity. A qualitative image of the parameters of detonation is shown in figure 2.9. Detonation wave front separates the initial gas mixture from the reaction products and it is also assumed that the thickness of the reaction zone is very less. At the front edge of the wave, the temperature increases rapidly and during the reaction it increase gradually and reaches to a maximum value. Further, in the reaction product zone the temperature decreases gradually from its maximum value as shown in figure 2.9(b). The specific mass is increased to the maximum all of a sudden at the beginning of the reaction and further it decreases gradually as shown in figure 2.9(c). The pressure increases gradually from the beginning of the reaction to the end of reaction zone and remains constant in the reaction product zone as shown in figure 2.9(d).

It is a well-known fact that, with lighter gases like helium and hydrogen the velocity of detonation increases whereas with heavier gases it decreases. The detonation wave velocity can be varied from 1000 m/s to 3000 m/s by varying the composition of the gas mixture. The velocity is independent of the gun barrel diameter, but the barrel diameter should be more than the critical diameter. The theoretical velocity (D in m/s) of the detonation can be calculated by following equation (50):

$$D = [2(\gamma^2 - 1)Q_0]^{1/2} \dots \qquad \dots (2)$$

Where Q_0 is the specific energy and γ is the ratio of specific heats of detonation. The temperature T_1 and pressure P_1 can be estimated by the following equations (50).

$$T_1 = (2\gamma Q_0)/(c_v[\gamma+1])$$
(3)

$$P_1 = 2(\gamma + 1)\rho_0 Q_0$$
(4)



Figure 2.9: Qualitative image of D-gun parameter variation in the gas (a) pressure, (b) temperature, (c) mass and (d) velocity of detonation (40)

All the parameters used for detonation are sensitive to the composition of the fuel and fuel to oxygen ratio. Figure 2.10, represents the varying velocities of detonation wave with varying oxygen/acetylene ratio at different volume percentages of nitrogen.

The detonation velocity increases when the quantity of oxygen is reduced for a stoichiometric oxy-acetylene mixture. With introduction of small amount of nitrogen, the velocity of the detonation is greatly decreased (the detonation velocity can be reduced by 600-800 m/s with an addition of 3 vol.% of nitrogen). This addition allows tailoring of the particle collision parameters.

Similarly by using equations 3 and 4 for hydrogen and oxygen gas mixtures the process parameters are obtained (as shown in table 2.3). Many similar sophisticated calculations on detonation parameters are proposed in literature (51-53). They account for the degree of filling, gun design, composition of oxy-fuel mixture and discontinuity of parameters at the exit of gun barrel.



Figure 2.10: Variation in detonation velocity for various oxy-acetylene mixtures with changing volume of N_2 . (40)

other gases				
Fuel mixture	p_2/p_1	T ₂ (K)	D (m/s)	
$2H_2+O_2$	18.0	3,283	2,806	
$(2H_2+O_2)+O_2$	17.4	3,390	2,302	
$(2H_2+O_2)+4H_2$	16.0	2,976	3,267	
$(2H_2+O_2)+N_2$	17.4	3,367	2,378	
$(2H_2+O_2)+3N_2$	15.6	3,003	2,033	
(2H ₂ +O ₂)+1.5Ar	17.6	3,412	2,117	

Table 2.3: Parameters of detonation wave in H_2/O_2 mixtures with addition of

2.4.1 Properties of particles during deposition

The heat and momentum transferred to the coating particles are estimated by using the traditional equations of heat transfer and motion (43, 45) with and without alterations of supersonic velocities. In D-gun thermal spraying process, the creation of gas-mixture-powder system is the main parameter. It is connected to the detonation mixture, size and morphology of the powder particles, mode of injecting the powder particles (the axial feeding is better than radial feeding) (44), and particle loading position.

The position at which particles are injected is an important aspect. The effect of the distance between the particle injection position and the point where detonation wave generates (loading distance) on the velocity of the particles is shown in figure 2.11. It is reported that for oxy-acetylene gas mixture, at loading distance of 20 cm and 60 cm the maximum velocity of the particle can be of 837 m/s and 1152 m/s respectively (54). In a study, D-gun barrels having 25 mm of diameter (internal) with varying length (L) are used. A mixture of C_2H_2 , O_2 and N_2 is used as detonation gas. Alumina particles with three different sizes (10, 20 and 30 µm) are sprayed. The stand-off distance value is kept around 150 mm, which is sufficient for allowing the gas to expand easily without shock reflection effects.



Figure 2.11: Al_2O_3 (20 µm) particle velocity against axial distance for O_2 - C_2H_2 and O_2 - H_2 mixtures for various injection positions (40)

The dependence of particle temperature and velocity on its axial loading positions (x_i) and the gas conditions at particle location are shown in figure 2.12(a) and 2.12(b) respectively. The high temperature of the gas mixture melts the powder particles and the degree of melting depends on the particle size and its injection location. It is well understood that the particle, powder loading position, geometry of the gun barrel and stand-off distance (up to certain limit) are very important factors to determine the final properties of the coating. An increase in stand-off distance increases the velocity of the particle but simultaneously decreases its temperature when it impacts the surface of the substrate. It also results in non-uniform properties of the deposited coating as the properties of a coating are dependent on the characteristics of the deposited splats. The axial loading condition of the powder particles has direct effect on the terminal velocity and temperature of the particle, and has weak dependency on radial loading position. In order to provide a coating layer which possesses uniform properties the powder particles should be loaded over a narrow range.

The quantity of the powder that is to be injected should be about 10-20% of the weight of the gas mixture. This is determined by the influence of the quantity on the properties of the sprayed coatings and not by the deficit of gas energy. For only one detonation shot the sprayed coating is composed of individual splats deposited at different locations. If the quantity of coating powder supplied for one cycle is too high then there are chances of formation of a continuous layer of coating. Due to rapid cooling effect cracks form in such type of coatings (48).

The size range of powder particles is one of the important factor on which the properties of a coating depends (53). The average surface roughness and porosity of the D-gun sprayed Al_2O_3 and Ni-Cr coatings are found to be decreased by spraying fine powder particles whereas very little effects are observed in case of WC-Co coatings due to the flow of soft binder (Co) phase. The presence of the W₂C phase in WC-Co coating and α -Al₂O₃ phase in Al₂O₃ coating have effects on the toughness of such coatings. Wear resistant property remains almost unaffected by the size of the powder in case of WC-Co coatings, whereas wear resistance of Al₂O₃ coating is very sensitive towards

the powder particle size. For thermal spraying, generally powder with a particle size distribution of 10-44 μ m is preferred (53).



Figure 2.12: (a) Variation in particle speed and gas velocity at different axial locations and (b) Variation in particle temperature and gas temperature at different axial location (54)

It is possible to produce dense coatings with the help of detonation gun process as it possesses high particle velocity and temperature. The basic phenomenon to form a coating by this process is the impact of high velocity semi-molten/molten particles on to the substrate. An estimation of the particle velocity (v_p) is derived from a condition where the heat energy and the kinetic energy of the powder particles are equal.

$$v_p = 100 \left([c_p T_p + L] / 1.195 \right)^{1/2} \dots (5)$$

Where,

 c_p is the specific heat of the particle,

 T_p is the particle temperature (°C),

and L is the latent heat of the particle (cal g^{-1}).

It is clear from the expression that the particle with higher value of specific heat requires larger velocity for the substrate surface in order to get equal contributions from both the kinetic and thermal energies to form the coating. For liquid/molten particles the velocity values required to balance the thermal and kinetic energy are also dependent on the latent heat of particles to some extent.

The materials which have low heat capacity are very sensitive to the velocity effects. The solid state nickel particles attain the critical velocity of around 1130 m/s whereas in liquid state this critical velocity is increased to around 1370 m/s. The tungsten particles have the critical velocities of 950 m/s and 1130 m/s in solid and liquid state respectively. Also, when two different types of materials are heated at same temperature then again their particle velocities differ from each other.

2.4.2 Graded coatings

The various process parameters of D-gun process can be efficiently controlled for each and every shot (55, 56). This gives an advantage of spraying both metal and ceramic materials by using optimum spraying parameters for each type of material (57). Hence, graded coatings, having a compositional gradient through the coating thickness can be developed by spraying several layers of coating with rising ceramic to metallic shot ratio in a series. Optimization of process parameters for other deposition methods such as mixed powder method is very difficult. The optimum process parameters depend on the properties of the feedstock material.

2.4.3 Properties of D-gun coatings

D-gun sprayed coatings are commonly applied for the enhancement of wear resistance, thermal protection and insulation properties of the metal substrates.

2.4.3.1 Thermal Barrier Coatings (TBCs)

(a) Bond coatings

D-gun sprayed Ti-Al-Cr and MCrAlY (M is metal like Ni/Co) coatings are investigated as thermal barrier bond coats (58-62). The functions of TiAlCr

coatings are found to depend upon the structure of substrate material which governs the nature of diffusion. NiCrAlY coating is found to be a good oxidation resistant coating due to the formation of an inert alumina layer at around 1000 °C temperature. The formation of Al₂O₃ takes place along the splat boundaries of D-gun sprayed NiCrAlY coatings (62). D-gun sprayed NiCrAlY coating has shown good oxidation resistance property when oxidized isothermally at around 1050 °C temperature. However, better oxidation resistance of NiCrAlY coating is achieved while spraying by LPPS process. D-gun sprayed NiCrAlY coating also possesses higher hardness. Such coating can be considered to apply for high dynamic working conditions (58). In another study, D-gun and HVOF techniques are employed to apply Ni-25Cr-5Al-0.5Y as a bond coat (BC) on a metal substrate before applying YSZ coating as TBC. It is found that the rate of oxidation of D-gun sprayed TBC is more than the same of HVOF sprayed TBC (60).

(b) Ceramic coatings

The D-gun sprayed ceramic TBCs are generally dense and possess less microcrack. In high temperature atmospheres, the less porous D-gun sprayed ceramic coatings can decrease the oxygen diffusivity in the coating and therefore, reduces the oxygen pressure at the interface of the bond coat and top coat (63). Various types of materials like NiCrAlY/NiAl/YPSZ and NiCrAlY/YPSZ are also successfully deposited as TBCs by this process (61).



Figure 2.13: Fractured cross-section of a D-gun sprayed Al₂O₃ coating

A fractured cross-section of a D-gun sprayed thermal barrier (Al_2O_3) coating is shown in figure 2.13. The lamellar microstructure is found to be similar to the plasma sprayed coatings. This is formed by layer wise deposition of splats resulted from the impact of melted/semi-melted particles. The splat formed is generally of 3-6 µm thickness and some hundred µm in diameter.

2.4.3.2 Wear resistant coatings

(a) Alumina (Al₂O₃):

It is reported that a high particle velocity helps in producing a rougher coating surface (64), which is beneficial for the adhesion of the coating splat to the substrate due to better interlocking. Such coatings also possess good wear resistant properties under abrasion and sliding wear conditions. An alumina coating produced by spraying 14 μ m sized particles by D-gun is believed to be a good erosion resistant material. It is reported that the hardness of alumina coating is influenced by the stand-off distance, oxy-fuel ratio, and carrier gas flow rate. A very high hardness value of 1363 H_v and less porosity of 1% can be achieved by varying these process parameters (65-69).

(b) Alumina-Titania/Alumina-Chromia/Alumina-Cerium coatings:

Al₂O₃-TiO₂ coating with 13 wt.% TiO₂ (22-45 µm particle size) sprayed by Dgun process is found to have very low porosity, high hardness of above 1000 Hv. This type of coating is capable of saving the AISI 1045 steel material from wear and friction. Many studies are conducted on Al₂O₃-TiO₂ coatings. The phases formed in Al₂O₃-TiO₂ by D-gun process are compared with the same of plasma sprayed Al₂O₃-TiO₂ (70). In another work, D-gun sprayed nano-structured Al₂O₃-TiO₂ coating is studied (71). The XRD peaks of α -Al₂O₃ and γ -Al₂O₃ obtained in the coating are used to determine the fraction of the melted powder. D-gun and plasma spray processes can be successfully employed for the deposition of nanostructured Al₂O₃-TiO₂ coatings. In a study it is observed that D-gun sprayed Al₂O₃ has 60% of γ -Al₂O₃ whereas plasma sprayed alumina coating has 98% of γ -Al₂O₃. Formation and retention of α -Al₂O₃ are also present in such coatings (71).

Addition of rare earth elements to thermally sprayed coating material with a small quantity can cause enhancement of coating properties. This

enhancement could be resulted from microstructural refinement, improved hardness, toughness and tribological properties (72, 73). Rare earth oxides are generally doped in the thermally sprayed coatings to combat severe wear and corrosion environments. It is reported in a study that cracking/spallation of a coating can be reduced by adding small quantity of rare earth oxides to the coating materials (74). Among various rare earth oxides Ceria or Cerium oxide has promising features which lead to improve properties of the deposited coatings (75, 76). Addition of cerium oxide (CeO₂) to Al₂O₃/Ni based coatings reduces the porosity and increases the micro-hardness and fracture toughness properties of as-sprayed coatings. The presence of Al₂O₃ in the developed coating provides high hardness while the presence of CeO₂ ensures the grain refinement of the coating. The low porosity, high hardness and grain refinement altogether makes the deposited coating to be a good wear resistant material (75). Alumina feedstock with 0.8wt% CeO₂ sprayed by D-gun process on AZ91 alloy produces a coating with better wear resistant property as the CeO₂ inhibits the formation of Mg and Zn oxides and refines the microstructure of the coating (77).

D-gun sprayed chromia (Cr_2O_3) coating is well known for its high corrosion and abrasion resistance properties. Such type of coating is very useful in ship building, water pumps, and printing rolls manufacturing. A lot of studies have been carried out on Al₂O₃-Cr₂O₃ coating systems where Cr₂O₃ is added to Al_2O_3 feedstock with different proportions. It is reported that α - Al_2O_3 phase gets stabilized on addition of 30wt% Cr_2O_3 in the staring powder (78). It is also reported that by adding 20wt% Cr_2O_3 and by utilizing water-stabilized plasma, only α -Al₂O₃ in the coating can be attained (79). The thermally sprayed Al₂O₃-50wt%Cr₂O₃ is found to have the highest fracture toughness property among different binary coating systems (80, 81). In a study, Al₂O₃-50wt% Cr₂O₃ is successfully deposited on a T22 boiler steel and Superfer 800H (Fe-based alloy) substrate with the help of D-gun process. Ni-20Cr is used as bond coat material for such coating applications. Al_2O_3 -50wt%Cr₂O₃ coating is found to improve the hardness of the substrate materials. Also, the cyclic hot corrosion tests are conducted on all the samples at 900 °C temperature in the Na₂SO₄-60%V₂O₅ atmosphere. It is found that D-gun

sprayed Al_2O_3 -50wt%Cr₂O₃ coating can save the Fe-based substrate from high temperature oxidation and hence enhances its life (82).

(c) Corrosion and wear resistant coatings:

D-gun sprayed Cr₃C₂-25NiCr coating on DIN 12CrMo44 structural steel surface is found to be dense, adherent, highly oxidation resistant and wear resistant material. Cr₃C₂-25NiCr coated superalloys (Superni 75 and Superni 718) have shown improved high temperature corrosion resistance properties compared to the same of their bare counterparts when exposed to 900 °C temperature in the presence of 75wt.% Na₂SO₄+25 wt.% K₂SO₄ salt mixture for 100 cycles. The formation of continuous protective oxide layer of nickel, chromium, and their spinel (83) is found to be helpful in increasing the material life. In a similar study, Cr₃C₂-25NiCr coating is applied on Superni 75 and Superni 718 superalloy materials (84). The developed coatings are found to be uniform, dense and adherent with less porosity (0.8%). These coatings have also showed higher corrosion protection in a molten salt environment of $Na_2SO_4-60\% V_2O_5$ at a temperature of 900°C for 100 cycles (84). Cr₃C₂-25NiCr coating deposited on Superfer 800H has shown higher hot corrosion resistance than the same coating deposited on Superni 75 and Superni 718 superalloy materials. It is found that the parabolic rate constant of Cr_3C_2 -25NiCr coated alloy substrates is lesser than their bare counterparts. The application of D-gun spray coatings is not just limited to superalloy materials; such coatings are also applied on steel components used in continuous casting rolls. D-gun sprayed Cr₃C₂-25NiCr coating is applied on the roll surface of material DIN 12CrMo44 in a steel manufacturing plant in China (85). The risk of failure of the components is reduced due to increased wear resistance property of the surface. It should be noted that the wear resistant property of D-gun sprayed Ni-Cr compounds is inferior to the same of D-gun sprayed WC-Co coatings (85). When exposed to high temperature conditions (above 600 °C) such WC-Co coatings have shown improved corrosion resistance property (86, 87).

It is reported that Ni-Al and Ni-Cr bond coat layers applied for intermetallic Fe-Al coating on a plain carbon steel surface are responsible for the improved thermal stability, bond strength, adhesive strength and hardness of the whole coating. The use of such type of bond coats on steel substrate reduces the negative gradients of temperature and enhances the adhesion of the coatings (88, 89).

