

HOT CORROSION AND OXIDATION ANALYSIS OF SS-304 AT 800°C UNDER CYCLIC CONDITION

**A Thesis Submitted
In Partial Fulfillment of the Requirement
For the degree of**

MASTER OF TECHNOLOGY

**In
Design Engineering**

By

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CERTIFICATE

It is certify that the work contained in this thesis entitled “**Oxidation and hot corrosion analysis of SS-304 at 800°C under cyclic condition**” by Mairaj Ahmad (Roll.No.1180456002) for the award of **Master of Technology** from **Babu Banarasi Das University** has been carried out under my supervision. I approved that thesis report embodies results of original work, and studies as out by the student themselves and contents of the project do not from the basis for the award of any other degree to candidate or anybody else from this or any other university.

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ACKNOWLEDGEMENT

I wish to express my sincere appreciation to my project guide; **Mr. Ravi Vishwakarma** for their knowledge, guidance and criticisms without which the collaborative work reported in this thesis would not have been possible. He always be a constant of encouragement and inspiration for me in spite of his busy schedule, I am very grateful to them for their valuable guidance and affection that turned my project into great success. Their constant efforts helped me a lot during entire journey.

I would also like to thank **Prof. (Dr.) Apurva Anand**, Head, Mechanical Engineering Department and **Mr. Sunil Kumar**, M.Tech Coordinator who has always been prepared to offer me help at any time, in spite of having busy schedule.

I am thankful to all faculty members of mechanical engineering department, School of Engineering, BBD University for providing help me directly or indirectly in bringing of this piece of work successful completion.

I would like to express endless gratitude to “**My Parents**” who gave me everything they could to enable me to reach the highest possible education level. I only hope that they know how their love, support and patience encouraged me to fulfil their dream.

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ABSTRACT

In power and energy sectors equipment like boiler, gas turbine, hot corrosion is very common and concerning problem as well as internal combustion engines, and industrial waste incinerators too. It deteriorate the materials at an unpredictably quick manner. Alloys used at high temperature, should carry strong mechanical properties, corrosion and oxidation resistance in order to sustain the frequent failures. Alloys are employed due to higher mechanical properties and creep resistance for air and salty environment. In current studies, Ni-20Cr and Ti coating has been sprayed on SS-304 alloys at 800 °C by Detonation Gun (D-Gun) sprayed technique. The characterization of coating been done by Scanning Electron Microscopy (SEM) morphology. The elevated temperature oxidation behavior of uncoated and coated alloy has been estimated by exposing the specimens at 800 °C for 50 cycles of 60 minutes heating followed by 20 minutes cooling in each cycle at ambient condition. At temperature below 600°C corrosion attack is relatively insignificant and significant above 750°C since contaminants are in the solid phase. The oxidation kinetics and hot corrosion kinetics of coated and uncoated alloys have been fixed with help of weight change measurement. The D-Gun sprayed coating has shown good contaminants to the substrate metal and lower weight gain in coated sample as compared to bare alloy SS-304. The oxidation behavior of SS-304 in salt of 50% Na₂SO₄ + 50% NaCl has been studied under the isothermal conditions at a temperature of 800°C in a cyclic manner. Squalor of components of boilers, gas turbines metallurgical furnaces, petrochemical installations are mainly due to the high temperature oxidation and hot corrosion. Super alloys find their wide applications in the gas turbines and marine engineering due to their good mechanical properties at elevated temperature.

It was observed that all the coated and uncoated stainless steel mapping techniques were used to analyze the oxidation products of coated and uncoated stainless steel. The coating showed better resistance to the air oxidation as compared to the uncoated stainless steel. The coating Ni-20Cr and Ti was found to be more protective. The formation of oxides and spinals nickel chromium and

titanium may be contributing to the development of air oxidation resistance in the coatings. The hot corrosion and oxidation analysis of SS-304 has been investigated at 800°C in air and molten salt 50% Na₂SO₄ + 50%Nacl under cyclic heating and cooling conditions for 50 cycles The kinetics of oxidation of coated and bare boiler steel has been established with help of weight change measurements. The kinetics of oxidation may be define by evaluation by parabolic rate constant value K_p, which was found by the following rate equation: $(\Delta W/A)^2/t = K_p$ where $(\Delta W/A)$ was the weight change measurement per unit surface area and K_p the parabolic oxidation rate constant, t the cooling time. It was observed that all the coated and bare stainless steel obeyed parabolic rate law of oxidation (K_p).The hot corrosion and oxidation of the coated and un coated stainless steel. The uncoated SS-304 are hot corrosion in the form of intense spalling and peeling of its oxide scale, which was perhaps due to the formation of unproductive oxide scale. The coatings showed better resistance to the air oxidation as compared to uncoated SS-304.The Ni-20Cr and Ti coating was found to be more protective. The formation of oxides and spinals nickel chromium and titanium may be contributing to the development of air oxidation resistance in the coatings. The FE-SEM micrograph as-sprayed Ni-20Cr and Ti coating is shown in fig. The microstructure consists of irregular sized particles.