2.4.4 Research work on thermally sprayed SiC and Al₂O₃-SiC

Silicon carbide (SiC) offers high structural and chemical stability due to which it is extensively used for tribological applications where low friction and high wear resistance is required. However, SiC powder is not easily sprayable by thermal spray techniques as it gets decomposed at above 2500 °C temperature (90). Plasma sprayed 'SiC' is found to be 30 times less wear resistant compared to the plasma sprayed WC-Co coatings. The decomposition of 'SiC' leads to formation of brittle silicon phase and increases the porosity of the sprayed coating, and hence reduces the wear resistance (90). Many researchers have tried to develop 'SiC' coatings by using different thermal spray techniques to achieve desired properties (90). All these studies have focussed mainly on the preparation of the 'SiC' feedstock material which is added with some other material (metal or ceramic) to restrict the decomposition of 'SiC' while spraying. In a study, mechanically activated Fe-SiC composite powder is successfully sprayed by D-gun process (91). The coating is found to be dense, homogeneous, and highly wear resistant. The XRD and SEM studies have indicated some reaction to take place between SiC and Fe during the deposition. The Fe-Si phase is formed and the presence of SiC has improved the strength of the coating. It is reported that copper (Cu) coatings with Al₂O₃-SiC ceramic particle inclusions (particle size $\geq 150 \text{ }\mu\text{m}$) increased abrasion resistance of concrete and grinding stones (92). Fine SiC powder added to FeTi feedstock produces a hard and dense coating (porosity <2%) (93). The phases present in the sprayed coating are TiSi₂, TiSi, Ti₅Si₃, and FeTiSi which suggest the decomposition of SiC while spraying. In another study, TiC_{0.5}N_{0.5} feedstock material is added with AlN, SiC and Ni-Cr materials and sprayed on the surface of 30KhGSNA steel. The resulting coating has offered more wear resistance property compared to the same of WC-15%Co hard alloy coating (94). SiC coatings with good adhesion can be successfully deposited by Dgun process on the surface of martensitic steel substrates (AISI 440C). The

wear resistance of such coating is improved due to the formation of SiO₂ during tribological test (90). In a suitable powder mixture with low SiC content the decomposition of 'SiC' can be avoided where melting of SiC takes place at a temperature lower than the decomposition temperature of 'SiC' (95-97). For example, decomposition of 'SiC' can be avoided if it is mixed in right proportion with other materials such as ZrB₂. On deposition, it is possible to form a eutectic mixture rich with SiC in the coating. Therefore, melting of SiC in the mixture can happen at lower temperature than the normal melting point. This way the stable liquid phase may form to preserve SiC in the final coating without decomposing it. Hence, it is possible to save SiC from getting decomposed when it is mixed with suitable material and with proper proportion. Al₂O₃-SiC composite coating can be deposited by using HVOF and plasma spray technique as the sintering temperature of 'SiC' is reduced by the introduction of Al_2O_3 (98, 99). Also, the Al_2O_3 addition is found to influence glass forming ability of 'SiC' coating (100). In a study, Al₂O₃-SiC coating is successfully deposited by HVOF process (101) without decomposing 'SiC'. Presence of 'SiC' in the Al₂O₃ feedstock results in a coating with an increased amount of α -Al₂O₃ content due to a rise in the melting temperature of the feedstock powder (102). Presence of 'SiC' in the coating helps to increase the transformation of metastable alumina phases to stable alumina phase.

Many researchers have tried to deposit SiC and Al₂O₃-SiC coatings by different thermal spray techniques. However, till date no such work is noticed in available literature where D-Gun spray process is used to successfully deposit SiC and Al₂O₃-SiC coatings.

2.5 Pre-treatment of steel substrate

Preparation of steel substrates is an important step before applying thermal spray coating on it. The effectiveness of a coating depends on its degree of adherence to the substrate. It is well known that proper surface preparation is essential for successful coating deposition. The presence of contaminants (such as oxides, grease, oil etc) can cause hindrance to the coating-substrate adhesion. Chemical impurities are generally not visible like sulphate and

chlorides, but they are very harmful as they attract moisture through the coating system and results in premature failure of the coating.

For each and every type of coating, the condition of the substrate surface is very critical in terms of the life of the coating. But different types of coating techniques require different types of surface preparation to achieve good coating-substrate adhesion. For example, for hot dip galvanizing it is very important to have a substrate free from impurities so that molten zinc can easily react with the steel surface to form a series of iron/zinc alloy layers. Organic paint coatings require polar adhesion with the substrate to have a successful coating.

Thermally sprayed coatings are much dependent on mechanical interlocking action to develop a good coating-substrate adhesion. Hence, the pre-treatment process should be able to provide proper surface roughness on the substrate surface. Hand and power tool cleaning, chemical etching, and abrasive blasting are some of the substrate preparation methods available for the job. Among those abrasive blasting (grit/sand blasting) process is generally used to prepare the substrate before applying thermally sprayed coating.

2.5.1 Surface treatment of steel by Sand blasting process

For thermally sprayed coating application the substrate surface should be rough enough to mechanically anchor the splats deposited on it (103). Sand blasting process can offer such roughness on steel substrates. This process is used for most of the thermal spray processes and it produces a surface suitable to achieve a coating with lesser residual stress, acceptable interface microstructure and good bond strength (104). In this process, abrasive grits (generally Al_2O_3/SiC) are accelerated by using compressed air towards the substrate surface to be coated. Other than producing a rough surface this process also cleans it by removing the surface contaminants (hard) present on it. Although the main reason behind the coating-substrate adhesion in thermally sprayed coating is mechanical interlocking, some physical/chemical bond formation may also take place at the interface zone due to the thermal energy transfer by heated particles to the chilled substrate. The roughness created on the substrate surface can be varied by adjusting various process

parameters such as grit size, stand-off distance, air pressure, blasting time, and spraying angle. Table 2.4 shows the effect of these parameters on roughness generated on the steel surface (105).

<i>Sicei</i> (105)						
S. No	Grit Size	Time	S.O.D	Angle	Pressure	Ra
	(Mesh No.)	(s)	(mm)	(Degree)	(Bar)	(µm)
1.	60	60	100	90	5	2
2.	24	60	100	20	7	3
3.	24	20	100	90	7	4
4.	24	150	100	90	7	5
5.	24	60	100	90	9	6

Table 2.4: Effect of grit blasting parameters on surface roughness of steel(105)

A lot of studies have been conducted on the effects of grit blasting process on the adhesion/bond strength of the thermally sprayed coating (106-109) with a major attention given to the roughness generated on the surface. Surface roughness created by grit blasting process is the main subject of many studies (107-110). It is noticed that by using coarser grits high roughness can be created on a steel surface (106). It is reported that the roughness value increases linearly with an increase in grit size whereas the roughness remains unaffected with changing blasting angle and the stand-off distance. An increase in blasting time initially increases the roughness on the substrate surface but after a certain period it does not change much (110). The maximum adhesion strength of the coating is achieved by blasting with alumina grits (20 μ m grit size) at an angle of 75° (111).

Surface distortion and grit contamination are two major limitation of sand/grit blasting process. Distortion of a surface occurs due to the impact of high velocity grit particles on the substrate which deforms the surface and produces a strain hardened zone beneath the top surface. Distortion can be minimized by using smaller grits and lower air pressure. Also, the surface distortion increases with an increase in number of passes without giving any change in the roughness generated. Hence, blasting time should be controlled properly to avoid distortion of the surface. Distortion is said to be related to almost all the process parameters used in a grit blasting process. Stand-offdistance has the least effect on the distortion of the surface compared to other

process parameters. The parameters which have a linear relationship with distortion of the surface are blasting pressure, grit size, blasting angle and working distance. The grit contamination is the defect caused by locking/embedding the grits on the substrate surface. Grit contamination is also believed to affect the adhesion of the coating and it can be calculated by counting total number of grits present in a constant area. It is reported that at high blasting angle more grit contamination occurs on the surface. The contamination level can be as high as 10% of the total substrate surface and can hinder the adhesion of the coating to the substrate (112, 113). It is reported that the grit contamination is the highest when using medium size grits. Grit contamination is found to be increased with increasing stand-offdistance, blasting pressure, and blasting angle. Also, it decreases with the increasing size of grits used for blasting operation. The average surface roughness (R_a) should be considered for measuring the roughness of a pretreated surface by grit blasting process. The other erosion processes which produce similar roughness are shot-peening and Electro-discharge machining (EDM) (103).

After grit blasting the treated surfaces are required to be ultrasonically cleaned in order to ensure best possible conditions for the bond formation (114). Also, some other methods like chemical etching (115-117) and ultrasonic cleaning (118-122) are used to clean the blasted surface. However, in many practical applications, ultrasonic cleaning and chemical etching are not possible to use on site due to the large size of the component and the working atmosphere of the site (123, 124). Hence, the most preferred way to clean the steel substrates after grit blasting is by blowing air over the surface (125, 126). But, this process is still incapable of removing micro-debris and broken fragments entrapped in the cracks generated due to plastic deformation effects of blasting. It is difficult to impart good wetting properties (which are crucial to achieve good bonding strength) to steel surfaces (127) by air blowing because of the relatively 'dirty' substrate condition. A new technique is proposed in a study in which a simple resin pre-coating (by using a resin and hardener) is done on the grit blasted steel surface to achieve a good wetting condition for onsite applications even when

the micro-dirt and grit particles are present in the interface zone. Around 32% improvement in the adhesive strength is achieved by using this new pre-treatment process (128).

Many times it is tried to replace the sand/grit blasting process by some other type of pre-treatment process before applying thermal spray coatings. One such replacement is by using dry ice pellet peening technique. The dry ice pellets are accelerated to the substrate by using compressed air with the help of Laval nozzle. This technique is known as dry-ice blasting/peening and is a pneumatic jet-based technology. The dry ice pellets have less abrasiveness compared to the ceramic grits used in grit blasting (129). However, being non-corrosive in nature this technology is widely used in cleaning delicate components such as, cleaning and decontamination of aircraft shells, nuclear plants, rust and paint removal, and removal of resin and oils (130). The roughening mechanism of dry-ice blasting is based on thermo-mechanical effects, which is particularly different from conventional grit blasting process. This process is capable of cleaning the substrate surface, reducing porosity and removing oxide scales present on the surface which in turn increases the adhesive strength of the deposited coatings. In addition to these, this process is less polluting compared to the traditional blasting process (131). However, the preparation of dry ice pellets makes this technology complicated and costly.

Grit blasting process followed by a chemical decontamination process is generally used as pre-treatment process for cleaning and roughening the steel substrates, but these processes are not environment friendly as they produce liquid waste, create noise and scatter sludge. It is reported that instead of using grit blasting for surface preparation before applying LPPS coating (132) one can also use a low pressure arc which neither generates noise nor any kind of sludge. The oxide scales present under the cathode spots can be vaporized and removed quickly. The distribution of the dust particles resulting from melting cathode is very important (132). A good bonding strength of the coating is proven to be achieved with a substrate roughness value of above 3 μ m. Addition of cathode spots on grit blasted surface increases the adhesion strength of the APS coatings (132). But, the process should be used carefully otherwise the projections formed by grit blasting may be vanished by cathode spot treatment.

2.5.2 Surface modification by Electric discharge machining (EDM) process

The Electric discharge machined surface is composed of craters, micro-cracks, micro-pores/voids and re-attached debris as shown in figure 2.14. As a result, EDM produces a surface with significant roughness. The formation of voids is believed to commence from a point which is on the interfacial surface of the overlapping craters. A little amount of gas gets entrapped under the craters due to the removal of the molten metal.



Figure 2.14: SEM images of (a) micro-crack (b) micro-pore/void (c) reattached debris particle and (d) cross-sectional view of a crater on EDMed *steel substrate*

The attachment of debris particles on the EDM processed surface changes the texture and the properties of the surface. The pressure drop at the end of pulseon-time (T_{on}) helps to remove the molten material from the crater. However, a portion of molten material remains intact on the surface and forms resolidified layer. This happens when the force of ejection is not large enough to overcome the viscous force of molten material. This re-solidified layer is commonly known as recast layer or white layer which is generally rough, brittle and contains some cracks. Formation of such layer is undesirable for engineering applications due to its brittle nature. EDM process parameters are directly related to the generation of roughness and the thickness of recast

layer. Higher spark energy yields higher roughness and more thickness of the recast layer. A lot of research work are carried out to find the thickness and properties of the white layer by both experimental (133) and theoretical (134) means. This white layer is generally has a fine-grained structure and is very hard in nature due to the rapid cooling effects (135). It is well adherent to the bulk material and is generally composed of spherical debris particles, voids and craters (136). The thickness of this recast layer depends on the thermal conductivity of the workpiece material. The materials with less thermal conductivity confine the heat produced by the spark in a very thin zone of the workpiece surface and hence the workpiece material gets easily melted (137). This process is capable of machining very complex shaped components with very high precision.

One of the commonly observed defects on the EDM processed surface is surface crack. The presence of cracks on the surface reduces its resistance to fatigue and corrosion. Figure 2.15 shows the presence of cracks on both the top surface and cross-sectioned surface of an EDM processed sample. It is observed that the surface cracks generated by EDM do not propagate in the bulk material and are terminated at the interface between the bulk material and the recast layer (137). The Electro-discharge machining has severe effects on the fatigue life of a tool steel component. This is due to the crack formation and crack propagation which lead the material towards failure (138, 139). Crack tip increases the stress concentration; hence it is important to eliminate the surface cracks induced by EDM process in order to improve the service life of EDM processed components subjected to cyclic loading conditions. The formation of crack is initiated by the tensile stress generated by the EDM process. Tensile stress generates when the molten material is cooled at a higher rate compared to the parent metal. When these surface stresses exceed the ultimate tensile strength of the material, cracks are generated. In a study, the relationship between the machining parameters and the crack formation is investigated. The crack formation in a thick recast layer is more as compared to the thin recast layer although the crack density in both the cases remains the same. A material with lower thermal conductivity experiences more crack formation and it increases with an increase in the values of the machining parameters such as pulse current and pulse-on-time. Pulse-on-time is believed to be the main contributor to the crack formation on the EDMed surface (140). In a study it is shown that low fracture toughness and low thermal shock resistance of the re-solidified layer are the main reasons behind the crack formation.



Figure 2.15: Cracks on the (a) top and (b) cross-sectional surface of an EDM processed steel sample

The average surface roughness (R_a) generated by EDM process is very important as EDM is generally used for mould and die making purposes. It is generally believed that the surface with very high roughness is more vulnerable to fretting and sliding wear conditions (141, 142). The effects of surface roughness of moulds on wear phenomenon and economy should be properly investigated (143). The surface cracks and its geometrical feature have strong effects on fatigue life of a component. It is reported via computer simulation and experimental verification that the height of asperities has a direct influence on the fatigue life of a component (144). The cavities present on the surface act as preferential sites for fatigue crack initiation (145). Hence, a control on the surface finish of the EDM processed surface and a reduction in stress concentration sites of an EDMed surface is important to improve fatigue life of a component. The surface roughness of an EDMed sample is directly proportional to the size of the craters produced on the surface. Larger craters produce higher roughness whereas smaller craters result in lower roughness of the workpiece surface. The large size craters are resulted due to high energy sparks and vice-versa (146). In the present scenario, attaining a

certain quality of surface texture is very important for the functionality of a part (147). The surface texture of the machined workpiece is influenced by the process parameters. The discharge energy of the pulse has large impact on the machined workpiece surface integrity. The electrical parameters on which discharge energy depends are peak current, pulse-on-time, pulse-off-time and voltage. Die-sinking EDM has the capability to create a surface with average roughness of 2-7 µm on tool steel surface by changing the process parameters like current, pulse-on-time and pulse-off-time as shown in table 2.5 (148). If larger value of pulse on time is selected then more material will be melted and much deeper craters will be formed (148). This crater formation is the basis of roughness creation on the workpiece surface by EDM process. A study examined the effects of pulse on time, peak current and pulse-off-time on surface roughness of AISI P20 steel sample. It is observed that lower peak current, lower pulse-on-time and higher pulse-off-time produces better surface finish (149). It is stated that the increase in spark energy (which is directly dependent on peak current and pulse on time) results in an increase of surface roughness. Dimensions of the cracks and the craters increase with increasing spark energy (150). The energy domain for material removal in electric discharge machining process is electro-thermal. Therefore, thermophysical properties like melting point, thermal conductivity etc. of the material are important aspects in EDM (151). Hence, the surface texture of the EDMed surface depends on its thermophysical properties as well.

roughness (R_a) of steel (148)						
S. No	Current	Pulse-on-time	Pulse-off-time	R _a		
	(A)	(µs)	(µs)	(µm)		
1.	8	2	2	2		
2.	16	4	3	3		
3.	8	4	2	4		
4.	16	4	2	5		
5.	16	24	3	7		

Table 2.5: Effect of EDM process parameters on the average surface roughness (R_a) of steel (148)

It is believed that the crater formed due to spark discharge has geometry of circular paraboloid (152) with a flat brim (no uneven re-deposited material present on its circumference) and uniformly disseminated re-solidified
material on the inner side as shown in figure 2.14. It is also assumed that uniform and optimum dielectric flushing helps to remove debris particles effectively from the gap between the tool and workpiece. This in turn reduces the occurrence of non-profitable or/and detrimental pulses (like shortcircuiting or arcing) and promotes a stable machining throughout the process (153). Theoretically each and every spark erodes only a single point, starting from a point where the distance between the workpiece and tool is the smallest. This process of erosion continues until the final surface profile is being created. The final surface produced after adequate number of spark discharges will be different from the initial surface profile. The shallowness of the craters resulted from the electro discharge machining generally represents peak to valley height distance. The microscopic images of an Electrodischarge machined surface are shown in figure 2.16 in which craters are clearly visible. There are two types of craters form on an EDMed surface as evident from fig. 2.16(a): one is the bare crater with no re-melted material inside it and the other is crater with re-melted material. The 3D view and 3D roughness shown in figure 2.16(b) and figure 2.16(c) respectively show the shallowness of the crater. Hence, the produced surface can be characterized mostly by estimation of its roughness.



Figure 2.16: Microscopic image of (a) top surface of EDM processed surface (b) 3 D view of top surface (c) 3 D roughness profile of the top surface

The formation of the new grain structures in the recast layer changes the mechanical properties of the component and hence, proper metallurgical characterisation of the EDM processed samples is required. Therefore, it is important to investigate the different phases observed in the recast layer by using XRD and SEM analysis (154, 155). In a study, recast layer formed on a steel surface by using various types of dielectric liquid and tool electrodes (156) is investigated. Austenite formation is reported due to absorption of carbon on the workpiece surface. But, this austenite phase is metastable in nature and it can change its form in different service environments. The amount of retained austenite in the recast layer is independent of the tool electrode material when carbon base dielectric is used. SEM and TEM are used to observe the complex nano-structure of the ferritic steel surface processed by EDM (136). The recast layer is found to be composed of residues of austenite, some martensitic needles and an austenite layer at the interface between the heat-affected zone and the recast layer. Presence of cementite is also spotted on the top surface of the recast layer measured by using Auger spectroscopy. The effect of EDM on the formation of recast layer and heat affected zones are analysed for different types of steels (157). It is observed that the metallurgical transformation of steel surface depends on its hardenability. Formation of three distinct layers happens in the case of martensitic steels which are hard in nature. The size of the top recast layer depends on the peak current value used during machining. A layer of 5-80 µm thickness can be developed by using a peak current of 2-50 A range. Below this recast layer a quenched layer forms, with martensite like structure. Beneath this guenched layer a transition layer forms which is much smaller in size than the other two layers. In case of austenitic steels and ferritic steels, the formation of a recast layer with a uniform structure is expected, below which almost no HAZ occurs. Therefore, it is easy to characterize the whole recast layer by assuming it as a single layer. Surface hardening by EDM process occurs in all the steels. However, it is reported that steels with an FCC structure are easily hardened by this process. Volumetric change in the workpiece due to structural and chemical changes caused due to carbon absorption and by rapid cooling and heating of the workpiece surface imparts

residual stresses of around 750 Mpa and 500 MPa in case of hardenable and non-hardenable steels respectively. The formation of retained austenite with some distorted martensite has a direct connection with the residual stress generated on the surface (156). This residual stress is considered to be detrimental for the workpiece. The residual stress concentration is highest on the topmost surface and it gets reduced with increasing depth (156, 158). In some cases, the presence of recast layer is found to be good for the fatigue properties of a material. It is found that Ti-Al based alloy has less crack formation on its surface when machined by EDM as compared to the same by conventional milling. Studies on this recast layer are conducted to increase the life of the EDMed components for engineering applications (159, 160).

In a study, modification of the workpiece surface by introducing sintered composite electrode material is reported (161). The electrode material gets attached to the workpiece surface in sufficient quantity to apply a coating on the workpiece surface. A 20 μ m thick coating of TiC ceramic material is observed on the surface of a steel workpiece in very short time of electric discharge machining and the hardness of the coating is found to be three times of the base material (162). The hardening/modification of a workpiece is also reported by developing TiC layer on it with the help of titanium powder suspended in the dielectric liquid (163). The tool life of drill bits have been improved by Electro-discharge machining. However, with high surface roughness the drill bits are found to have limited applications (164). Application of hard layers on workpieces by EDM process is reported in many other studies (165-167).

Hence, it can be concluded that surface treatments are possible by using EDM technique. In fact, electrical discharge surface treatment machines are being manufactured by Mitsubishi Electrical (Japan) in order to produce functional coatings to improve durability of the components.

2.6 Research gaps

It is found from the literature that the sand/grit blasting is mostly used as a pretreatment process (to impart roughness and to clean the surface) before applying thermal spray coatings on steel samples and Electro-discharge

machining process is another type of process which can create roughness on the steel substrate. A lot of researchers tried to improvise the use of sand blasting process (by using dry ice blasting, cathode spot generation technique, and by using single resin primer) in order to increase the bonding strength between the coating and the substrate material. The average surface roughness (R_a) created on the steel substrates by both sand blasting and EDM processes can be varied by varying the process parameters. The EDM process is found to be used to modify various types of materials for functional applications. Although, no study is found so far, on the usage of EDM as a pre-treatment process prior to the application of thermal spray coatings.

Silicon Carbide 'SiC' has many engineering applications like in cutting tools for machining. Alumina inserts added with 'SiC' whiskers are proven to be good cutting tool materials which can easily machine almost any kind of material with very less distortion of the tool. But this material (SiC) has limited application in the field of thermal spray coatings. Thermally sprayed alumina coatings are been extensively used in many industries like aerospace, petroleum, etc. A lot of studies have been conducted on increasing the wear and corrosion resistance of alumina base coatings by adding some dopants (like TiO₂, Cr₂O₃, and CeO₂ etc.) to the feedstock powder. Few researchers have tried to deposit 'SiC' material by thermal spray process but their success is minimal due to the decomposition of 'SiC' at high temperature produced by the processes. Hence, it is not suitable to deposit 'SiC' by using thermal spray process and this is the main reason behind the rarity of literature related to thermally sprayed 'SiC' coating. Although, it is claimed by a researcher who used HVOF technique to deposit a mixture of Al₂O₃-SiC that if 'SiC' can be deposited without getting decomposed then it will be beneficial for the properties of final coating. But no such claims are noticed regarding the deposition of Al₂O₃-SiC by D-gun process.

Also, the literature on Al₂O₃-SiC coating used as TBC is rare and no literature is found so far on the high temperature oxidation behaviour of these coatings sprayed by D-gun process.

2.7 Objectives

The objectives of present work are formulated based on the observations and research gaps found in the literature. The point wise objectives are mentioned below.

- To check applicability of electro-discharge machining (EDM) process as a pre-treatment process to replace the grit/sand blasting process before applying Ni-5Al bond coat by D-gun process. In order to achieve this, comparisons between EDM processed steels and sand blasted steels are to be made.
- To develop D-gun sprayed Al_2O_3 coatings by spraying crushed powder and to analyse the features of the coating, such as microstructure, porosity, micro-hardness, fracture toughness and wear properties.
- To produce D-gun sprayed Al₂O₃-SiC coatings by adding low quantity (3, 5 and 7 wt%) of SiC to Al₂O₃ feedstock and to study the effect of 'SiC' addition on the phase formation of Al₂O₃.
- To study the wear behaviour of D-gun sprayed Al₂O₃-SiC coatings by using ball-on-disc (BOD) type tribometer. The effect of 'SiC' addition on the wear behaviour of Al₂O₃-SiC coatings is to be investigated.
- To study the oxidation resistance of bare steel, D-gun coated Al₂O₃ and D-gun coated Al₂O₃-3wt%SiC by high temperature cyclic oxidation tests. The applicability of D-gun sprayed Al₂O₃-3wt%SiC as a TBC (Thermal barrier coating) is to be judged.

2.8 Summary

It has been concluded from the literature survey that very less work has been done so far on thermally sprayed Al_2O_3 -SiC coatings and also no work is reported on the quantity of Al_2O_3 phases present in the as-sprayed Al_2O_3 -SiC coatings. This research work also aims on the detailed study on tribological and mechanical properties of the D-gun sprayed alumina based coatings. The effect of SiC addition on the oxidation resistance property of the D-gun sprayed alumina coating is studied. In addition, the mechanical properties of the oxidized coatings are estimated. Moreover, it is also tried to replace the sand/grit blasting technique by the Electro-discharge machining (EDM) process as a substrate preparation technique to be used before applying Ni-5Al bond coat by D-gun spray process.

In the consecutive chapter, a detailed description of the materials and methods used in this study is furnished.

Chapter 3 Materials and Methods

In this chapter, all the experiments conducted for this study are explained in detail:-

3.1 Deposition of coatings

3.1.1 General introduction

D-gun sprayed Ni-5Al coating is deposited on pre-treated (by sand blasting and EDM) EN 31 steel samples with a diameter of 25 mm and thickness of 10 mm. Ni-20 bond coat and Al₂O₃ based coatings are deposited on sand blasted AISI 1020 steel substrates (size: $100 \times 50 \times 8 \text{ mm}^3$ and $10 \times 10 \times 5 \text{ mm}^3$) by D-gun technique. Ni-5Al, Ni-20Cr and Al₂O₃-SiC powder mixture (with variable quantity of SiC) are used as feedstock materials. The detonation is created by igniting an oxy-acetylene gas mixture. The particulars of all the powders used are shown in table 3.1. The details of the feedstock powders used for the deposition of coatings are shown in table 3.2. The compositions of EN 31 and AISI 1020 steel substrate are shown in table 3.3

3.1.2 Blending of powders

SiC powder with low quantity (3wt%, 5wt% and 7wt%) is mechanically mixed homogenously with Al_2O_3 feedstock with the help of a ball mill (Retsch PM 100). The mixing is performed at 120 rpm for 2 hours in normal atmospheric conditions without using any ball in the vial.

3.1.3 Preparation of substrate

In the present study, EN 31 and AISI 1020 steel substrates are used for the deposition of the Ni-5Al coating and Ni-20Cr bond coats and Al₂O₃-SiC top coat. All the substrates are first cleaned by chemical cleaning method to remove the loose dirt, oils, grease etc. In order to get the required roughness on the substrates sand blasting process is employed with Al₂O₃ grits. The sand blasted samples ($R_a = 3\mu m$, $5\mu m$, $7\mu m$) are then cleaned by using ultrasonic

cleaning method. Immediately after this, the substrates are directly taken to develop coating on their surface.

Name	Size	Composition	Туре	Make &
				specification
Crushed	–45 μm	Al ₂ O ₃ 99.5 wt%,	fused &	Oerlikon
Al_2O_3	$+5\mu m$	$SiO_2 0.020 wt\%$,	crushed	Metco, USA,
		$Na_2O 0.300 \text{ wt\%},$	(Angular /	(Amdry 6060)
		CaO 0.050 wt%,	blocky)	purity: 99.5%
		$Fe_2O_3 0.050 \text{ wt\%}$		
Ni-20Cr	-106 µm	Ni 76.3 wt%,	Mechanically	Oerlikon
	+45 µm	Cr 19.5 wt%,	Clad	Metco, USA,
		Si 1.2 wt%,	(Spheroidal)	(METCO 43
		Fe 1.0 wt%,		C-NS)
		Mn 1.5 wt%,		
		Others 0.5 wt%		
Ni-Al	–90 μm	Ni 95 wt%,	Mechanically	Oerlikon
	+45 μm	Al 5 wt%	Clad	Metco, USA,
			(Spheroidal)	(450 NS)
SiC	-40 µm		Angular /	SNAM
	$+5 \ \mu m$		Blocky	abrasives
				Private
				Limited
				Chennai (SiC-
				M)

Table 3.1: Types of coating powders used

Die-sinking EDM is another pre-treatment process used to prepare EN 31 steel surfaces as detailed in chapter 4. The machine used simple jet flushing technique to flush out the melted material from the gap between the tool and electrode. Hydrocarbon oil is used as dielectric material for all machining experiments.

The detailed description of sand blasting and die-sinking electro-discharge machining techniques used to create roughness over the steel surfaces in this research work is given below.

Coatings	Contents		Nomenclatures
Top coat	Ni - 5wt.%Al		Ni-5Al
Bond coat	Ni - 20wt.%Cr		Ni-20Cr
Top coat	Pure Alumina	Al ₂ O ₃	A0SiC
	Mechanically	Al ₂ O ₃ -	A3SiC
	blended alumina-	3wt%SiC	
	SiC	Al ₂ O ₃ -	A5SiC
		5wt%SiC	
		Al ₂ O ₃ -	A7SiC
		7wt%SiC	

Table 3.2: Various powders and their composition for D-gun spraying

Table 3.3: Chemical Composition of EN 31 and AISI 1020 material (168)

Element	С	Mn	Si	Р	Cr	S	Fe
EN 31	0.9-	0.6-	0.15-	_	0.9-	_	Balance
	1.1%	0.9%	0.35%		1.2%		
AISI 1020	0.17-	0.3-	_	0.4%	_	0.05%	Balance
	0.23%	0.6%					

3.1.3.1 Sand blasting

Sand blasting is performed on steel substrates by Sandstorm made (SEC-SB-9090) blasting equipment. The process parameters used for the operation are shown in table 3.4. Alumina grits with variable size (36, 24 and 16 mesh) are used for blasting. Three different surface roughness of 3, 5 and 7 μ m are obtained by the process.

3.1.3.2 EDM

In die-sinking EDM process (Electronica Sinker EDM, model PS50 CNC), cylindrical copper electrode (having 99.5% purity) with a diameter of 25 mm and a length of 250 mm is used as the tool and hydrocarbon oil is used as the dielectric medium. During the machining process, the workpieces are totally submerged in dielectric fluid (hydrocarbon oil) and two external nozzles are used to continuously flush the dielectric fluid at a pressure of 2 Kg/cm². The openings of both the nozzles are positioned at an angle of 30° from the workpiece surface. Figure 3.1 shows the position of flushing nozzles during the Electro-discharge machining process. A servo mechanism is used to automatically control the gap between the workpiece and the tool electrode. The properties of electrode material are shown in table 3.5 and the parameters used for Electro-discharge machining are shown in table 3.6. The workpiece is set as anode whereas the tool electrode is set as cathode for the EDM operation. Based on trial and error, the parameters of EDM process are selected in such a way that an average substrate roughness (Ra) of 3 µm, 5 μ m, and 7μ m can be achieved.

	Sample 1	Sample 2	Sample 3
Grit Size (in mesh)	36	24	16
Time (s)	30	30	30
Pressure (bar)	3	5	5
Stand-off-distance (mm)	100	100	100
Avg. Roughness (R_a) (μm)	3	5	7
$R_{z}(\mu m)$	32.95	36.32	41.92
Peak to valley (R_t) (µm)	33.46	36.90	42.35

Table 3.4 Process Parameter.	s used for	Grit Blasting	process
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Figure 3.1: Schematic diagram of workpiece and nozzle position

Table 3.5: Properties of copper el	ectrode (168)
Density (Kg/m ³)	8910
Thermal Conductivity (W/mk)	158
Melting Point (°C)	1083

Table 3.6: P	rocess Parameter	rs used for EDM pr	ocess
	Sample 1	Sample 2	Sample 3
Current (A)	1	3	5
Voltage (V)	10	30	30
Pulse on Time (µs)	50	75	100
Pulse off Time (µs)	32	32	32
Dielectric Material	Kerosene	Kerosene	Kerosene
Avg. Roughness (R _a)	3	5	7
(µm)			
$R_{z}(\mu m)$	34.45	37.64	44.02
Peak to valley (R _t)	34.83	38.44	44.21
(µm)			

 Table 3.6: Process Parameters used for EDM process

3.1.4 D-gun spraying

The D-gun thermal spray technique (SVX Pvt. Ltd. Noida, India) is used for the deposition of coating materials. The original set-up is shown in figure 3.2. The process parameters used to deposit Ni-5Al bond coat on grit blasted and

EDMed EN 31 steel are shown in table 3.7. Using the same process Ni-20Cr and Al_2O_3 based top coats are applied on AISI 1020 steel substrates. The D-gun process parameters used for such experiments are shown in table 3.8. The range of coating thickness for Ni-20Cr and Al_2O_3 based coatings are kept 80-100 µm and 250-300 µm respectively. Oxy-acetylene gas mixture is used as fuel and N₂ is used as purging gas for the D-gun process.



Figure 3.2: The original set-up of D-gun spray equipment

Parameters	Value
Air pressure (in Mpa)	0.4
Nitrogen pressure (in Mpa)	0.4
Oxygen pressure (in Mpa)	0.2
Acetylene pressure (in Mpa)	0.14
Spray distance (in mm)	165
Acetylene flow rate (in kg/cm ²)	2240
Oxygen flow rate (in kg/cm ²)	2800
Nitrogen flow rate (in Kg/cm ²)	1040
Firing rate (shots/s)	3-5

 Table 3.7: D-gun process parameters used for Ni-5Al deposition

Ch	ap	ter	3

	AI2U3-SIC
2800	4800
2320	1920
1200	800
170	200
0.2	0.2
0.14	0.14
0.4	0.4
0.4	0.4
	2800 2320 1200 170 0.2 0.14 0.4 0.4

 Table 3.8: D-gun parameters used for Ni-20 Cr and Al₂O₃-SiC coatings

 demosition

3.2 Characterization of coatings

3.2.1 Phase analysis and quantification

The phases present in the grit blasted and EDMed surfaces, in the powders and the deposited coatings are examined by XRD technique (Rigaku Smart Lab, 3 kW). Nickel-filtered Cu-K α radiation (λ =0.15406 nm) operating at a voltage of 30 kV is utilized in the process. The data is collected for a range of 20°- 100° angles with a step size of 0.01° . The data is further analysed with the help of X'pert High score software (Philips Analytical B.V., Netherlands) and the peaks are identified by JCPDS data files. Rietveld refinement analysis is performed by using the XRD data to estimate the quantity of different phases present in the coatings. In this technique, the ICSD data is used to collect the standard patterns and create the theoretical plot. Finally, theoretically obtained plot is compared and fitted with experimentally obtained pattern. The refinement has been done by changing number of parameters such as scale factor, flat background, zero shift, lattice parameters, half width, orientation parameters, atomic coordinates, (x, y, z), U V W parameters, peak shape parameters etc., in order to get the minimum value of goodness of fit (GOF). Goodness of Fit (GOF) is measured from the difference pattern and is used as an index to judge the accuracy of the fitment. Generally, GOF value close to 1 is considered as good fitment. For each sample the refinement is performed for atleast 10 times to get the average value.