CHAPTER 1

1. INTRODUCTION

Corrosion is deterioration of material or its properties because of reaction with its environment. Sometimes the deterioration is a weight gain, sometimes it a weight reduction, sometimes the mechanical properties are affected. Solid particle erosion (SPE) is a serious problem for the electric power production, costing a projected US\$300 billion per year in lost efficiency, forced outages, and repair costs [1]. Metals and alloys sometimes experience accelerated oxidation when their surfaces are covered with a thin film of fused salt in an oxidizing gas atmosphere at elevated temperatures. This is known as hot corrosion where a porous non-protective oxide scale is formed at the surfaces and sulphides in the substrate. Alloys that are developed for heat and oxidation resistance typically form a protective layer of chromia or alumina. The more rapidly this layer is established, the better protection is offered. As this layer grows or as it reforms over areas from which the original layer was removed, it must withdraw chromium or aluminum from the metal in order to provide for further scale growth [2]. The super alloy have been developed to enhance their oxidation resistance by utilizing the concept of selective oxidation which are affected by alloy composition, surface condition, gas environment and cracking behavior of the oxide scale [3]. Squalor of components of boilers, gas turbine, metallurgical furnaces, petrochemical installations are mainly due to the high temperature oxidation and hot corrosion. Super alloys find their largest applications in the gas turbine industry due to their good mechanical properties at elevated temperature [4]. Oxide scale is constituted by a layered structure with

compositional and microstructure variations from the substrate to the outer interface [5]. Residual fuel oil used in energy generation system contains sodium, vanadium, and sulphur as impurities. During combustion sodium and sulphur react with each other and forms Na_2SO_4 , Vanadium reacts with oxygen to form V_2O_5 . These impurities react together to form low melting point complex compounds, known as ash, which deposit on the surface of materials and induce accelerated oxidation (hot corrosion). Corrosion occurs when these molten compounds dissolve the protective oxide layers that naturally form on materials during boiler/gas turbine operation due to high temperature oxidation. The inability to either totally prevent the hot corrosion or at least detect it at an early stage has resulted in destruction of engines/ infrastructures [6]. According to Stott when a clean component is exposed to an oxygen rich gas, small impinging nuclei of all the thermodynamically stable oxides develop on the surface and collapse rapidly to give a complete layer during the initial or transient stage, all the elements in the alloy oxidize and the amount of various oxides in the layer are approximately proportional to the concentration of the elements in the alloy [7]. For achieving enhanced efficiency, it is necessary that the developed superalloy should exhibit excellent high temperature oxidation resistance as it is detrimental at elevated temperatures. It reduces the superalloy component life by forming oxides at a faster rate, thereby reducing the load-carry capacity and potentially leading to catastrophic failure of components. Therefore, high temperature oxidation resistance of new superalloy is as important as its high temperature strength properties.

It is understood that the high temperature capability of superalloys depends on their chemistry such as nature of alloying elements and concentration of each alloying element. The major change is the addition of rhenium or of both

ruthenium and iridium at the cost of chromium, which are named as the 3rd or 4th or 5th generation superalloys respectively. Therefore, the chemistry of an advanced superalloy that belongs to 3rd generation was greatly influenced by reducing chromium (Cr) content and increasing the rhenium (Re) content. Similarly, the 4th and 5th generation superalloys contain only about 3% Cr but instead contain about 6% Re, 1.5% ruthenium (Ru) and/or iridium (Ir), which is a great contrast to the earlier generation superalloys containing about 10% Cr and no Re, Ru or Ir. These are unique elements, which can increase high temperature creep properties considerably, but make the superalloys susceptible to high temperature corrosion *i.e.* hot corrosion and high temperature oxidation. It is due to the fact that the new superalloys cannot form corrosion resistant alumina or chromia scale because of the presence of high rhenium content and small amounts of ruthenium and iridium. Their effect is similar to Mo on oxidation *i.e.* the high vapour pressure of its oxide. Therefore, the new alloying elements are harmful for high temperature corrosion resistance of advanced Ni-based super-alloys. Several failures of gas turbine engine blades were reported during service [8]. Newer materials with improved properties are essential in order to enhance the efficiency of gas turbine engines. Efforts made in this direction made it possible to develop a new super-alloy for aero engines. The developed super-alloy exhibits excellent high temperature strength properties [9]. It was attributed primarily to high temperature corrosion of different types and established their relevant theories. Extensive amount of work was carried out in the laboratory on hot corrosion of several super-alloys and established their degradation mechanisms [10]. It was shown that the hot corrosion of super-alloys takes place through electrochemical reactions and it is an electrochemical phenomenon [11]. Further, high performance protective coatings were