3.2.2 Microstructural study

Microstructures of the pre-treated and coated samples are studied by observing the polished cross-sections of the samples under different microscopes. The cross-sectional analysis of the samples is done by cutting the samples in the transverse direction with the help of a slow speed diamond cutter (Struers, Labopol 25). In order to perform the metallographic study, the cross-sections of the samples are mounted by using cold mounting technique and then these cold mounted samples are wet polished by using SiC abrasive papers of different sizes ranging from 220 mesh to 2500 mesh. Then the polished samples are further mirror finished by using diamond pastes applied on selvyt cloth. The polished samples are then cleaned ultrasonically in an isopropanol bath to remove the impurities from the surface. The as pre-treated samples (grit blasted and EDMed), the as-deposited coatings, the individual powders, mixed powders and the polished cross-sections are examined under field emission scanning electron microscopy (FE-SEM, (Zeiss Supra-55)). Also, the elemental compositions of different zones of the samples are identified with the help of energy dispersive spectroscopy (EDS, (INCA Oxford Instruments, UK)) attached to the FE-SEM. The scratches performed on coating surface are observed and studied by using inverted microscope (Leica, DFC 295).

3.2.3 Vickers micro-hardness test

For thick coatings such as thermally sprayed coatings the hardness is judged by Vickers micro-hardness tests. In this process, indentations are made on the coating cross-section by using a highly polished, square based diamond pyramid with 136° of face angle. The Vickers hardness number (H_v) is defined as the ratio of the load applied on the sample by the indenter to the surface area of the indentation. This is calculated by using the following equation,

$$H_v = (2P\sin(\alpha/2))/D^2 \qquad \dots (6)$$

Where, P is applied load (Kgf),

 α is the face angle,

and D is the mean diagonal length of the indentation mark (mm).

This micro-hardness value is generally expressed in kgf/mm². In the present study, the coating hardness is estimated by using a UHL-002 micro-hardness

tester with a load of 200 gf and a dwell time of 15 s. An average of 10 readings is considered for a specific sample.

3.2.4 Nano-indentation test

Nano-indentations are performed on the mirror polished cross-sections of the pre-treated surfaces with the help of a Nano-mechanical test instrument (Hysitron, T1750). The experimental set-up considers data at each point during the loading and unloading conditions. The Nano-indentations have been performed with a peak load of 10 mN and a dwell time of 2 s. The Oliver & Pharr model has been used to measure the hardness of the samples at each point of indentation (169). In the present study, a Berkovich probe indenter with a tip radius of 150 nm, a total included angle of 142.35°, a semi angle (θ) of 65.35° and an aspect ratio of 1:8 has been used. The Nano-indentation results have been shown in chapter 4.

3.2.5 Roughness and porosity measurement

The average roughness (R_a) and the maximum height of the roughness profile (R_t) of the pre-treated samples are estimated with the help of a contact type stylus profilometer (Taylor-Hobson Surtronic 25). The 2D and 3D roughness profiles are obtained and studied with the help of optical surface profiler (Veeco, NT 9100). The porosity of the as-sprayed coatings is predicted by using image analysis technique with the help of Image J software. In the captured magnified images the spherical voids are assumed as the pores as shown in figure 3.3. The crater marks originated from removal of unmelted cores during polishing are not considered as pores. The area fractions of the pores present at atleast 10 different positions are evaluated to get the average value of percentage porosity present in the coating.



Figure 3.3: Image analysis using Image J software

3.2.6 Wear test

The ball-on-disc wear tests are carried out on the polished top surface (Ra=0.2µm) of the as-sprayed coatings by using Ducom TR-20LE ball-on-disc tribometer. With a speed of 300 rpm the coated samples have experienced a normal load of 2.5 kgf during the tests. A 10 mm track diameter of rotation has been maintained during each test for 15 minutes duration. All the variables are selected according to the ASTM standards and available literature. A minimum of 3 tests are performed on each coating with similar conditions to get average specific wear rate. Prior to the application of wear tests, the top surface of the coating is polished and an average roughness (Ra) of approximately 0.2 µm is achieved. The loose debris particles which remain stuck on the wear track after the completion of wear test are removed by ultrasonic cleaning of the specimens in an acetone bath. After this the specimens are dried with the help of a hair drier. The depth of the wear track has been measured with the help of contact type stylus profilometer (Taylor-Hobson Surtronic 25) in order to calculate the volume lost due to the wear test. The wear track is examined under optical microscope (Leica DFC 295 inverted type) to observe the wear mechanism of each coating. The specific wear rate is estimated by using the following equation,

$$\omega_{\rm d} = (V/dL) \times 10^{-9} \qquad \dots (7)$$

Where,

 ω_d = Specific wear rate in m³/(N.m), d = Sliding distance in m, L = Normal load in N,

and $V = Volume of wear track in mm^3$.

Now,
$$V = \pi Ad_w$$
(8)

Where,

 d_w = Diameter of wear track in mm,

and A = cross- sectional area of wear track in mm².

It is assumed that the wear scar on the tested sample has a shape of a truncated sphere. The cross-sectional area of wear track 'A' can be estimated by using the following equation,

$$A = R^{2} [Sin^{-1}(h_{T}/2R)^{0.5} - 0.25 Sin \{ 4(Sin^{-1}(h_{T}/2R)^{0.5}) \}]$$
(9)

Where,

 $h_T = avg.$ depth of wear track in mm,

and R = Radius of WC ball counterpart in mm.

3.2.7 Scratch test

The scratch hardness and fracture toughness of the coating is estimated through scratching the polished top coating ($R_a = 0.8 \ \mu m$) surface by using a scratch tester (DUCOM, TR- 101) attached with a Rockwell C diamond indenter (blue star, tip radius: 200 μm , apex angle: 120°). All the tests are conducted at normal atmospheric conditions with 50% humidity and 24°C of room temperature. Fracture toughness (K_c) of the coating is evaluated by using following equation (170).

$$K_c = F_{eq} / (2pA)^{0.5}$$
 ...(10)

$$F_{eq} = (F_T^2 + 0.6 F_V^2)^{0.5} \qquad \dots \dots (11)$$

For Conical Probe:

$$(2pA)^{0.5} = (4d^3 (Tan \emptyset / Cos \emptyset))^{0.5}$$
(12)

Where, $K_c =$ Fracture toughness,

 F_{eq} = Contributions of both the vertical and the horizontal forces,

(2 pA) = Scratch probe shape function {p= Perimeter of indenter; A= Area of indenter},

 F_V = Vertical force,

 F_T = Horizontal force,

Ø = Half-apex angle of conical indenter,

and d = Penetration depth.

Scratch hardness (H) = $8F_n/\pi w^2$ (13)

Where, $F_n = Normal force (N)$

w = Scratch width (mm)

The average values of fracture toughness and scratch hardness are obtained by considering at least three scratches performed at three different locations of the same coating surface.

3.2.8 Oxidation tests

For cyclic oxidation tests all the six surfaces of the rectangular steel substrates are coated with D-gun sprayed Al₂O₃ based coatings with uniform (approximately 250 µm) thickness. All the six surfaces of bare and coated samples are wet polished to achieve an average roughness (R_a) value of less than 0.5 µm. Then the specimens are ultrasonically cleaned in acetone bath (Bio-Techniks, India) for 5 minutes. The cleaned polished coatings are subsequently dried and made ready for cyclic oxidation tests. A vernier calliper (digital) is used to measure the dimensions of the samples in order to calculate the surface area of each sample. The alumina boats $(40 \times 40 \times 30 \text{ mm}^3)$ are used to carry the specimens inside the muffle furnace. The boats are preheated to 700 °C for 10 hours, so that during the high temperature cycles their weights remain unchanged. The initial weight of each specimen along with the boat is measured prior to the oxidation tests. The cyclic heating of the bare AISI 1020, AOSiC and A3SiC samples are carried out in a muffle furnace (UniX 96, Bio-Technik) at a temperature of 900 °C. Each cycle is constituted of heating the samples for 1 hour at 900 °C followed by 20 minutes of air cooling. After completion of a cycle the weight of each specimen along with its boat is measured by an electronic balance (capable of weighing 0.0001 gm) and the same process is repeated for 50 cycles. The consistency of the results is checked by performing same test on three identical samples of each type. The XRD analysis, microstructural study and evaluation of mechanical properties of oxidized samples (after completion of 50 cycles) are done in the same way as described above.

In the next chapter, a comparison between the sand/grit blasted steel samples and EDMed samples is done to examine the possibility of using EDM as a pretreatment process for steel surfaces before applying thermal spray coating.

A comparative study of sand blasted and electro-discharge machined surfaces of steel substrates

4.1 Introduction

The commonly used substrate preparation technique for steel is sand blasting which creates desired roughness by erosion mechanism (171, 172). The erosion of the material can be controlled by varying shape, size and the kinetic energy of the abrasive particles impinging on the surface (173). Die-Sinking Electro-discharge machining (EDM) is a non-conventional machining process used to remove material from steel workpiece by spark erosion mechanism. It is observed that the produced surface by EDM process is a superposition of discharge craters (174), pores, melted drops, and micro-cracks. The average size of the craters is directly proportional to the discharge energy (175, 176). Grossly, the average radius of the crater represents the theoretical roughness (h_m) of the machined surface. The discharge energy of EDM depends on various process parameters such as current intensity, gap voltage, pulse-on-time, and pulse-off-time. Hence, the resulting surface roughness can be controlled by controlling those process parameters.

In this chapter, the suitability of such rough surface produced by EDM for the application of thermally sprayed coating on it is investigated. For this purpose, the sand blasted steel surface is compared with EDMed steel surface with same average surface roughness (R_a).

4.2 2D Surface Roughness Analysis

The surface roughness profiles of sand blasted and EDM processed samples with an average roughness of 3 μ m are shown in figure 4.1. Lesser number of peaks and valleys is observed in the profile of EDMed sample compared to the same of sand blasted sample. Also, the asperities observed in the sand blasted surface profile are sharper than the same observed in the EDMed surface

profile. Hence, the EDMed surface has less chance to grip the splats deposited on it by thermal spray process. Higher sharpness of asperities promotes higher mechanical anchorage to the coating material.



Figure 4.1: Surface profiles of sand blasted (SB) and electro discharge machined (EDM) samples with a roughness of 3 μm

The surface roughness profiles of EDMed and sand blasted samples of 5 μ m and 7 μ m roughness is shown in figure 4.2 and figure 4.3 respectively. Apparently, there is not much difference between the profiles of sand blasted and EDMed processed surfaces in both the cases shown in figure 4.2 and figure 4.3. However, a decreasing trend in the sharpness of asperities is noticed with increasing Ra of sand blasted surface. This is because of using larger sized grits, to produce rougher surfaces. Also, by close observation of figure 4.2 it is revealed that the density of peak in case of sand blasted surface is more than the same of EDM processed surface. It is evident from figure 4.3 that the surface profiles of both the samples are similar when Ra reaches to 7 μ m.

The crater diameter of the samples is calculated using the following formulae:

Total Length = Evaluation length -0.4 mm - 0.5 mm = 7.1 mm

Density of peaks / mm = Total number of peaks / Total Length

Avg. Crater Diameter = 1 / (Density of peaks / mm).



Figure 4.2: Surface profiles of sand blasted (SB) and electro discharge machined (EDM) samples with a roughness of 5 μm



Figure 4.3: Surface profiles of sand blasted (SB) and electro discharge machined (EDM) samples with a roughness of 7 μm

Figure 4.4 shows the variation in crater diameter with varying Ra for both sand blasted and EDMed surfaces. It is clear that, with an increase in Ra value

the difference in crater diameter between sand blasted and EDMed samples is decreased. Also, both the samples have possessed almost same crater diameter when Ra value reaches to $7 \mu m$.



Figure 4.4: Variation of Crater Diameter with changing avg. surface roughness of SB and EDM processed samples

The mechanism of material removal in sand blasting is erosion by impacting high-velocity abrasive particles. The removal takes place through indentation followed by crack propagation and brittle fracturing of the substrate. With smaller grits (36 mesh) the density of peak is increased by forming smaller craters. As a result, low Ra is achieved with sharp peaks. While blasting with larger particles (16 mesh), the diameter of the crater is increased which increases the overall Ra of the sample. However, in fixed evaluation length the number of peaks is reduced significantly. Also, while blasting with larger particles, a significant amount of plastic deformation takes place, due to which the sharpness of the peaks is reduced. On the other hand, the mechanism of material removal in EDM is controlled by heating, melting and evaporation of substrate material through the formation of sparks. During pulse-off time, some amount of molten material from the crater re-solidifies and deposits over the machined surface. It is because of these re-solidified deposits, the peaks of EDM processed surface are not very sharp.

4.3 Surface profile study by 3D optical microscopy technique

The 2D surface profiles (obtained by optical microscopy technique) of sand blasted and EDMed sample with 3 μ m roughness (R_a) are shown in figure 4.5(a) and figure 4.5(b) and their respective 3D profiles are shown in figure 4.6(a) and 4.6(b). It is clear from the figures that the crater size of sand blasted sample is lesser than the EDMed sample. Also, the peaks present on the surface of sand blasted sample are found to be sharper than the same of EDMed sample.

The 2D surface profiles (obtained by optical microscopy technique) of sand blasted and EDMed sample with 3 μ m roughness (R_a) are shown in figure 4.7(a) and figure 4.7(b) and their respective 3D profiles are shown in figure 4.8(a) and 4.8(b). Very less difference is observed between the surfaces of sand blasted sample and the EDMed sample. Also, the sharpness of the peaks in case of sand blasted sample with a roughness (R_a) of 5 μ m is found to be lesser than the same of the sand blasted sample with a roughness (R_a) of 3 μ m. The 2D surface profiles (obtained by optical microscopy technique) of sand blasted and EDMed sample with 7 μ m roughness (R_a) are shown in figure 4.9(a) and figure 4.9(b) and their respective 3D profiles are shown in figure 4.10(a) and 4.10(b). The surface profiles of both sand blasted and EDMed samples with a roughness of 7 μ m are similar to each other.



Figure 4.5: 2D Optical microscopy of (a) sand blasted and (b) EDM samples with an average roughness of $3 \mu m$.



Figure 4.6: 3D Optical microscopy of (a) sand blasted and (b) EDM samples with an average roughness of 3 µm.



Figure 4.7: 2D Optical microscopy of (a) sand blasted and (b) EDM samples with an average roughness of $5 \mu m$.



Figure 4.8: 3D Optical microscopy of (a) sand blasted and (b) EDM samples with an average roughness of $5 \mu m$.



Figure 4.9: 2D Optical microscopy of (a) sand blasted and (b) EDM samples with an average roughness of 7 µm.



Figure 4.10: 3D Optical microscopy of (a) sand blasted and (b) EDM samples with an average roughness of 7 μ m.

4.4 Phase analysis

Figure 4.11 shows the XRD patterns of all six samples. The presence of α -Fe in the sand blasted samples suggests that, during blasting no surface contamination occurred and the metallurgy of the surface remains unchanged. On the other hand, in EDMed samples austenite (CFe15.1) and cementite (Fe3C) phases are observed on the surface. Also, by observing the relative intensity of the austenite (CFe15.1) peaks it is noticed that the formation of austenite phase has increased with increased surface roughness. To obtain high surface roughness high energy is invested in EDM. The high energy sparks produce a number of carbon radicals and ions through dissociation and ionization of the hydrocarbon-based dielectric material (177). These unstable

carbons are impregnated to the EDMed surface (178). At high temperature, these carbon radicals/ions react with molten iron to form ion diffusion compounds which deposit and re-solidify over the asperities. The stability of Fe3C phase increases with an increase in the absorption of carbon in the recast layer during EDM process.



Figure 4.11: XRD patterns of Electro Discharge Machined and Sand Blasted EN 31 steel samples with average roughness (R_a) of (a) 3 µm, (b) 5 µm and (c) 7 µm

The austenitic phase formation is common on EDM processed steel samples when mineral/hydrocarbon-based oil is used as the dielectric (179). It is reported that, with an increase in carbon content in dielectric material, the formation of martensite decreases (180). The absence of martensite phase in the re-solidified layer is confirmed by many researchers (181).

However, some amount of martensite formation is still possible on the top surface with a suitable cooling rate in case of oil-based EDM (178). The formation of martensite is so little that quite often it is not detectable by XRD analysis.

4.5 Microstructure study

Figure 4.12(a-b) shows the scanning electron micrograph (SEM) of the top surfaces of the sand blasted and EDMed surfaces with Ra of 3 μ m. The sharp irregular surface morphology observed in Figure 4.12(a) suggests the brittle fracturing of the surface during sand blasting operation. On the other hand, large craters with a relatively smoother surface of re-solidified layers are observed in case of EDMed samples. More number of microcracks is observed in sand blasted sample compared to the same of EDMed surface. The cracks observed in sand blasted sample are with wider openings. Few re-solidified spherical metallic drops are visible on the EDMed surface. Due to high cooling rate those are solidified before deposition. Sharper asperities are observed on sand blasted sample. The thin cracks formed on EDMed sample are due to the introduction of thermal stress during solidification of the recast layer (182).



Figure 4.12: SEM micrograph of (a) Sand blasted and (b) EDM processed EN 31 sample with average roughness of 3 µm

The SEM micrographs of the cross-sections of sand blasted and EDMed surface with 3 μ m roughness are shown in Figure 4.13(a) and 4.13(b) respectively. Many large sub-surface cracks are noticed in sand blasted samples whereas very few small cracks are found in the cross-section of EDMed sample.