successfully identified for protection of super-alloys under hot corrosion conditions [12]. Efforts made by other researchers in developing protecting coatings helped in understanding their behaviour [13]. Basically, the high temperature corrosion can be divided into oxidation and hot corrosion. The hot corrosion can be further divided into type I (800°C - 950°C) and type II (600°C - 750°C). As already mentioned above, any new super-alloy material that is developed for gas turbine engine applications should exhibit excellent high temperature corrosion resistance apart from excellent mechanical properties. Super-alloys find extensive use in gas turbines, especially for fabricating hot section components to provide superior strength and creep resistance in high temperature environment. During operation, blades and vanes of gas turbines are subjected to severe thermal cycling and mechanical loads. In addition, they are also attacked chemically by both high temperature oxidation and hot corrosion. It is impossible to impart both high temperature strength and high temperature oxidation resistance to the superalloys simultaneously along with ease of manufacturing. It is possible only with the composite materials to meet such requirements, where the base material provides the necessary mechanical strength and the coating provides the protection against wear, erosion–corrosion, and oxidation [14-15]. Among the commercially available thermal spray coating techniques, Detonation Spray (DS) and High Velocity Oxy Fuel (HVOF) spray are the best choices to get hard, dense and wear resistant coatings as desired [16]. The objective of the work is to analyze the role of detonation gun spray coating to enhance the properties of surface of substrate to counter the problems like erosion, residual stress, fretting fatigue, thermal behavior and corrosion etc. Thermal spraying has emerged as an important tool of increasingly sophisticated surface engineering technology. The different functions of the coating, such as

wear and corrosion resistance, thermal or electrical insulation can be achieved using different coating techniques and coating materials [17]. There are many thermal spray coating deposition techniques available, and choosing the best process depends on the functional requirements, adaptability of the coating material to the technique intended, level of adhesion required, (size, shape, and metallurgy of the substrate), and availability and cost of the equipment.[18] Thermal spray processes that have been considered to deposit the coatings are enlisted below:

(1) Flame spraying with a powder or wire, (2) Electric arc wire spraying, (3) Plasma spraying, (4) Spray and fuse, (5) High Velocity Oxy-fuel (HVOF) spraying, (6) Detonation Gun. Oxidation behavior of Ni-20Cr metallic coatings using high-velocity oxy-fuel (HVOF) and air plasma spray process on 9Cr-1Mo substrate steel was observed in the temperature range of 600- 7500C [19]. The kinetics of hot corrosion like formation of protective oxide scale of Ni-20Cr,Ti diffusion of nickel from the coatings to the substrate and the diffusion of iron from the substrate to the coatings for longer exposures to steam oxidation was investigated. The trend of formation of scale initiation with temperature and time duration was also observed at the interface between the coating and the substrate in case of the APS coating.

This paper is intended as a contribution to the knowledge of the oxidation behavior of the SS-304 in an air and molten salt 50% Na₂SO₄+ 50% NaCl atmosphere under isothermal conditions in cyclic manner. In this experimental study emphasis is also given to oxide scales which were separated and fell down in boat while oxidation process was going on.

CHAPTER 2

2. LITERATURE REVIEW

T.S. Sidhu et. al. [20] have evaluated the hot corrosion performance of high velocity oxy-fuel (HVOF) sprayed Ni-20Cr wire coating on a Ni-based super alloy for 1000hrs at 900°C under cyclic conditions in a coal-fired boiler. The HVOF sprayed Ni-20Cr coating was found to be effective in imparting hot corrosion resistance to Superni 75 in the actual working environment of a coal fired boiler as compared to the uncoated super alloy. Buta Singh Sidhu et al. [21], while studying Ni3Al coatings on boiler tube steels through plasma spray process (where Ni-Cr-Al-Y was used as a bond coat before applying Ni3Al coatings) observed that the Ni3Al coating was very effective in decreasing the corrosion rate in air and molten salt at 900°C in case of ASTM SA210- Grade A1 and ASTM-SA213-T-11 type of steel where as the coating was least effective for ASTM-SA213-T-22 type of steel. Uncoated ASTM SA213- T-22 type of steel had shown very poor resistance to hot corrosion in molten salt environment and also indicated spalling of oxide level.

Kamal et al. [22] investigated the hot corrosion resistance of detonation gun sprayed (D-gun) Cr3C2–NiCr coatings on Superni 75, Superni 718 and Superfer 800 H superalloys. The deposited coatings on these superalloy substrates exhibit nearly uniform, adherent and dense microstructure with porosity less than 0.8%. Thermogravimetry technique is used to study the high temperature hot corrosion behavior of bare and Cr3C2–NiCr coated superalloys in molten salt environment (Na2SO4–60% V2O5) at high temperature 900 °C for 100 cycles. The corrosion products of the detonation gun sprayed Cr3C2–NiCr coatings on super-alloys are

analyzed by using XRD, SEM and FE-SEM/EDAX to reveal their micro structural and compositional features for elucidating the corrosion mechanisms. It is shown that the Cr₃C₂-NiCr coatings on Ni- and Fe-based superalloy substrates are found to be very effective in decreasing the corrosion rate in the given molten salt environment at 900 °C. Particularly, the coating deposited on Superfer 800 H showed a better hot corrosion protection as compared to Superni 75 and Superni 718. The coatings serve as an effective diffusion barrier to preclude the diffusion of oxygen from the environment into the substrate superalloys. It is concluded that the hot corrosion resistance of the D-gun sprayed Cr₃C₂-NiCr coating is due to the formation of desirable micro structural features such as very low porosity, uniform fine grains, and the flat splat structures in the coating.