Figure 4.13: Cross- sectional SEM micrographs of (a) Sand blasted (b) EDM processed sample with an average roughness of 3 μm

The SEM micrographs of the top surfaces of sand blasted and EDMed samples with Ra of 5 μ m are shown in figure 4.14(a) and 4.14(b) respectively. Large craters and relatively lesser number of cracks are observed in figure 4.14(a) compared to the same of sand blasted sample of 3 µm Ra. This is due to the increased grit size (24 mesh) which has not only removed material by brittle fracturing but also deformed the surface plastically by indentation. The reduced sharpness of the peaks in roughness profile shown in figure 4.2 also indicates surface deformation while blasting with larger grits. Plastic deformation of the surface helps to suppress cracks to some extent. Few hair cracks are observed on the EDMed surface as shown in figure 4.14(b). The width and number of surface cracks are more on sand blasted surface compared to the same of EDMed surface. It is also noticed that the area coverage of the re-solidified layer is increased with increased Ra from 3 µm to $5 \,\mu\text{m}$. This is due to the higher energy investment during discharge in order to obtain higher surface roughness. As a result, more melting and resolidification has occurred. This enhanced re-solidified layer has covered the surface cracks formed during material removal by spark erosion. This is why the number of cracks formed in EDMed surface of 5 µm Ra is lesser compared to the same of 3 μ m Ra. However, increased number of pores and blow holes are noticed in figure 4.14(b) due to the inclusion of gas bubbles at elevated temperature.



Figure 4.14: SEM micrograph of (a) Sand blasted and (b) EDM processed EN 31 sample with average roughness of 5 µm

The SEM micrographs of the cross-sections of sand blasted and EDMed surface with 5 μ m Ra are shown in figure 4.15(a) and 4.15(b) respectively. Figure 4.15(b) reveals that the crater size of EDM processed sample is slightly bigger than the same of sand blasted sample. The cracks observed in figure 4.15(a) are identical to the crater wall, which shows how the brittle fracturing takes place before separation during blasting. However, number of cracks on cross-section is lesser than the same observed in sand blasted sample of 3 μ m roughness. On the other hand, almost crack-free surface is observed on the cross-section of EDMed sample of 5 μ m roughness. However, deposition of recast layer is found to be more, especially on the crests of the asperities. Very few surface cracks are observed in EDMed sample.



Figure 4.15: Cross- sectional SEM micrographs of (a) Sand blasted (b) EDM processed sample with an average roughness of 5 µm

Figure 4.16(a) and 4.16(b) are showing the SEM micrographs of sand blasted and EDMed surfaces with 7 μ m Ra. Less number of cracks with shorter length and width are observed in sand blasted sample. This is due to the enhanced effect of deformation by the indentation of larger grits. The large grit (16 mesh) produces large crater which in turn increases surface roughness. On the other hand, from figure 4.16(b) it is observed that the EDMed surface is completely covered with re-solidified layer.

Due to very high energy investment craters with larger diameter are achieved. Due to more melting and re-solidification a thick recast layer is deposited. All the minor cracks formed during spark erosion are suppressed by a thick envelope of re-solidified layer. In addition, at higher temperature this resolidified/recast layer has included number of gas bubbles and increased the porosity.



Figure 4.16: SEM micrograph of (a) Sand blasted and (b) EDM processed EN 31 sample with average roughness of 7 μm

Figure 4.17(a) and 4.17(b) show the cross-sectional SEM images of sand blasted and EDMed surfaces of 7 μ m Ra. Few cracks observed in sand blasted sample (figure 4.17(a)) are indicating incomplete propagation of cracks under impact load of high-velocity grit to achieve hemispherical material removal. However, formation of cracks on the cross-section of sand blasted sample of 7 μ m roughness is lesser compared to the same of other sand blasted samples. This is due to the effect of enhanced material deformation by compressive load applied by larger sized grit particles. On the other hand, multiple thick recast layers are observed all over the area of EDMed surface. The thickness

of this layer is found to be more on the crests than the same on the valleys. By shock wave the liquid metal from the crater wall erupts and spreads over the edges/banks of the crater. Hence, the thickness of recast layer is found to be more than the same of valley regions. Figure 4.18(a) and 4.18(b) again shows the cross-sectional SEM images of sand blasted and EDMed surfaces of 7 μ m Ra at a different location. It is clear from the figure that both sand blasted and EDMed samples have the same crater diameter of size approximately 160 μ m.

EDMed surface with 3 μ m roughness has a significant amount of crater zones where no recast layer is deposited. As the surface roughness is increased gradually, the number of uncovered craters is decreased with an increase in thickness of the recast layer. To create an average roughness of 7 μ m by EDM, the input energy is high enough to cover the entire surface with a thick recast layer. The XRD pattern of this sample confirms the presence of higher amount of austenite phase.



Figure 4.17: Cross- sectional SEM micrographs of (a) Sand blasted (b) EDM processed sample with an average roughness of 7 µm showing presence of sub-surface cracks



Figure 4.18: Cross- sectional SEM micrographs of (a) Sand blasted (b) EDM processed sample with an average roughness of 7 µm showing crater size of both samples

4.6 Nano-indentation

Nano-indentations by Berkovich Nano-indenter are performed on the polished cross-sections of all the samples with a load of 10 mN. The indentations are performed from 8 μ m depth to 16 μ m depth in a vertical manner with a regular interval of 4 μ m as shown in figure 4.19(a). Due to experimental constraints, it is not been possible to indent in close proximity of the top surface and a safe distance of 8 μ m is maintained. An average of five data points is considered as the hardness of that zone. Hardness of peak zones and valley zones are considered separately as shown in figure 4.19(b).



Figure 4.19: (a) Schematic Diagram of indent positions during Nanoindentation process and (b) SEM image of indent positions

The hardness data are graphically presented with varying depth in figure 4.20(a-f). It is noticed from figure 4.20(a-b) that on an average 7 GPa Nanohardness is achieved at all points of a sand blasted sample. There is no change in hardness value with increasing depth of sand blasted sample of 3 μ m Ra. Also, no significant change is observed between the hardness values of peak and valley regions of the same sample. However, the hardness value (7 GPa) is found to be higher than the same of the base material. Using same loading condition, the hardness of base metal is found to be of 6.5 GPa. This suggests the formation of hard strain hardened zone having a thickness more than 16 μ m. Also, the hardening effect is found to be homogenous up to 16 μ m depth. On the other hand, the hardness properties of EDMed sample do not differ much from the same of sand blasted sample. On an average 7 GPa hardness is noticed at all points of EDMed sample. The variation in hardness up to 12 μ m depth is due to the effect of improper grain refinement of heat-affected zone

(HAZ). However, hardness beyond 12 μ m depth is found to be uniform and unchanged. This suggests the homogenous nature of HAZ. As the improvement in hardness is not very high from the base metal's hardness value and from SEM micrographs thin recast layer is observed, the selected points for hardness measurement lie in the HAZ. Hence, the thickness of HAZ of EDMed sample with 3 μ m Ra is expected to be more than 16 μ m.

The variation in hardness values with varying depth of sand blasted and EDMed sample with Ra of 5 μ m is shown in figure 4.20(c-d). The hardness of sand blasted sample is not changing much with varying depth for both peak and valley regions. This suggests the uniform nature of strain hardened zone which is extended beyond 16 µm of depth. The difference in hardening effect between peak and valley region is also not noticeable. However, increased hardening effect is noticed than the same of sand blasted sample with 3 µm Ra. This is due to more deformation effect by the high-velocity grits with relatively larger mass (183). On the other hand, the hardness of valley region of EDMed sample with 5 µm Ra shows no significant variation in hardness with increasing depth and the value is close to 7.25 GPa. This suggests the increased grain refinement of the HAZ at the depth up to 16 µm. However, in peak region of same EDMed sample significant variation is observed. Highest hardness is noticed at 8 µm depth and it has a decreasing trend with increasing depth. At 16 µm depth the hardness obtained is of 7.25 GPa. This suggests the presence of thick recast layer up to 16 µm thickness in peak region. The cementite (Fe3C) phase formed on EDMed surface is found to have orthorhombic crystal structure. With high carbon content (6.67%) it possess high density (7.73 gm/cc) also. On the other hand, the austenite phase formed on EDMed surface is found to have cubic crystal structure. The carbon content of austenite is relatively lower and possess lower density (7.45 gm/cc). The highest hardness (\geq 7.5 GPa) obtained in the top surface of peak region suggests the presence of mostly Fe3C phase in it. Having more carbon radicals or ions on the top surface formation of Fe3C in that zone is mostly expected. Gradual decrease in hardness with increasing depth suggests the formation of austenite in more quantity. The high variation of hardness value up to 12 µm depth of peak region also suggests the non-homogenous nature of the microstructure. The high hardness value upto 12 μm suggests the formation of Fe3C upto the 12 μm depth.

Nano-hardness data of sand blasted and EDMed samples of 7 µm Ra is shown in figure 4.20(e-f). Uniform hardness value of sand blasted sample is observed with variable depth. Also, the hardness of valley region is found to be higher than the hardness of peak region of the same sample. Enhanced deformation leading to enhanced strain hardening is the key reason for such behavior. The sub-surface hardness of sand blasted sample of 7 µm Ra is the highest among the same of all other sand blasted samples. On the other hand, significant change in hardness value of EDMed sample is observed with variable depth (184). The high hardness (approx. 7.5 GPa) at 8 µm depth of both peak and valley region suggests the formation of more amount of Fe3C phase in those regions. However, the thickness of such layer in valley region is lesser as the hardness is decreased sharply with an increase in depth. At the depth of 16 µm in valley region the hardness is reached to 7 GPa. Hence, it indicates that the recast layer containing mostly Fe3C is limited upto 8 µm depth and the recast layer containing mostly austenite is limited upto 16 µm depth in case of valley region. On the other hand, the highest hardness (approx.. 7.5 GPa) is retained upto 12 µm depth in peak region. This indicates the formation of Fe3C upto 12 µm depth. Also, from 12 µm to 16 µm the hardness is dropped from 7.5 GPa to 7 GPa. This indicates the major presence of austenite in that zone. The wide deviation in error bar suggests the formation of inhomogeneous microstructures of both Fe3C and austenite. However, the average value of hardness suggests the mostly present phase in the zone. Very high hardness suggests the presence of mostly Fe3C phase, relatively lower hardness suggests the presence of mostly austenite phase and hardness value below around 7 GPa suggests the presence of heat affected zone (HAZ). Also, thicker re-cast layer with more hardened phase is formed on peak region than the valley region.





Figure 4.20: Variation of nano-hardness with changing depth: (a) Valley hardness for 3 μm roughness samples (b) Peak hardness for 3 μm roughness samples(c) Valley hardness for 5 μm roughness samples (d) Peak hardness for 5 μm roughness samples (e) Valley hardness for 7 μm roughness samples (f) Peak hardness for 7 μm roughness samples.

4.7 Application of thermally sprayed coating

With an attempt to apply coating of thermal spray grade Ni-Al (METCO 450 NS) on the above mentioned sand blasted and EDM processed samples, D-gun coating method has employed. The SEM micrographs of the top surfaces of both the coatings are shown in figure 4.21(a) and 4.21(b) respectively. The successful coating is achieved on the sand blasted sample, whereas coating on EDM processed sample is found to be unsuccessful as spallation of coating is
occurred due to poor adhesion. Local welding between the Ni-5Al splats and EDMed surface could not take place. This suggests that to achieve proper coating adhesion in thermally sprayed coatings the physical/chemical bond formation is equally necessary along with mechanical anchorage by the roughness of the substrate. Presence of Fe3C and austenite phase on the EDMed surface has restricted such physical/chemical bond formation with the deposited Ni-Al coating.



Figure 4.21: Top surface of (a) grit blasted and (b) EDMed sample after applying coating by D-gun process

4.8 Concluding remarks

In this chapter, a detailed study of both sand blasted and EDM processed samples are made with an aim to use the EDM processed sample as a substrate material in thermal spraying. It is found that at lower surface roughness such as 3 μ m the density of asperity is more in sand blasted samples whereas at higher roughness values such as 7 μ m the density of asperity of sand blasted sample is same with that of EDM processed sample. The sand blasted surface contains a uniform strain hardened zone. The hardening effect increases with increasing kinetic energy of grits. The hardness of peak region is comparatively lower than the hardness of valley region of sand blasted sample is uniform and close to 7 GPa. The high hardness obtained at lower depth due to the presence of hardened recast layer on the surface of 5 μ m R_a and above. The thickness of recast layer on surface of 3 μ m R_a is less than 12 μ m and the thickness of recast layer on surface of more than 5 μ m R_a is more than 16 μ m.

At high surface roughness value of the sample, the hardness of peak region of EDMed surface is more than the same of valley region. This is due to formation of higher amount of hardened phases on peak regions. Presence of austenite and Cementite over EDM processed surface makes it unsuitable for application of thermally sprayed Ni-Al coatings. For successful thermally sprayed coating application along with surface texture of the substrate, the metallurgical compatibility of the substrate with the coating material is a necessary aspect.

In the next chapter, an attempt has been made to apply thermally sprayed Al_2O_3 -SiC coatings on Ni-20Cr bond coated AISI 1020 steel substrates. For this study conventional sand blasting technique is used to prepare the substrate. The effect of the SiC addition on the Al_2O_3 phase stabilization and microstructures of the as-sprayed coatings is also studied.

Stabilization of Al₂O₃ phases by SiC addition in D-gun sprayed Al₂O₃-SiC coatings

5.1 Introduction

Thermally sprayed Al₂O₃ coating contains different phases of Al₂O₃ such as α , γ , δ , θ etc. Among them formation of α and γ is predominant (185). Depending on the nature of the feedstock and it's melting and solidification behaviours these phases form. α -Al₂O₃ is superior over the metastable phases of alumina in terms of mechanical properties. Hence, to improve the mechanical properties of thermally sprayed Al₂O₃, in many occasions dopants (TiO₂, Cr₂O₃, ZrO₂ etc.) are added to the Al₂O₃ feedstock (186-188). In very few cases SiC is added to Al₂O₃ feedstock in thermal spray applications. The presence of SiC is found to increase the α -Al₂O₃ in the resulting coating prepared by HVOF. A high chance of decomposition of SiC in thermal spray processes makes it an unsuitable material. Therefore, it is rare to find thermally sprayed SiC coating in available literature. In this chapter, micron size SiC powder is added to sprayable alumina feedstock in low quantity (3-7 wt. %) and deposited on low carbon steel substrates by using detonation gun technique. The effect of SiC addition on the phases and microstructure of Dgun sprayed Al_2O_3 is thoroughly studied in this work.

5.2 X-ray diffraction (XRD) analyses

The XRD patterns of the pure Al_2O_3 and SiC powders are shown in figure 5.1 and the XRD patterns of all the four Al_2O_3 based coatings are shown in figure 5.2. It is noticed in figure 5.1 that the Al_2O_3 peaks are of mainly α -phase and many peaks of 'SiC' are coinciding with some significant peaks of Al_2O_3 . On identification of phases shown in figure 5.2 it is noticed that in all coatings mainly α -Alumina and γ -Alumina phases are formed. The presence of α -

Alumina in the coating is mainly because of the presence of the un-melted cores of Al₂O₃ particles in the coating whereas; the formation of γ -alumina is due to the rapid solidification of the molten droplets on the metal substrate (189). The broad humps found at 32° and 62° angles suggest the presence of amorphous phases in the as-sprayed coatings. It is found in literature that formation of amorphous phase in any thermally sprayed coating takes place due to rapid cooling of coating material (190). The quantity of amorphous phase formed in the coating depends on the process, process parameters and the coating material. The molten or semi-molten particles with a supersonic velocity hit the substrate to form disc shaped splats with larger diameter and producing lamellae with large surface area that increases the rate of solidification to form amorphous phase. Full sintering state of SiC coatings is not been possible to achieve by thermal-spraying processes till date especially by High-frequency pulsed detonation (HFPD) process (191). Being unstable at high temperature (more than 2500 °C) SiC dissociates in Si and C which makes it difficult to achieve SiC phase in the resulting coating (192). Peaks of rhombohedral SiC in the XRD patterns suggests the retention of SiC phases in the resulting coating with in-significant dissociation effect. It is observed from figure 5.2 that few Al₂O₃ peaks are overlapped with SiC peaks (193). Having peaks of both materials at same 2θ angles is the reason behind this. It suggests the possible presence of 'SiC' in the deposited coatings. In past, a mixture of Al₂O₃-SiC powders with varying SiC content was successfully deposited on the steel substrates by using HVOF while keeping the maximum flame temperature at 2400° C (98).

The maximum temperature which can be attained by Detonation Gun process is approximately 3850 °C and it offers a very high velocity of around 800-1200 m/s (62, 194). The detonation gun process is able to minimize the decomposition of feedstock powder due to lesser time involved in deposition and lower heat generation (195). The temperature of the powder particles attained by D-gun process depends on the X_i/L ratio where ' X_i ' is the axial loading position and 'L' is the length of gun barrel (54). In the present work, this ratio is maintained at approximately 0.3 which suggests that the flame temperature to be less than 2400 °C. Therefore, no decomposition of SiC has

occurred. In few past research work, the possibility of obtaining thermally sprayed SiC coating without any decomposition is claimed (98).



 α - α Al₂O₃ 1000 γ- γ-Al₂O₃ A7SiC 0 1.92 o- SiC à α aol α α g α A5SiC α α Relative Intensity o} α, α 500 A3SiC aαa 8 α_0 α A0SiC 0 ò 20 40 60 80 20 (Degrees)

Figure 5.1: XRD Patterns of the pure Al₂O₃ and SiC powders

Figure 5.2: XRD patterns of D-gun sprayed Al₂O₃-SiC coatings

From the XRD analysis report shown in figure 5.2 it is clear that not only the formation of 'SiC' phase is ensured, but also no evidence of decomposition is obtained. Even if decomposition occurred to form compounds of Si and C, it is not been possible to detect those by X-ray due to their negligible presence.