H.Singh et. al. [23] have studied high temperature oxidation behavior of plasma sprayed Ni₃Al coating. In their investigation, Ni₃Al powder was prepared by mechanical mixing of pure nickel and aluminium powders in a ball mill. Subsequently Ni₃Al powder was deposited on three Ni-base super alloys: Superni 600, Superni 601 and Superni 718 and, one Fe-base super alloy, Superfer 800H by shrouded plasma spray method. Oxidation studies were conducted on the coated superalloys in air at 900°C under cyclic condition for 50 cycle. Each cycle consisted of 1 hrs heating followed by 20 min of cooling in air. The thermo gravimetric method was used to approximate the kinetics of oxidation. All the coated super alloys nearly followed parabolic rate law of oxidation. X-ray diffraction, SEM/EDAX and EPMA technique were used to analyze the oxidation products. The Ni₃Al coating was found to be successful in maintaining its adherence to the super alloy substrates in all the cases. The oxide

scales created on the oxidized coated superalloys were found to be intact and spallation-free.

Kamal et al. [24] investigated the microstructure and mechanical properties of detonation gun sprayed NiCrAlY + CeO₂ alloy coatings deposited on superalloys. The morphologies of the coatings were characterized by using the techniques such as optical microscopy, X-ray diffraction and field emission scanning electron microscopy/energy-dispersive analysis. The coating depicted the formation of dendritic structure and the microstructural refinement in the coating was due to ceria. Average porosity on three substrates was less than 0.58% and surface roughness of the coatings was in the range of 6.17–6.94 μm. Average bond strength and micro hardness of the coatings were found to be 58 MPa and 697–920Hv, respectively. S.B. Mishra et. al. [25] have investigated plasma sprayed metallic coating of nickel-aluminide deposited on Fe-based super alloy. The coating had shown better erosion resistance as compared to the uncoated samples.

Wang et al. [26] designed the separation device for detonation gun spraying system and studied its effects on the performance of WC–Co coatings. The WC–Co coatings were synthesized by the D-gun spraying system with and without using a separation device, respectively. The results showed that the use of the separation device resulted in better properties of the D-gun sprayed WC–Co coatings, e.g., lower the surface roughness, lower the porosity, higher the microhardness, higher the elastic modulus, and higher the interfacial adhesive strength. Also, the tribological performance of the WC–Co coatings was improved. The relationship of surface roughness, microhardness, elastic modulus, adhesive strength, and wear resistance of the WC–Co coatings with porosity was discussed. At the same time, there is an inevitable disadvantage for

using the separation device, i.e., the relatively lower effective utility rate of the feedstock powder. Therefore, the separation device is suitable to be applied in occasions of high performance requirements where increased costs are acceptable.

CHAPTER 3

3. HOT CORROSION & OXIDATION

Hot corrosion can occur at high temperatures, where the deposit is in the liquid state right from the beginning, or the solid deposit turns into liquid during exposure as a result of reaction with the environment. These two types of hot corrosion processes are termed as High Temperature Hot Corrosion (HTHC) or Type I and Low Temperature Hot Corrosion (LTHC) or Type II respectively [27]. Hot corrosion was first recognized as a serious problem in 1940s in connection with the degradation of fireside boiler tubes in coal fired steam generating plants, internal combustion engines, gas turbines, fluidized bed combustion and industrial waste incinerator. Hot corrosion is considered as a major failure mode for high temperature components of many important engineering systems such as aircraft and land-based gas turbines. Hot corrosion has been defined by Rapp and Zhang (1994) as the accelerated oxidation of materials, at elevated temperatures, induced by a thin film of fused salt deposit [28]. In hot corrosion, metals and alloys are subjected to degradation at much higher rates than in gaseous oxidation, with a porous non-protective oxide scale formed at the surface and sulphides in the substrate. The kinetics of the oxidation process, as well as the characteristics of the oxidation products is critically dependent on the oxygen partial pressure of the aggressive environment. Hot corrosion on metallic coatings can be classified into Type I and Type II. The temperature range and the damage on the coatings are illustrated in Fig.1 [29]. Type I hot corrosion occurs above a certain temperature (800-950 °C) when the detrimental salts (e.g. sulphates like Na_2SO_4 , K_2SO_4) are melted to dissolve the

oxide scale. This process usually produces a porous oxide layer and the underlying alloy/coating with a sulfidation attack. At lower temperature (600-800 °C), pitting attack with minimal sulfidation is commonly found, leading to the type II hot corrosion. The damage by the hot corruptions depends on many factors such as coating composition, thermomechanical condition, contaminant composition, flux rate, temperature, corrosion time, gas composition and velocity, and erosion [30]. Some corrosive salts, oxides and eutectics with their melting points are shown in Table 1; note that the eutectics of some salts have a lower melting point than the single salts. Oxidation is a type of corrosion involving the reaction between a metal and air or oxygen at high temperature in the absence of water or an aqueous phase. It is also called dry-corrosion. The rate of oxidation of a metal at high temperature depends on the nature of the oxide layer that forms on the surface of metal [31]. Metals and alloys may experience accelerated oxidation when their surfaces are coated by a thin film of fused salt in an oxidizing gas. This mode of attack is called hot corrosion. Hot corrosion was first recognized as a serious problem in the 1940s in connection with the degradation of fireside boiler tubes in coal-fired steam generating plant. Since then the problem has been observed in boilers, internal combustion engines, gas turbines, fluidized bed combustion and industrial waste incinerators [32]. But, hot corrosion became a topic of important and popular interest in the late 60s as gas turbine engines of military aircraft suffered severe corrosion during Viet Nam conflict during operation over sea water. Metallographic inspection of failed parts often showed sulfides of nickel and chromium, so the mechanism was initially called “sulfidation” [33]. However, studies by Goebel and Pettit and by Bornstein and DeCrescente [34] showed that sulfide formation indeed resulted from the reaction of the metallic substrate with a thin film of fused salt

of sodium sulfate base, the phenomenon has been renamed “hot corrosion”. Thus, hot corrosion may be defined as accelerated corrosion, resulting from the presence of salt contaminants such as Na₂SO₄, NaCl, and V₂O₅ that combine to form molten deposits, which damage the protective surface oxides [35].

Table 1. Melting point of some salts, oxides and eutectics [42, 43]

Species	Melting Point (°C)
NaCl	800
Na ₂ SO ₄	884
NaCl-Na ₂ SO ₄	620
Co-Co ₄ S ₃	877
Ni-Ni ₃ S ₂	645
CoSO ₄	735
CoSO ₄ -Na ₂ SO ₄	565
NiSO ₄ -Na ₂ SO ₄	671
V ₂ O ₅	690
NaVO ₃	630
Na ₃ VO ₄	850
Na ₄ V ₂ O ₇	635
Al ₂ (SO ₄) ₃	770
Na ₂ O	1132
NaAlO ₂	1800
CaO-Al ₂ O ₃ -SiO ₂	1170
CaO-MgO-SiO ₂	1320

3.1 GENERAL CLASSIFICATION OF HOT CORROSION

Hot corrosion is often divided into two forms of attack: Type I or High temperature hot corrosion (HTHC) above about 900°C where pure sodium sulfate is above its melting temperature, and Type II or Low temperature hot corrosion (LTHC), between about 700°C-750°C where a liquid salt phase is only formed because of significant dissolution of some corrosion products [36]. Various parameters may affect the development of these two forms, including alloy composition and thermo-mechanical condition, contaminant composition and flux rate, temperature and temperature cycles, gas composition and velocity, and erosion processes.

3.1.1 HIGH TEMPERATURE HOT CORROSION

This form of hot corrosion is observed mainly within the temperature range 850–950°C. HTHC starts with the condensation of fused alkali metal salts on the surface of the components. A cycle of subsequent chemical reactions takes place, initially attacking the protective oxide film and progressing to deplete the chromium element from the substrate materials. With chromium depletion, oxidation of the base material accelerates and porous scale begins to form. The macroscopic appearance of HTHC is characterized in many cases by severe peeling of metal and by significant colour changes. For instance, a greenish tone appears on the surface of metals and alloys due to the formation of NiO in the area of accelerated attack. Microscopically, the morphology of Type I is characterized by a sulphidation and depletion region beneath the porous, non-

protective scale. The reaction products frequently exhibit oxide precipitates dispersed in the salt film [37].

3.1.2 LOW TEMPERATURE HOT CORROSION

LTHC is observed mainly within the temperature range 650–800 C. In this form of hot corrosion, low melting point eutectic mixtures of Na_2SO_4 and CoSO_4 (the melting temperature of the Na_2SO_4 – CoSO_4 eutectic is 5400C) cause typical pitting in the localized areas. The localized nature of attack is related to localized failure of the scale as a result of thermal cycling, erosion or chemical reactions. As opposed to Type I hot corrosion, in Type II corrosion neither microscopic sulphidation nor chromium depletion is generally observed [38]

3.2 MECHANISM OF HOT CORROSION

Several mechanisms have been suggested to explain the process of hot corrosion [39]. The hot corrosion degradation process of the superalloys usually consists of two stages [40] 1. An initiation stage during which the alloys behave much as they would have behaved in the absence of the deposits and 2. A propagation stage where the deposits cause the protective properties of the oxide scales to become significantly different than those that they would have been had no deposit been present.

Khana et al. [41] , in their review of degradation of materials under hot corrosion conditions , stated that corrosion-resistant alloys depend on selective oxidation to form the dense, compact protective scales of Cr_2O_3 and Al_2O_3 for their resistance. During hot corrosion a degradation sequence consisting of the eventual displacement of a more protective reaction product barrier by a less protective product is usually followed. The hot corrosion degradation sequence is not clearly evident, and the time for which the protective scales are stable

beneath the salt layer is influenced by a number of factors, which affects the initiation of hot corrosion. The propagation stage of the hot corrosion sequence is the stage for which the superalloy must be removed from service since this stage always has much larger corrosion rates than for the same superalloy in the initiation stage [42].