5.3 Rietveld refinement

To study the effect of 'SiC' addition on the phase of Al₂O₃ coating Rietveld refinement is performed by using the XRD patterns of all the coatings. The major parameters and phases are shown in Table. 5.1. In the refinement process the amorphous phase content in the coating is considered to be negligible for all the samples. Refinement is performed on each sample for atleast 10 times. Only those results are accepted for which very low (≤ 2) G.O.F (Goodness of fitment) are obtained. The averages of accepted results are considered to be the estimated quantity of phases. Further, the change in α -Al₂O₃ content of the coating against SiC addition to the feedstock is plotted in figure 5.3. The maximum α -Al₂O₃ formation is noticed in A3SiC coating. With further increase in 'SiC' content the quantity of α -Al₂O₃ phase shows a decreasing trend. The starting α -Al₂O₃ phase of the powder transforms to γ phase in the resulting coating due to the rapid solidification of the molten volume.

ICSD	ICDD	Name	Chemical	Space	a[A°]	b[A°]	c[A°]	α[°]	B[°]	γ[°]	Z
			formula	group							
26790	01-	Aluminum	AlO	R-3c	5.1280	5.1280	5.1280	55.270	55.270	55.270	2
	074-	Oxide (a)	2 0					0	0	0	
	1081										
85137	01-	Aluminum	AlO	R-3c	4.7607	4.7607	12.997	90.00	90.00	120.00	6
	088-	Oxide (a)	2 5				0				
	0826										
39014	01-	Aluminum	(Al 0)	Fd-3m	7.9060	7.9060	7.9060	90.00	90.00	90.00	8
	077-	Oxide (y)	2 3 1.3								
	0396		33								
30267	01-	Aluminum	(Al 0)	Fm-3m	3.9500	3.9500	3.9500	90.00	90.00	90.00	1.00
	075-	Oxide (y)	2 3 1.3		0	0	0				
	0921		33								
43727	01-	Silicon	SiC	R3m	3.0790	3.0790	438.20	90.00	90.00	120.00	174
	089-	Carbide					00				
	3067										
42868	01-	Silicon	SiC	R3m	3.0730	3.0730	218.65	90.00	90.00	120.00	87
	089-	Carbide					70				
	2226										

Table 5.1: Parameters used during Rietveld refinement

The unmelted/partially melted volume of Al_2O_3 particles has retained its α -phase in the coating. The presence of α -Al_2O_3 in AOSiC coating is mainly because of retention of unmelted cores of Al_2O_3 particles (196).

The increased α -Al₂O₃ in the Al₂O₃ coating suggests proper/slow solidification of molten volume of Al_2O_3 (197). By the addition of 3 wt. % SiC to the Al_2O_3 feedstock, the melting and solidification behaviour of Al₂O₃ is affected due to the great mismatch of the thermal properties between the two materials. As a result slow cooling of solidifying Al₂O₃ takes place around the deposited 'SiC'. However, this is only possible if SiC melts and deposits as a splat or the Al₂O₃ melts at lower temperature than its normal melting point. The selected process parameters are such that the temperature of combustion does not reach to the melting point of 'SiC'. But the results suggest that with same heat content/temperature A3SiC powder mixture possibly melted at a temperature which is at or below 2400 °C. For given process parameters this specific temperature of 'SiC' can be reached when the feedstock quantity of SiC is close to 3 wt. %. When the feedstock quantity of SiC is more than 5 wt.%, with same process parameters/energy input the 'SiC' is not been able to get the desired temperature for melting or stabilization of Al₂O₃ phase through slow cooling.



Figure 5.3: Change in percentage of α -alumina with change of SiC content in feedstock powder

5.4 Microstructure Study

The SEM micrographs of the pure Al₂O₃ powder and Al₂O₃-SiC powder mixtures are shown in figure 5.4. The irregular and angular shaped pure Al₂O₃ powder (AMDRY 6060) suggests that the powder was manufactured by crushing. Also, no significant change in the size of Al₂O₃ powder is noticed on mixing with hard 'SiC'. The very low quantity of 'SiC' possibly could not cause much harm to the final size of Al₂O₃ particle. The micrograph of SiC powder shows the irregular and crushed nature of SiC particles. The micrographs of the coatings are shown in figure 5.5(a-d). All the coatings are well adhered to Ni-20Cr bond coat. Voids, cracks and defects are observed in all the coatings. Among all, A3SiC coating shows the minimum defects present in it. With further increase in the quantity of SiC, the formation of voids, cracks and defects increases. Pure Al₂O₃ coating contains more defects mainly due to the presence of partially melted Al₂O₃ particles. Partial melting is a commonly observed phenomenon in thermally sprayed Al_2O_3 (196). In D-Gun coating, as the residence time is less mostly the Al₂O₃ particles experience partial melting and due to the presence of unmelted portion the defect of the coating increases. This is one of the major reasons for the retention of starting phase of Al_2O_3 (in the present study α -Al₂O₃) in the resulting coating. On polishing, those loosely adhered unmelted cores of Al₂O₃ particles are removed from the surface and deep pockets are exposed. These deep pockets or defect marks are termed as 'crater marks' in the thesis. Severe defect is observed in A7SiC coating as shown in figure 5.5. Through EDS mapping of A7SiC, presence of SiC is traced in a limited zone as shown in figure 5.5(d). The small area coverage of Si rich zone suggests the entrapment of unmelted 'SiC' particle in such coating. The embedded 'SiC' particle probably has hindered the proper growth of Al₂O₃ crystals surrounding it. In addition, the blasting/bombardment effect of unmelted SiC particles on the A7SiC coating surface is also an important factor for increasing defects. The presence of SiC in the A3SiC coating is confirmed by EDS analysis as shown in figure 5.6. The white coloured part in the figure 5.6 represents the 'Si' rich zone. Also the wavy nature of the zone suggests the formation of SiC splat. The splat formation suggests the melting of SiC in A3SiC coating. The

SEM/EDS mapping analysis of A5SiC coating is shown in figure 5.7 below. The figure clearly shows a white area which is rich with 'Si' in it. It is a good indication of the presence of SiC in A5SiC coating. However, the small size of such zones suggests limited spreading of SiC splats. Figure 5.8 (a, b, c) shows the SEM images of the cross-sections of all three coatings along with their EDS analyses. Many SiC splats distributed inside A3SiC and A5SiC coatings are observed in 5.8 (a, b). The thin wavy shape of the SiC splats observed in A3SiC coating (figure 5.8 (a)) suggests good melting of SiC particles. The limited spreading of SiC splats observed in A5SiC coating suggests improper/partial melting of SiC particles. Also, in both A3SiC and A5SiC coatings the areas where the SiC splats are present contain no/less defects. On the other hand, no such SiC splat is visible in A7SiC coating. Also, lot of defects are observed in A7SiC coating. EDS analysis of a defective zone of A7SiC coating has revealed negligible presence of Si in it. However, no splatlike shape or white coloured area (as seen in A3SiC and A5SiC coatings) is visible in such zone. This suggests no/negligible melting of SiC in A7SiC coating. The incoming SiC particles with high velocity have caused damage to the already deposited alumina coating and created more defects in the A7SiC coating. Therefore, inclusion of SiC in the A7SiC coating is negligible and the



Figure 5.4: Morphology of (a) A0SiC (b) A3SiC (c) A5SiC (d) A7SiC powders

In Thermal Spraying, coating porosity is an important aspect to study as the mechanical properties depend on it (198). The detonation process is an intermittent process due to which few pores get developed in the coatings. An average of at least 10 readings taken at 10 different cross-sectional locations of each sample is considered to estimate the porosity and presented in figure 5.9. The low porosity (<2%) of the coatings suggests the impact velocity of the droplets to be very high by the D-gun process (199). It is evident from figure 5.9 that the porosity first decreases and then increases with an increase in the SiC content. The minimum porosity of about 0.4% is achieved when 3 wt. % SiC is added to the Al₂O₃ feedstock. This is due to the increased formation of α -Al₂O₃ phase with the improved the wettability property of the deposited droplets. With high spreading of splats dense coating is achieved. On the other hand, because of bombardment effect and inclusion of few 'SiC' particles the porosity of A7SiC coating is the maximum.



Figure 5.5: SEM images of cross-sections of (a) A0SiC (b) A3SiC (c) A5SiC (d) A7SiC coatings



Figure 5.6: EDS analysis of A3SiC coating



Figure 5.7: SEM/EDS analysis of A5SiC coating



Figure 5.8: SEM/EDS analysis of (a)A3SiC (b) A5SiC and (c) A7SiC coatings



Figure 5.9: Percentage porosity graph of coatings

5.5 Scratch hardness

Scratch hardness of the coatings is evaluated by scratching the polished ($R_a \le 0.5 \ \mu m$) top surfaces of coatings by a Rockwell diamond indenter mounted on a scratch tester (DUCOM TR-101). With lesser porosity content A3SiC shows higher scratch hardness value compared to the other three as-sprayed coatings. Figure 5.10 and figure 5.11 shows the scratch hardness values and SEM micrographs of scratches performed on the surface of the coatings respectively. It can be clearly seen that due to scratching less/no crack formed on the surface of A3SiC coating whereas due to scratch formation on A0SiC and A7SiC coating cracks formed on the surface. With higher α -Al₂O₃ phase content the mechanical property such as scratch hardness of A3SiC coating is higher compared to the same of other as-sprayed Al₂O₃-SiC coatings. Presence of 'SiC in A3SiC coating also helps to restrict the crack formation and propagation of the same.



Figure 5.10: Scratch hardness value of coatings



Figure 5.11: High magnification SEM images of scratch performed on (a) A0SiC (b) A3SiC (c) A5SiC (d) A7SiC coatings

5.6 Concluding remarks

Al₂O₃-SiC can be successfully deposited on Ni-20Cr bond coated AISI 1020 steel samples by D-Gun technique without decomposing SiC. Dense coatings of Al₂O₃-SiC are obtained with less than 2% of porosity. A very low quantity of 'SiC' is found to affect the melting and solidification behaviour of D-gun sprayed Al₂O₃. Deposition of 'SiC' helps to improve the α -Al₂O₃ phase content of A3SiC and A5SiC coating. Hence, Phase stabilisation of Al₂O₃ is possible in D-gun sprayed coating with 3-5 wt. % of SiC addition to the Al₂O₃ feedstock. Scratch hardness of as-sprayed A3SiC coating is found to be highest amongst the four coatings as A3SiC coating has the highest α -Al₂O₃ phase content and lowest porosity amongst all as-sprayed coatings developed. In the next chapter, detailed description on mechanical properties and wear behaviour of these four as-sprayed coatings is made.

Wear analysis of D-gun sprayed Al₂O₃-SiC coatings

6.1 Introduction

Addition of SiC to Al_2O_3 for the preparation of cutting tool is a popular approach, as SiC whiskers provide transformation toughening property to the ceramic tool (200). Being harder in nature SiC enhances the wear resistance behaviour of Al_2O_3 -SiC composites. SiC particles facilitate the grain growth of Al_2O_3 , which in turn improves the mechanical property of overall coating (98). Such property of SiC can be beneficial for a coating if it is obtained with its original form. Due to vulnerability of 'SiC' material at high temperature exposures it is rare to find thermally sprayed SiC coating and the effect of SiC addition on the mechanical properties of the coating in available literature. In this chapter, the effect of SiC addition on the mechanical properties and wear resistance of D-gun sprayed Al_2O_3 is thoroughly studied.

6.2 Micro-hardness test

The Vickers micro-hardness tests are carried out on the polished cross-section of the coatings with a load of 200 gm. The average hardness value of each sample is calculated by considering at least 10 indentations with the same load. The micro-hardness values of all coatings are graphically shown in figure 6.1. Among all, the A3SiC coating is found to be the hardest. The coating hardness decreases significantly with further increase in SiC content. One of the reasons of such behaviour is the density of the coating which is the maximum for A3SiC coating. With more than 3 wt. % SiC content as the density of the coating decreases, the hardness of the same decreases too. However, as we have observed (figure 5.7) very low change in porosity (< 1%) of the coatings, density cannot be the only reason for the significant change in hardness. Therefore, other reasons for such behaviour are to be found out. It is well known that amongst different phases of Al₂O₃ the stable

 α -phase possess the highest mechanical properties (34, 196). Hence, more the presence of α -Al₂O₃ in the coating more will be the hardness. The Vickers indentation marks of all the samples are shown in figure 6.2



Figure 6.1: Variation in micro-hardness of Al₂O₃-SiC coatings with changing SiC content



Figure 6.2: Micrographs of Vickers indent marks produced by applying 200gm of load on the cross-section of (a) A0SiC (b) A3SiC (c) A5SiC (d) A7SiC coatings

The cracks formed at the corners and edges of the rhomboidal indent mark on A3SiC are the minimum among all. The presence of SiC splats helps to restrict the formation/propagation of cracks (201). On the other hand, the indent marks created on A0SiC coating and A7SiC coating show higher crack formation due to their high brittleness properties owing to high γ -Al₂O₃ content. The highest quantity of α -Al₂O₃ together with few molten/semi-molten 'SiC' makes the A3SiC coating to be hardest and toughest among all.

6.3 Fracture Toughness by Scratch test

Fracture toughness of the coating is estimated by scratching the polished coating surface with conical diamond indenter. The applied load and scratching speed used during the tests are of 15 N and 0.1 mm/s respectively. The average fracture toughness values of the coatings are graphically shown in figure 6.3 and the SEM images of scratch marks are shown in figure 6.4.



Figure 6.3: Fracture Toughness graph coatings with different SiC content

The scatter of fracture toughness values observed in this work represents the non-homogenous nature of the coating micro-structure (202). The A3SiC coating shows the highest fracture toughness property among all four coatings. With further increase in SiC content in the feedstock the toughness of the coating reduces significantly. 'SiC' imparts toughness property to the coating through transformation toughening. It also possesses crack deflection property. To achieve these properties in the coating the primary condition is to include the 'SiC' in the coating as a splat with proper adhesion. Inclusion of well

adhered 'SiC' in the coating is reduced as the quantity of SiC increases in the feedstock. This is due to the limited energy input by D-gun process. Also, the high velocity unmelted 'SiC' particles have caused damage to the coating to form a non-homogenous coating micro-structure. The high scatters obtained in the results of A5SiC and A7SiC suggests these coatings to be non-homogenous in nature.



Figure 6.4: *Microscopic images of scratch marks produced on (a) AOSiC (b)* A3SiC (c) A5SiC (d) A7SiC coatings

6.4 Ball-on-disc type wear test

Ball on disc type wear test is carried out on the polished ($R_a=0.8 \mu m$) top surfaces of the coatings with an average thickness of 250 μm each. The specific wear rate of the coatings is shown in figure 6.5 and the depth profiles of the wear tracks are shown in figure 6.6. The specific wear rate is reduced significantly from A0SiC to A3SiC coating. Also, further increase in SiC content results in rapid wear of coating materials. From the depth profiles of wear track shown in figure 6.6 it is observed that the depth of wear track is the

minimum for A3SiC coating. Also, the maximum value of the same is obtained for A7SiC coating. The irregularities on the track wall are more in both A0SiC and A7SiC coatings. A sudden increase in depth is observed in the wear track of A7SiC coating due to the dislodgement of embedded SiC particle from the track depth. On the other hand, smoother track walls are found in case of A3SiC and A5SiC coatings. Having high toughness property such coatings have shown some plastic deformation prior to the material flow.

The microscopic images of the worn surfaces of all the coatings are shown in figure 6.7. The distinguished wear tracks of the coatings suggest the major mode of failure to be spallation. Under cyclic loading condition fatigue stress developed on the deposited splats which resulted in the formation of fatigue cracks in the transverse direction of the wear tracks. Being brittle in nature the coating material helps the crack to propagate quickly across the wear tracks and between two splats of similar lamellae. The cyclic loading of the coating surface leads to crack propagation along the splat boundary due to which material spallation has taken place. Spallation or delamination is the major mode of adhesive failure observed in both A0SiC and A5SiC coatings. On the other hand, for A7SiC coatings, in the first few cycles the defects are exposed and spallation has occurred. With further loading in next few cycles the embedded SiC particles are dislodged and entrapped in between the work surface and WC ball. This leads to start three body wear mechanism due to the abrasive action of those entrapped SiC particles. The next major portion of material removed from A7SiC coating is due to abrasion. The severe scratch grooves and furrows formed in the longitudinal direction of wear track suggest the major mode of wear for A7SiC coating is to be abrasive. A very less amount of spallation is noticed on the wear track of A3SiC coating. The burrs formed due to ploughing action of the WC ball are visible at the edges of wear track (figure 6.7(b)). This suggests the improved ductility and toughness of A3SiC coating material. In the later stage of cyclic loading action few spalled off hard particles have caused abrasion to the surface. The fine scratches and furrows are in good agreement with this. Due to the ductile nature of the coating material, separation of material is little in case of A3SiC coating.





Figure 6.5: Specific wear rate of the coatings



Figure 6.6: Depth profiles of wear tracks of (a) A0SiC (b) A3SiC (c) A5SiC (d) A7SiC coatings

The magnified view of wear debris collected from all samples is shown in figure 6.8(a-d). The powder nature of debris of AOSiC coating suggests that mostly loose unmelted particles are detached from the wear track. Broken laminar fragments along with few powder type debris are observed in case of

A3SiC coating. This suggests the removal of solidified splats along with unmelted powder of Al₂O₃. However, having comparatively low quantity of unmelted Al₂O₃ particles suggests good melting of Al₂O₃ in A3SiC coating. In case of A5SiC, the quantity of unmelted particles is increased. Therefore, in the debris both broken fragments and fine particles are observed equally. Debris of mostly fine particles and few lamellar fragments are observed in case of A7SiC coating. In addition, few 'SiC' particles are also observed in the debris. The EDS analysis confirms the presence of Si and C in the debris of A7SiC.