3.3 INITIAL STAGE OF OXIDATION

The adsorption of gas the metal surface is the very fast stage of oxidation. This process involves a decrease in free energy and entropy which means enthalpy decreases and makes this process normally exothermic. There are two type of adsorption, chemical (chemisorptions) and physical. Chemisorptions involve the adsorbed species forming a chemical bond with surface atoms via the transfer of electrons. Physical adsorption involve physical or Vander Walls forces bonding the gases to the surface and is reversible. Chemisorptions tend to take place at much higher temperature and many involve activation energy [43]. Very rapid chemisorptions can be seen with gases and clean metals where there appears to be no activation energy. It continuous only until a monolayer of the adsorbent is created on the surface. After the adsorption where the surface has been converted by chemisorptions oxygen isolated oxide nuclei nucleated at random points for instants at impurity atoms surface imperfection etc. on the metalsurface. The growth of individual crystallite enable the oxidation of the surface continue until the oxide patched grown from individual nuclei connect and the entire surface is converted with oxide which acts as a diffusion barrier [44].

3.3.1 OXIDE TRANSPORT MECHANISMS

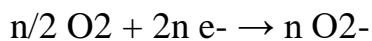
Oxidation Corrosion is brought about by the direct attack of oxygen at low or high temperature on metal surfaces in the absence of moisture. Alkali metals (Li, Na, K etc.,) and alkaline earth metals (Mg, Ca, Sn, etc.,) are rapidly oxidized at low temperature. At high temperature, almost all metals (except Ag, Au and Pt) are oxidized. The reactions of oxidation corrosion are as follows:

Mechanism:

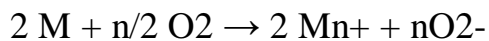
1) Oxidation takes place at the surface of the metal forming metal ions M^{2+}



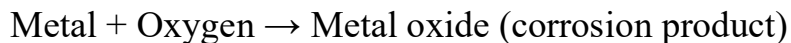
2) Oxygen is converted to oxide ion (O^{2-}) due to the transfer of electrons from metal.



3) The overall reaction is of oxide ion reacts with the metal ions to form metal oxide film.



The Nature of the Oxide formed plays an important part in oxidation corrosion process.



The formed oxide separates the metal from the gas and the only way for oxidation to proceed is via of solid-state diffusion can only take place due to the presence of defect of the reactants. This type of diffusion can only take place due to the presence of defects in the oxide structure. Point's defects such as interstitial atoms and misplaced atoms are required for solid-state diffusion in the oxide. Scales growth occurs by the diffusion of the cat ion and anions cat ion diffusion causes oxide formation at the oxide gas interface and anion diffusion leads to oxide growth the metal- oxide interface as show in figure. Oxide can

show non stoichiometric and either mainly contain defects or mainly contain oxygen defects.

3.3.2 OXIDATION OF ALLOYS

All of the principles that have been described previously have been for simple oxidation of pure metal but this theory can also be applied to alloys. However the oxidation of alloys can be a lot more complex due to metal in the alloys having differing affinities to oxygen because of the different free energies of formation of the oxide. The different metal will also have varying diffusivities in the alloys and their ions will have different mobility in the oxide phase. This makes the prediction of oxidation behaviour much more difficult for alloys. To have effective oxidation resistance the alloy needs to form a continuous scale via external oxidation. Ineffective protection can occur by precipitates forming inside the alloy during oxidation. This is called internal oxidation. To achieve effective oxidation resistance alloys aim to form compact scale with small rates of diffusion of the reactant ions. The oxidation of alloys generally produce more than one oxide. Selective oxidation occurs where the least noble alloying element in the alloy is oxidized first to form the outer protective layers. The alloying elements have oxide which demonstrates large difference in stability however the temperature, partial pressure of the oxygen and concentration of the active alloying element also affects selective oxidation [45]. Selective oxidation has led to alloys being designed to have certain alloying additions in them to increase their oxidation resistance in high temperature applications.

3.3.3 OXIDATION RESISTANCE

The ability to protect refined metals from reactive environments is vital to many industrial and academic applications. Current solutions, however, typically introduce several negative effects, including increased thickness and changes in the metal physical properties. In this paper, we demonstrate for the first time the ability of grapheme films grown by chemical vapour deposition to protect the surface of the metallic growth substrates from air oxidation. SEM, Raman spectroscopy, and XRD studies show that the metal surface is well protected from oxidation even after heating at 800°C in air and molten salt for 1 hr heating and 20 min. Cooling at room temperature. Our work further shows that grapheme provides effective resistance against hydrogen peroxide. This protection method offers significant advantages and can be used on any metal the catalyses grapheme growth use of refined metals is widespread, but they are often chemically reactive, requiring protective coatings for many applications. Protecting the surface of reactive metals has developed into a significant industry which employs many different approaches, including coating with Ni-20%Cr and Ti.

However, these conventional approaches can suffer from a variety of limitations, such as susceptibility to damage by heat, limited chemical stability, cost and formation of waste products. In addition, most conventional methods modify the physical properties of metals being protected. The addition of a protective coating changes the dimensions of the metal due to the finite thickness of the coating, changes the appearance and the optical properties of the metal surface, and often decreases the electrical and thermal conductivity. One important approach to overcome these problems would be to develop a novel protection coating with an exceptional chemical and thermal stability with minimum

changes to the physical properties of the protected metal. Grapheme as a two-dimensional one-atom-thick sheet of carbon has attracted increased interest for both fundamental reasons and due to its potential for a wide variety of applications. A world-wide effort is underway on developing new and improved methods of growing grapheme on metal substrates; our group included [46]. In particular, chemical vapour deposition (CVD) techniques have been successfully applied to grow high quality single and multilayer grapheme onto various metal substrates, including single-layer growth on Ni-20%Cr,Ti and multilayer growth. The growth temperature ranges from 800°C.

3.4. EROSION

Solid particle erosion (SPE) is the progressive loss of original material from a solid surface due to mechanical interaction between that surface and solid particles. Erosion is a serious problem in many engineering systems, including steam and jet turbines, pipelines and valves used in slurry transportation of matter, and fluidized bed combustion systems[46]. Solid particle erosion (SPE) is a serious problem for the electric power industry, costing an estimated US\$150million a year in lost efficiency, forced outages, and repair costs [47]. Erosive, high temperature wear of heat exchanger tubes and other structural materials in coal-fired boilers are recognized as being the main cause of downtime at power generating plants, which could account for 50-75% of their total arrest time. Maintenance costs for replacing broken tubes in the same installations are also very high, and can be estimated up to 54% of the total production cost. High temperature oxidation and erosion by the impact of fly ashes and unburned carbon particles are the main problems to be solved in these applications, especially in those regions where component surface temperature is

above 600°C. Therefore, the development of wear and high temperature oxidation protection systems in industrial boilers is a very important topic from both engineering and an economic perspective. Erosion-corrosion at high temperature is a field within high temperature corrosion that is growing in importance. Degradation of materials is a function of many parameters. These are normally classified in terms of properties of the particle (size, shape, velocity, impact angle, hardness), target (hardness, ductility, corrosion resistance) and the environment (temperature, partial pressure of the gaseous environments) [48]. A few different types of erosion-corrosion behavior are frequently observed. The model by Kang et al. [48], describes four regimes, which were assigned “erosion of oxide only”, “erosion enhanced oxidation”, “oxidation affected erosion”, and “erosion of metal only”. The order follows that of increasing erosion and decreasing oxidation rate.

3.5. FACTOR AFFECTING HOT CORROSION

Various important factor affected hot corrosion are

1. Alloy compositions.
2. Fabrication conditions.
3. Gas compositions.
4. Salt compositions
5. Salt depositions rate.
6. Conditions of salt.
7. Temperature.
8. Erosion.
9. Specimen geometry.

3.6. METHOD OF EVALUATION

Along laboratory test the discontinuous measurement of the high temperature corrosive attack of the material is widely used. The most common method are.

Crucible test - In this test specimens are totally or partly immersed in crucible a molten salt.

Salt coat test- In this test the specimens is coated with salt prior and exposed to high temperatures.

Burner rig test- This type of testing is done by exposing the specimens to a burner into which flame contaminants can be injected.

Electrochemical - In this type of testing the acts an electrode and molten salt acts as electrolyte.

Silicon tube furnace –Hot corrosion test is carried out silicon tube furnace. The hot zonentemperature is able to maintained to +50C of the desired test point temperature through the use of PID temperature controller.

3.7 CONTROLLING METHOD FOR HOT CORROSION

3.7.1 Alloy selection- The resistance of super alloys against hot corrosion is directly related to the chemical composition of the alloy and its thermo mechanical history. Unfortunately many alloying element have an adverse effect on mechanical properties of the super alloy at high temperature and on its resistance to hot corrosion. For example such as tungsten, vanadium and molybdenum are excellent in improving the mechanical properties but their presence make the alloy highly susceptible to hot corrosion.

3.7.2. Protecting coating - A major challenge in technological development is to meet requirements for new materials in progressively more severe conditions.

Usually one or more properties of materials are incompatible with the conditions prevailing in the operating environment. In the material environment configuration, the surface of a component is a vital parameter in determining its optimum performance. This is the basis for the development of the coating technology. It is not possible for a single material to have different properties to meet the demand of today's industry. Therefore, a composite system of a base material providing the necessary mechanical strength with a protective surface layer different in structure and/or chemical composition can be an optimum choice in combining material properties. In the past two decades, the need for protective coatings has dramatically increased on hot section parts of gas turbine engines and other heat engines used in non-flight applications. High-temperature corrosion problems become much more significant for these alloys with increasing operating temperatures of modern heat engines. This led to an increased attention given to the development of coatings, which offer significant compositional flexibility. The purpose of a coating is to serve as an effective solid state diffusion barrier between oxygen (or other gases) and the base alloy. The coating should have a composition that will react with the environment to produce the protective oxide scale, which should not react with the corrosive environment and at the same time should not allow the corrosive species to diffuse into the coating. Therefore, the identification/development of suitable alloys and coatings are of great interest for such applications.

3.7.3. Air filtering- a limiting level of 0.008 ppm (by weight) has been suggested for the content of Na in the air below which hot corrosion not exist. Therefore secondary protection against hot corrosion may be attained by installation of high efficiency air filters.