In D-Gun coated Al₂O₃, due to low heat generation and less dwell time the Al_2O_3 particle experiences partial melting. However, with a very high velocity those unmelted particles spread well and dense coating is achieved. With addition of low quantity 'SiC' to Al₂O₃ feedstock significant change in porosity, hardness and wear behaviour is observed in the Al_2O_3 coatings. The selected process parameters are not sufficient to melt 'SiC' as its melting point is much more than the same of Al₂O₃. Also, the thermal conductivity and toughness of SiC are higher. For the given process parameters/heat content the 3% SiC is the optimum quantity to add with Al₂O₃ feedstock for the deposition of 'SiC' splats. This improves the α -Al₂O₃ phase formation and toughness of the overall coating. With enhanced α -Al₂O₃ quantity the hardness of the coating is enhanced. Also, the well adhered 'SiC' of A3SiC coating imparts toughness to the coating material. However, with given heat input further increase in SiC addition to Al₂O₃ feedstock is not been able to deposit 'SiC' in splat form. Therefore, enhancement of the α -Al₂O₃ phase content and so the properties of coating are not noticed.

The limited energy produced in per shot has restricted the amount of melting volume of SiC. The few 'SiC' particles embedded in A5SiC and A7SiC coatings makes weak bond with the surrounding Al₂O₃. Also, with high velocity some of the unmelted SiC particles have bombarded the just deposited Al₂O₃ coating and created defects. The improved α -Al₂O₃ phase content by addition of 3 wt. % SiC suggests the stabilization of Al₂O₃ phase in A3SiC coating. The enhanced mechanical properties of such coating once again support the fact of improvement in α -Al₂O₃ phase content. As the

addition of SiC is very less, the significant improvement in mechanical properties is not only due to the presence of 'SiC' in such coating. Presence of higher amount of α -Alumina also contributes to the enhancement of the overall mechanical properties of the coating.



Figure 6.7: Wear track images of (a) A0SiC (b) A3SiC (c) A5SiC (d) A7SiC coatings captured by inverted microscope



Figure 6.8: SEM micrographs showing wear debris of (a) A0SiC (b) A3SiC (c) A5SiC (d) A7SiC coatings

6.5 Concluding remarks

A3SiC is found to be the highest wear resistant material among the selected coatings as it possesses highest hardness and toughness properties amongst the sprayed coatings. 3-5wt.% of SiC addition to the Al_2O_3 feedstock improves the mechanical properties of D-Gun coated Al_2O_3 . For selected process parameters, more than 3% of 'SiC' addition to the feedstock tends to decrease the mechanical properties of Al_2O_3 coating. The high velocity unmelted 'SiC' particles damage the just solidified Al_2O_3 by bombardment.

In the next chapter, the effect of 3 wt.% 'SiC' addition on cyclic oxidation behaviour of the thermally sprayed Al_2O_3 coatings is thoroughly studied. The oxidation resistance, micro-hardness and fracture toughness of AOSiC and A3SiC coatings are also compared after exposing these coatings to cyclic oxidation tests conducted at a temperature of 900 °C for 50 cycles.

Chapter 7 Oxidation behaviour of D-gun sprayed Alumina based coatings

7.1 Introduction

Low carbon steel is a potential material to produce engineering components due to its several beneficial properties. It's low cost, high toughness and machinability makes it suitable for industrial application. However, due to its proneness to oxidation such material has limited application and it is not preferred to use at high temperature environment. Iron (Fe) which is the main constituent of such steel reacts easily with the oxygen present in the atmosphere at high temperatures to form oxides such as Fe₂O₃, Fe₃O₄, FeO etc. (203). This reduces the performance life of the component. The application of a protective layer (coating) on the surfaces of steel components used in boilers is mainly to counteract oxidation (204). Ceramic thermal barrier coatings are well known to decrease the temperature of the metal beneath the coating by 100-300 °C which in turn improves the longevity of the metal component (205). It is believed that oxidation resistance of a surface can be improved by the formation of Al_2O_3 scales over it (206, 207). Among the common oxides, Al₂O₃ material shows the least diffusivity towards oxygen (208). This helps in protecting the surface of the substrate material from oxidation and hence improves the robustness of the system under high temperature conditions (209). The mechanical properties of Al₂O₃ coating can be improved by adding other compounds (Cr₂O₃, TiO₂, CeO₂, SiC etc.) to it in small quantities. It is reported that addition of CeO₂ to Al₂O₃ refines the microstructure of the coatings sprayed by D-gun process (77). In another study, it is reported that the addition of SiC in the Al₂O₃ results in increased transformation of metastable alumina polymorphs to the stable α -Al₂O₃ phase (98). An addition of SiC has helped in increasing oxidation resistance of Al_2O_3 coating sprayed by low velocity oxy-fuel (LVOF) thermal spray process (210).

Addition of SiC microfibers to thermally sprayed YSZ is found to be beneficial in terms of oxidation resistance property of the coating (211). In this chapter, detonation gun technique is used to deposit pure Al_2O_3 and Al_2O_3 -3wt.%SiC coatings on AISI 1020 steel substrates. The cyclic oxidation tests are carried out at 900 °C for 50 cycles on the uncoated and coated samples to evaluate the oxidation resistance in a muffle furnace. Further the mechanical properties of the oxidized samples are estimated and compared with the properties of as-sprayed coatings.

7.2 Characterization of as-sprayed coatings

The average roughness of the as-sprayed coating surface is found to be around 5 μ m. Also, no significant change in surface roughness (R_a) value is observed between the two different coatings. The porosity percentage, Vickers microhardness and fracture toughness values of the as-sprayed coatings are shown in figure 7.1.

With changing depth/thickness no significant difference in coating porosity is observed in any type of coating. However, notable difference is noticed in the porosity content between the two coatings. The SEM micrographs of the cross-sections of both the coatings are shown in figure 7.2. The presence of more cracks and pores is noticed in AOSiC coating whereas very less pores and cracks are present in A3SiC coating. The reason of this difference is described in chapter 5. For any coating type the hardness is found to be increasing with increasing thickness of the coating. This is because of formation of different phases at different zones of the coating. Initially, the bond coated substrate is at low temperature and the first few layers of Al₂O₃ coating material on deposition have experienced a very high rate of cooling effect. Transfer of heat is taking place by conduction through metallic bond coat and substrate, and by convection to atmospheric air. Due to this, metastable phases (e.g. γ etc.) and amorphous phases are formed at the interface/low thickness zones of the coating. These metastable and amorphous phases are brittle in nature and possess relatively lower hardness than the stable phase such as α -Al₂O₃. As deposition is continued the already deposited layer of coating along with the substrate has become hot and further solidification of newly deposited coating material is prolonged. The already

deposited ceramic coating has restricted the newly deposited Al₂O₃ coating to transfer heat through conduction. Also, with high substrate temperature the top layer coating material has experienced annealing effect. With increased solidification time and annealing effect the formation of α -Al₂O₃ phase at higher thickness region is increased and so the hardness of the zone. At any zone the hardness of A3SiC is found to be more than the same of A0SiC. This is due to the effect of phase stabilization by low quantity SiC addition. With high α -Al₂O₃ content the hardness of A3SiC is more than A0SiC (189, 197). The A3SiC coating also possesses higher toughness property than the same of A0SiC as shown in figure 7.1(c). Presence of 'SiC in A3SiC coating also helps to restrict the crack propagation through its transformation toughening property. It is found in previous chapters that addition of 3wt% SiC to Al₂O₃ coating helps to stabilize the phases of Al₂O₃. In D-gun sprayed A0SiC coating due to rapid cooling effect formation of γ -Al₂O₃ is more in quantity. With low hardness value the γ -Al₂O₃ has low toughness property as well. On the other hand, due to Al₂O₃ phase stabilization A3SiC contains high quantity of α -Al₂O₃ in it. α -Al₂O₃ is not a brittle phase as γ -Al₂O₃ and possess higher toughness property than the later. Therefore, with high amount of α -Al₂O₃ the as-sprayed A3SiC coating possess higher toughness property than the same of A0SiC coating.

Chapter 7



Figure 7.1: The comparisons of (a) Porosity percentage (b) Vickers microhardness (c) Fracture toughness of AOSiC and A3SiC as-sprayed coating



Figure 7.2: SEM micrographs of cross-sections of (a) A0SiC and (b) A3SiC as-sprayed coatings

7.3 Weight change of coatings after oxidation tests

The bare AISI 1020 steel sample grows a fragile greyish oxide scale just after the completion of 1st cycle of oxidation. Very high weight gain is observed in case of bare steel sample. Spallation of oxide scale starts from 5th cycle. The formation of irregular scale and cracks are increased with an increase in oxidation cycle. In case of A0SiC coated sample, after the completion of 1st oxidation cycle the colour of coating changed from white to yellow and it remained the same till the completion of 50th cycle. On the other hand, the colour of A3SiC coating changed from light grey to dark grey colour after 1st cycle of oxidation and it remained unchanged up to 50th cycle. Formation of cracks is noticed in both the coated samples. However, A0SiC sample shows more number of cracks compared to the A3SiC coating.

Figure 7.3 shows the plot of changing weight of the samples with an increase in oxidation cycle. The very low increase in weight of A0SiC and A3SiC coatings suggests the coating materials to be highly oxidation resistant. On the other hand, the high weight gain of bare steel sample proves the material to be very less oxidation resistant. The A3SiC coating is found to have more resistance against oxidation than A0SiC coating. Significant change in weight gain between the two coated samples is observed after 40th cycle of oxidation. For better observation the magnified view of the plots for A0SiC and A3SiC samples are shown in the set of figure 7.3.

The square of weight change per unit area of sample versus number of cycle graphs for bare AISI 1020 steel, A0SiC and A3SiC coated samples are shown in figure 7.4(a), figure 7.4(b) and figure 7.4(c) respectively. It is observed that oxidation behaviours of all the samples have almost followed the parabolic rate law. This parabolic rate is generally expressed by the square of weight increment of the specimen per unit area, as shown in the following equation (212),

 $\left(\Delta W\right)^n = K_p t + C$



Figure 7.3: Plot of Weight change/area versus number of cycles

Where, ΔW is the weight change per unit area, n is the exponent of rate, K_p is the constant for rate of oxidation, t is the total heating time in furnace. The constant for rate of oxidation (K_p) depends on the temperature (213, 214). The average values of constant for rate of oxidation are evaluated from the linearly fitted parabolic regression curves shown in figure 7.4 and the estimated K_p values are presented in table 7.1.

The K_p value of the bare steel sample is far more higher compared to the K_p values of A0SiC and A3SiC coated samples. With high K_p value bare steel sample is found to be oxidation prone material (215). The A3SiC coated

sample has the lowest value of Kp which proves the D-gun sprayed A3SiC to be a thermal barrier coating material (216). The low Kp value of A0SiC coated sample makes the AOSiC coating to be a thermal barrier material too. However, significant improvement in thermal protection is observed if low quantity of 'SiC' is added to the Al₂O₃ especially when the number of oxidation cycles is more than 40.



Figure 7.4: The plots for square of weight change per unit area versus number of oxidation cycles

Table 7.1: The values of parabolic rate constants (\mathbf{K}_p)							
$K_{\rm p} \begin{pmatrix} -10 & 2 & -4 & -1 \\ 0 & {\rm gm} \ {\rm cm} \ {\rm s} \end{pmatrix}$							
Bare	2508						
A0SiC	7.3						
A3SiC	5.33						

7.4 XRD analysis

The XRD profiles of oxidised bare AISI 1020 steel, as-sprayed A0SiC and A3SiC, and oxidized A0SiC and A3SiC coated samples after 50 cycles are shown in figure 7.5(a), 7.5(b, d) and 7.5(c, e) respectively. The phase formed

on the surface of oxidized bare steel sample is found to be iron oxide (Fe_2O_3) only. It is reported that at elevated temperatures (above 570 °C), normally a layer of the Fe₂O₃ is formed on top surface of the steel sample due to oxidation and beneath this layer Fe_3O_4 and FeO phases are formed (217). Due to the formation of very thick scale of Fe_2O_3 after 50 cycles of oxidation, with limited penetration depth the X-ray could detect the Fe₂O₃ phase only. The assprayed coating of AOSiC consists of α -Al₂O₃ and γ -Al₂O₃ phase. On cyclic oxidation the γ -Al₂O₃ experiences annealing effect due to which some amount of γ -Al₂O₃ is converted to θ -Al₂O₃ and α -Al₂O₃ phase (189, 197, 218). The reduced intensity of γ -Al₂O₃ and increased intensity of α -Al₂O₃ are in good agreement with this. In addition to α -Al₂O₃, γ -Al₂O₃, and θ -Al₂O₃ the oxidised A0SiC coating also contains Fe₂O₃ and NiCrO₄ phases in it. NiCrO₄ and Fe_2O_3 phases generally form due to the oxidation of Ni-Cr (219) and Fe respectively. The presence of NiCrO₄ and Fe₂O₃ minor phases on the top surface of AOSiC coating suggests the diffusion of such phases from the Ni-20Cr bond coat and the steel substrate material to the AOSiC coating during the oxidation tests. The EDS analysis of top surface of oxidized A0SiC coating is discussed in the next segment.

The as-sprayed A3SiC coating contains α -Al₂O₃, γ -Al₂O₃ and SiC phases in it. However, in the oxidised A3SiC coating, along with these phases the presence of some minor phases such as θ -Al₂O₃ and SiO₂ are also observed. By annealing effect of heat treatment few γ -Al₂O₃ is converted into θ -Al₂O₃. In the feedstock powder of SiC; Si and SiO₂ were present as impurities with very low quantity. In the as-sprayed coating of A3SiC with uniform distribution the presence of such impurities is negligible.

Hence, the peaks of Si and SiO₂ are not detected in as-sprayed A3SiC coating (figure 7.5(d)) by x-ray. However, during oxidation diffusion of Si and SiO₂ phases from the depth to the top surface of the coating has occurred. This 'Si' is oxidized to form SiO₂. This increases the SiO₂ content of top surface. Therefore, such SiO₂ phase is detected by XRD as shown in figure 7.5(e).

Presence of detectable amount of Si on top surface is confirmed by EDS analysis. The absence of phases like Fe_2O_3 and $NiCrO_4$ in the XRD pattern of

oxidised A3SiC coating proves that no diffusion of bond coat or substrate material is taken place during oxidation tests. Hence, the safety of substrate material is ensured even after 50th cycle of oxidation test.



Figure 7.5: XRD patterns of (a) bare AISI 1020 after oxidation (b) as-sprayed A0SiC (c) A0SiC after 50 cycles of oxidation test (d) as-sprayed A3SiC and (e) A3SiC after 50 cycles of oxidation test

7.5 SEM/EDS and mapping analysis

The SEM images of the top surfaces of the AOSiC and A3SiC coated steel samples after oxidation tests are shown in figure 7.6(a, b). It is clear from the figure that more cracks are formed on the AOSiC coating as compared to the A3SiC coating. Also, the cracks of A0SiC sample are wider than the same of A3SiC coating. The Al₂O₃ coating produced by spraying α -Al₂O₃ powder contains metastable phase like γ -Al₂O₃. During cyclic oxidation tests, some amount of γ -phase is transformed into θ -Al₂O₃ and α -Al₂O₃ through annealing effect. As a consequence of this phase transformation, micro-cracks form in the coating due to the change in volume of the phases (220, 221). Also, due to the difference in expansion and contraction of the different phases under cyclic heating and cooling effect cracks start forming. With time due to the effect of cyclic thermal load these inherited cracks propagate and connect with already present cracks and defects of the coating (figure 7.2). These cracks grow almost in every direction in the coating. With further thermal load the cracks grow further in length and width and degrade the performance of TBC (222). This mechanism of crack formation is similar for both the type of coatings. However, severe damage is observed in case of A0SiC compared to A3SiC coating after 50th cycle.



Figure 7.6: SEM images showing surface of (a) A0SiC and (b) A3SiC samples after completion of cyclic oxidation tests

Figure 7.7 shows the cross-section of damaged A0SiC coating. It shows the cracks reaching to the substrate through the Ni-Cr bond coat. At 900° C temperature after 50 cycles of oxidation the Ni-Cr bond coat has lost its toughness property and cracks are formed. Through these cracks diffusion of materials occurred. The EDS analysis confirms the presence of Al_2O_3 in Ni-Cr bond coat and also confirms the presence of Fe and Ni-Cr in Al_2O_3 coating zone. Some amount of Ni-Cr and Fe has managed to reach the top surface of the coating through these cracks. The presence of NiCrO₄ and Fe₂O₃ on the top coating surface is in good agreement with this. On the other hand, the damage of A3SiC coating is not as severe as A0SiC coating. Figure 7.8 shows the cross-section of A3SiC coating after 50 cycles of oxidation. The already present cracks in as-sprayed coating are now increased in length. However, those are not much inter-connected and also the Ni-Cr bond coat is found to be unharmed. With less/no crack in Ni-Cr bond coat the diffusion of substrate material and bond coat material is not taking place.



Figure 7.7: SEM and EDS analysis of oxidized A0SiC coating

The as-sprayed A3SiC coating has possessed lower defects, porosity and higher mechanical properties compared to the same of as-sprayed A0SiC coating. With high toughness property the growing of cracks in A3SiC coating is lesser. Also, 'SiC' has a property of deflecting cracks through

transformation toughening mechanism. At elevated temperature the stress field near the crack tip triggers the initial Moissanite 24R (synthetic) phase of SiC to transform into Moissanite 174R (synthetic) phase, which has higher volume of cell. This volume expansion causes compressive stress at the crack tip. As a result the crack loses its energy/velocity and gets deflected. In other words, the work associated to this phase transformation contributes to the improvement of toughness. In figure 7.6(b) one such location is shown in the bottom of the figure. A crack is being deflected by a SiC splat. The EDS analysis confirms the presence of 'SiC' at the bend of the crack path.



Figure 7.8: EDS analysis of (a) top and (b) middle surface of A3SiC coating after oxidation

In figure 7.8 the EDS analysis of oxidized A3SiC coating is shown. It is performed to find the presence of 'Si' at the top and middle zone of A3SiC coating. It shows that the presence of 'Si' is more at the top surface compared to the same at middle zone. The XRD analysis shows the presence of SiO₂ in the coating after oxidation tests. In the feedstock powder of SiC as detected by XRD analysis (figure 5.1), Si and SiO₂ were present as impurities. Those impurities were deposited as SiO₂ in the resulting alumina-silicon carbide coatings. Due to low quantity and uniform distribution such SiO₂ was not detected by XRD of as-sprayed A3SiC coating (figure 5.2). However, during

oxidation tests this SiO_2 is diffused out through the cracks and accumulated at the top surface of the A3SiC coating. EDS analysis of figure 7.6(b) shows the presence of 'Si' in a crack. After 50 cycles of oxidation the concentration of 'SiO₂' is increased at top surface and hence, SiO₂ is detected by the XRD analysis. In addition to this, the temperature of oxidation tests was not sufficient enough for SiC to decompose and form Si. Therefore, the possibility of decomposition of SiC and forming SiO₂ is ignored.

The EDS analysis shown in figure 7.8 also reveals the presence of Fe at the top and middle zones of the A3SiC coating. As the Ni-Cr bond coat material is dense in nature, for the substrate material to diffuse out crack formation through the bond coat is a mandatory requirement. Also, diffusion of bond coat material is required to take place too. After 50 cycles of oxidation tests unlike A0SiC coating no crack formation in Ni-Cr bond coat is noticed in A3SiC coating. Figure 7.9 shows the cross section of A3SiC coating where the bond coat material is found to be intact. However, many cracks are observed in the top coat region.



Figure 7.9: SEM micrograph of cross-section of A3SiC coating after oxidation
Also, through the EDS analysis shown in Figure 7.8 no such bond coat material (Ni/Cr) is detected at both top and middle zones of the A3SiC coating. Therefore, possibility of diffusion of Fe from the substrate is ignored. The presence of Fe at top and middle surface of the top coating is due to the improper cleaning of the samples. During the cutting and polishing operations of the oxidised coated sample for metallographic study, the loose steel particles were possibly locked inside the cracks and defects of the A3SiC coating.

7.6 Characterization of oxidized coatings

The mechanical properties of the top coats are highly affected by the cyclic oxidation at high temperature (about 900 °C). The formation of micro-cracks in the coatings is a very important aspect as the severity of the condition is increased with time and temperature. The formation of micro-cracks increases lineally with the increase in exposure time. Hence, degradation of the coating in terms of mechanical properties is expected. In figure 7.10(a, b, and c) the porosity, micro-hardness and fracture toughness data of oxidized coatings are shown. From figure 7.10(a) it is noticed that the porosity of both the oxidized coatings is increased from same of their as-sprayed coatings. At high temperature, the volume of the entrapped gas in the pores/inter-splat region increases and so the overall porosity of the coatings. A3SiC coating has lesser porosity compared A0SiC coating.

With increasing coating thickness the porosity value decreases. This is because of the annealing effect which is pre-dominant at the top layer of the coating due to the exposure to high temperature. Conversion of metastable phases to stable phases and suppression of pores is maximum at the top layer. Therefore, both the coatings have maximum porosity in deep regions and minimum at the top. However, at all the zones the porosity of oxidized coating is more than the same of as-sprayed coatings. Having more α -Al₂O₃ and less defects the hardness of the oxidized coating is found to be lesser than the same of as-sprayed coatings. This is due to the overall increase in porosity of the oxidized coatings. It also shows increasing trend with an increase in coating thickness. With minimum annealing effect the amount of stable α -

Al₂O₃ is lesser at the deeper zone of the coatings. Also, the porosity at this deep zone is the maximum. Hence, the hardness at the depth is minimum. On the other hand, the annealing effect is the maximum at the top surface of the coatings. This leads to more stable phase formation. With highest quantity of stable α -Al₂O₃ and lowest amount of porosity the hardness at the top surface zone is the maximum for any coating. With higher α -Al₂O₃ content A3SiC shows higher hardness than A0SiC coating at any zone of the coating. Also, at the top coating surface of A3SiC coating the decrease in hardness is not much from the same of as-sprayed A3SiC coating. On the other hand, for oxidized A0SiC is very high at any zone of the coating. This is because of the diffusion of bond coat and steel substrate to the top ceramic coating. Presence of Ni-Cr and Fe in the oxidized coating makes it less hard than the as-sprayed A0SiC coating.

Figure 7.10(c) shows the fracture toughness values of oxidized A0SiC and A3SiC coatings. Having more α -Al₂O₃ in the coating the oxidized A3SiC coating has higher fracture toughness property than the oxidized A0SiC coating. However, decrease in toughness value of both the coatings is noticed than the same of their respective as-sprayed coatings. The decrease in toughness property of coatings is due to increased porosity, reduced hardness and increased cracks at the top surface of the coatings. Material spallation has taken place at many places of oxidized A0SiC coating surface during the scratch test. On the other hand, no such spallation has occurred on the surface of oxidized A3SiC coating during scratch tests and a smooth scratch is performed as shown in figure 7.11(b).





Figure 7.10: The comparisons of (a) Porosity percentage (b) Vickers microhardness (c) Fracture toughness of AOSiC and A3SiC as-sprayed coatings after cyclic oxidation tests



Figure 7.11: Microscopic image of scratch on the surface of oxidized (a) AOSiC and (b) A3SiC samples

7.7 Concluding remarks

In this chapter, it is observed that AISI 1020 steel is not a suitable material for high temperature applications due to its very high oxidation rate. However, the thermal resistance of this steel can be enhanced significantly by applying Ni-20Cr bond coat and pure Al₂O₃ (A0SiC) or Al₂O₃-3wt%SiC top coat materials on it by D-Gun technique. Both A0SiC and A3SiC coatings possess thermal barrier property. During cyclic oxidation tests both the coatings follow parabolic rate law. With lower parabolic rate constant (K_p) value A3SiC is found to be more oxidation resistant than A0SiC coating. During the oxidation test wider and longer cracks are formed in pure Al₂O₃ coating than the same of A3SiC coating. Diffusion of materials occurs through the cracks of the coatings. Bond coat and substrate materials diffuse to top coating surface and form oxides in case of A0SiC coating. No bond coat and substrate material diffuse in case of A3SiC coating. Presence of 'SiC' helps to reduce the crack propagation in A3SiC coating through transformation toughening property. The mechanical properties such as micro-hardness and fracture toughness of oxidised A3SiC coating are found to be higher than the same of oxidised A0SiC The change in micro-hardness property of the top surface of A3SiC coating is much lesser compared to the same of A0SiC coating due to oxidation. Hence, the A3SiC coating has more ability to retain mechanical properties at elevated temperature.

The next chapter is the final chapter of this thesis and it presents consolidated conclusions made to summarize the entire research work. It also contains the future scope of this research work.

Chapter 8 Conclusion

8.1 Introduction

This chapter highlights the conclusions made from the research work presented in this thesis. In first part, comparative study is made between sand blasted steels and EDMed steels to judge the applicability of die-sinking EDM as a substrate preparation process prior to thermally sprayed coating application. In the second part of the thesis, D-gun sprayed Al₂O₃ based coatings are developed by varying SiC content in the feedstock powder at constant process parameters. The characteristics of the developed coatings are thoroughly studied. Some general conclusions have been drawn in accordance to the observed performance and nature of the coatings.

8.2 General conclusions

It is found that both die-sinking EDM and sand blasting processes are able to produce similar type of roughness profiles on steel substrates. Both EDM and sand blasting process harden the surface of the treated substrates, although EDM treated samples gain much more hardness compared to the sand blasted samples. The increased hardness of the surface produced by EDM is due to the metallurgical changes occurrence on the steel surfaces. Such metallurgical changes are the result of carbon impregnation on the steel surface which leads to form austenite and cementite phases on the surface of the EDMed samples. No such metallurgical change is found on the steel surfaces produced by sand blasting operation. The hardness increment of sand blasted surfaces is attributed to work hardening phenomenon caused by impact of alumina grits on the substrate surface. The adhesion of D-gun sprayed coatings with steel substrate depends not only on the mechanical interlocking but also on the local welding phenomenon. This local welding takes place between the surface asperities and the deposited splats by physisorption or chemisorption mechanism. Failing to achieve a coating on the EDMed surface suggests that the metallurgical change occurred on the steel surface would not allow any

local welding phenomenon between the steel substrate and the Ni-5Al coating. It is concluded that for successful thermally sprayed coating deposition both surface roughness and proper metallurgy are the essential requirements.

It is possible to deposit 'SiC' by detonation gun spraying technique without decomposing it by selecting proper process parameters. The low 'SiC' content (3wt%-5wt%) in the alumina based coating stabilizes the α -Al₂O₃ as it affects the melting and solidification behaviours of as-sprayed Al₂O₃ coating. However, the parameters used for coating deposition are good enough to stabilize the Al₂O₃ phase with only 3wt% to 5wt% of SiC addition. If 'SiC' content is more than 5wt% then the 'SiC' particles start damaging the already solidified Al₂O₃ splats by bombardment effect.

The mechanical properties of the Al_2O_3 -3wt%SiC coating is found to be the best among all the four types of sprayed coatings. Also, the high values of hardness and fracture toughness of the Al_2O_3 -3wt%SiC have made it the best wear resistant coating material among the sprayed coatings.

Both D-gun sprayed pure Al₂O₃ and D-gun sprayed Al₂O₃-3wt%SiC coatings are found to have good oxidation resistance property as these are able to save AISI 1020 steel surface from high temperature cyclic oxidation. Both of these coatings have showed very less values of parabolic rate constant (K_p) compared to bare AISI 1020. Hence, such type of coatings can be applied on boiler walls made of alloy steels. Between the two coatings, D-gun sprayed Al₂O₃-3wt%SiC coating is found to have the highest oxidation resistance property as it has the lowest value of parabolic rate constant. Also, the effect of oxidation is found to be more on the pure Al₂O₃ coatings as compared to Al₂O₃-3wt%SiC coating. A significant number of cracks are formed on both the top and cross-sectional areas of pure Al₂O₃ coating. Presence of 'SiC' in the latter has reduced the crack propagation in the coating as 'SiC' has the ability to stop crack propagation through transformation toughening mechanism. Also, the mechanical tests on both the coatings after completion of 50 cycles of oxidation have showed that Al₂O₃-3wt%SiC have retained more hardness and fracture toughness compared to the pure Al₂O₃ coating.

8.3 Contribution to the science

For long it is believed that the adhesion of thermally sprayed coatings depends mostly on the mechanical interlocking at the coating-substrate interface. This research work proves that for successful coating deposition along with mechanical interlocking, the local welding phenomenon is equally important to take place. Without the local welding by physisorption/chemisorption mechanism it is impossible to obtain a coating on a steel substrate.

The D-gun thermal spray process can be used to successfully deposit a material like "SiC" without decomposing it. D-gun sprayed Al_2O_3 -3SiC coating is a potential material to protect steel substrates from wear and tear as compared to pure Al_2O_3 coatings. The D-gun sprayed alumina coatings with 3wt% of 'SiC' content can withstand very high temperature and hence can be used as TBC applied on components like boilers.

8.4 Future scope of work

In the present research work die-sinking EDM is tried as a substrate preparation process and compared with the already established sand blasting process used prior to the application of thermal spray coatings on steels. The die-sinking EDM can produce a roughness profile which is similar to sand blasting process. However, the metallurgical changes occur on the steel surface due to EDM processing with hydrocarbon based dielectric material making it unsuitable to be used before applying thermal spray coatings. Hence, other types of EDM processes and non-hydrocarbon based dielectric materials may be tried to prepare the substrate.

The stabilization of phases of D-gun sprayed Al_2O_3 can be tested for higher amount of SiC addition to the feedstock powder and for variable process parameters. It will be interesting to find how the maximum stabilizing points vary with changing process parameters. In the present study, the process parameters are not varied. However, from the results it is evident that melting of 'SiC' and stabilization of Al_2O_3 phases heavily depend on the selected process parameters. It is well predicted that for higher energy input the quantity of 'SiC' can be more to stabilize the Al_2O_3 phase present in the D-gun sprayed Al_2O_3 -SiC coatings. However, the increase of energy input may be limited upto certain point, beyond which all the 'SiC' will start decomposing into 'Si' and 'C'.

Also, other than oxidation resistance, high temperature corrosion resistance (in molten salt) and quench test can also be performed on D-gun sprayed Al_2O_3 -SiC coatings.

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A. Details of technique used for mechanical mixing of coating powders A1. Ball Mill



Make and model	Retsch, PM100, Germany
Speed	10 – 2000 rpm
Bowl size range	12 - 500 ml
Ball size range	5 - 40 mm

B. Details of the instruments used for the characterization of samples

B1. Leica Inverted Microscope



Make	DM IL, Leica Microsystems, Germany
Optics	Leica HC optics (infinity corrected) HC objectives: 2.5x–100x
Transmitted-light	5 watt LED, external power supply
illuminator	(in 100-240, out 5 V/2 A) Filter holder for TL filter Ø 32 mm,
	collector, scattering filter
Focus	Coaxial coarse and fine adjustment, travel path 7 mm, nosepiece focusing

B2. Field Emission Scanning Electron Microscope (FESEM) coupled with EDS



Make and model	SUPRA 55, Carl Zeiss NTS GmbH,
	Germany
Resolution	1.0 nm @ 15 kV
	1.7 nm @ 1 kV
	4.0 nm @ 0.1 kV
Acceleration Voltage	0.1 – 30 kV
Magnification	12x – 900,000 x
Stages	5-Axes Motorized Eucentric
	Specimen Stage X = 130 mm, Y =
	130 mm and Z = 50 mm, T = -3° to
	$+70^{\circ}, R = 360^{\circ}$

B3. Vickers Microhardness Tester



Make and model	VMH002 V, Walter UHL Technische Mikroskopie
	GmbH, Germany.
Load Range	1 gram – 2000 grams
Type of intender	Diamond square base hexagonal Pyramid

B4. X-ray Diffraction



Make and model	Rigaku, SmartLab, USA
X-ray generator	3 kW
Tube voltage variable range	20 – 60 kV
Tube current variable range	2 – 50 mA

B5. Scratch Tester



Make and model	Ducom TR-101, India
Stroke	1-25 mm
Normal load	0-20 N
Loading rate	0.1-2 N/mm
Tractional force	20 N max.
Scratching speed	0.25 mm/s to 5 mm/s
Indenter	Rockwell C, 200 µm tip radius



B6. Nano-mechanical Test Instruments (Nano-indenter)

Make and model	Hysitron, TI750, USA	
	Z-Axis	X-Axis
Maximum Force	10 mN – 30 mN	2 mN
Maximum Displacement	5 μm	15 μm
Load Resolution	1 nN	3 μN
Displacement Resolution	0.04 nm	4 nm
Load Noise Floor	100 nN	10 μN
Displacement Noise Floor	0.2 nm	10 nm
Thermal Drift	< 0.05 nm/sec	< 0.05 nm/sec

- C. Facility to test wear resistance of coatings
- C1. Ball-on-disc Tribometer



Make and model	Ducom TR-20LE , India
Disc speed	150 – 2000 rpm
Normal Load range	0.5- 20 kg
Sliding speed	0.5- 12 m/s
Wear track diameter	10 – 140 mm
Frictional force	Max. 200 N

D. Instruments used during oxidation tests

D1. Semi Micro Balance



Make and model	CITIZON, CX 265N, India
Capacity	80/220 gm
Readability	0.01/0.1 mg
Readability (+/-)	0.02/0.1 mg
Response time	$3-5 \sec$
Display	Backlit LCD Graphical Display
Calibration	Perfect internal calibration
Tare Range	Full
Operating Temperature	5°C to 40°C
D2. Muffle furnace



Make and model	Bio-Techniks, India
Heating Element	Kanthal A-1 Wire
Max Working Temperature	1160 deg. C
Power Supply	230V

(A) Publications from PhD thesis work:

- Vishal Sharma, Sabiruddin Kazi, "An investigation on D-gun sprayed Al₂O₃-SiC coatings, Surface and Coatings Technology", Vol. 375, pp. 303-314, 2019.
- Vishal Sharma, Kazi Sabiruddin, "A Comparative Study of Sand Blasted and Electro Discharge Machined Surfaces of Steel Substrates", Sadhana, Vol. 45:50, pp. 1-13, 2019.
- Vishal Sharma, Sabiruddin Kazi, "Oxidation Behavior of D-gun sprayed Al₂O₃-3wt.% SiC coating, Surface and Coatings Technology", Vol. 383, pp. 125238, 2020.

(B) Other publications during PhD:

- V. Sharma, K. Sabiruddin "Effect of process parameters on the roughness parameters of EDM processed EN 08, EN 09 and EN 31 steel samples" (Under Preparation).
- V. Sharma, M. Sharma, K. Sabiruddin " Development of Explosive coating setup to deposit Ni-Al coating on steel substrates" (Under Preparation)