3.8. EFFECT OF ALLOYING ADDITION

The various alloying addition and their role in steel is summarised below. All the alloying element are added to optimised the steel's properties so that they do not fail in services.

Nickel – Stabilized the austenitic structure during the arsenisation treatment.

Manganese- Stabilized the austenitic structure during the arsenisation treatment.

Nitrogen – Increased the tensile strength through solid solution strengthening.

Niobium – stabilized carbon and improves the creep strength by forming NbC carbides.

Carbon –Increased the tensile strength through solid solution strengthening.

Copper – Improves the creep strength by the precipitation of a copper rich phase. Also has austenitic stabilizing effects.

Chromium –Improves the oxidation/corrosion resistance. Resistance increased with increased content.

Silicon – Improves the oxidation/corrosion resistance.

Phosphorus – Improving in increasing hardenability and strength.

CHAPTER 4

4. COATING

A major challenge in technological development is to meet requirements for new materials in progressively more severe conditions. Usually one or more properties of materials are incompatible with the conditions prevailing in the operating environment. In the material environment configuration, the surface of a component is a vital parameter in determining its optimum performance. This is the basis for the development of the coating technology. It is not possible for a single material to have different properties to meet the demand of today's industry. Therefore, a composite system of a base material providing the necessary mechanical strength with a protective surface layer different in structure and/or chemical composition can be an optimum choice in combining material properties. In the past two decades, the need for protective coatings has dramatically increased on hot section parts of gas turbine engines and other heat engines used in non-flight applications. High-temperature corrosion problems become much more significant for these alloys with increasing operating temperatures of modern heat engines. This led to an increased attention given to the development of coatings, which offer significant compositional flexibility [49]. The purpose of a coating is to serve as an effective solid state diffusion barrier between oxygen (or other gases) and the base alloy. The coating should have a composition that will react with the environment to produce the protective oxide scale, which should not react with the corrosive environment and at the same time should not allow the corrosive species to diffuse into the coating. Therefore, the identification/development of suitable alloys and coatings are of

great interest for such applications. The compositions and structures of the coatings are determined by the role that they have to play in the various material systems and performance environments. Recourse is made to materials composed of metal alloys and metal–ceramic mixtures, forming specially developed composite systems and aiming at predetermined mechanical and physical– chemical properties [50]. The materials used as coatings must ensure an effective protection against oxidation as well as have a high thermal conductivity (heat–exchangers) in order to provide a good service behavior and an effective and economical maintenance layout. The primary aim of the coating/surface treatment is the ability to produce a stable, slow–growing surface oxide providing a barrier between the coated alloy and the environment. The important feature of a protective hard coating is its high hardness and chemical inertness. Conventional methods such as carburizing, nitrating, electroplating are being used over a century to protect tools; however, the development of the hard protective coatings in the narrower sense, started in the sixties with the discovery of chemical vapour deposition (CVD) and physical vapour deposition (PVD) techniques. In recent times, modern deposition techniques such as thermal spray and laser cladding have become more popular and can give large throughput in shortest possible time. Currently, diffusion and overlay coatings are used to provide corrosion and oxidation resistance to extend the component life [51]. However, as the operating temperatures of the heat engines have increased, it has become impossible to achieve the required service lives using diffusion coatings, whereas overlay coatings have performed better in aggressive environments at elevated temperatures with respect to environmental and material factors affecting corrosion processes, the corrosion behaviour of the coatings depends on the following elements:

1. Corrosive media.
2. Substrate and their surface state.
3. Environmental temperature.
4. Composition, structure, porosity.

Thickness adhesive strength and other properties of coatings. It is standardized that coating thickness is approximately 300–500 μm in the case of a cermet coating, while metallic alloys such as stainless steel could be deposited getting a final thickness of 2 mm. Good adherence of a coating to its substrate is one of the most important aspects of a successful coating. It has been speculated that an excellent coating is obtained when bonds between the film and the substrate is produced before a strong bond within the film is formed. Strong bonding between the coating and the substrate has a unique significance when the coated metals are used in aggressive corrosive environment. The corrosion resistance is also associated to the surface roughness, in a way that higher the surface roughness, higher will be the corrosion attack due to higher surface area. Protective coatings may be used on structural alloys, such as ferrite and austenitic steels, in such systems to decrease surface degradation by erosion–oxidation. The ability of the coating to protect the base metal against the oxidizing environment and the mechanical attack by eroding particles is primarily a function of morphology, i.e., high density and low porosity, small grain size, good adhesion and absence of cracks. The morphology of the coating, in turn, is dependent, for example, on the method of application. Thermal sprayed coatings are economical; can be produced by means of relatively simple techniques, and offer excellent corrosion and wear protection. It is a versatile technology that has been successful as a reliable cost–effective solution for many

industrial problems [52]. It is further reported to be the most flexible with respect to the sprayed materials. In fact, coatings are playing a significant role in today's military and gas-turbine engines to extend the life or enhance the performance of components. Enormous challenge exists to develop and to apply the coating technologies to other high-temperature applications.

4.1 CLASSIFICATION OF COATING METHOD

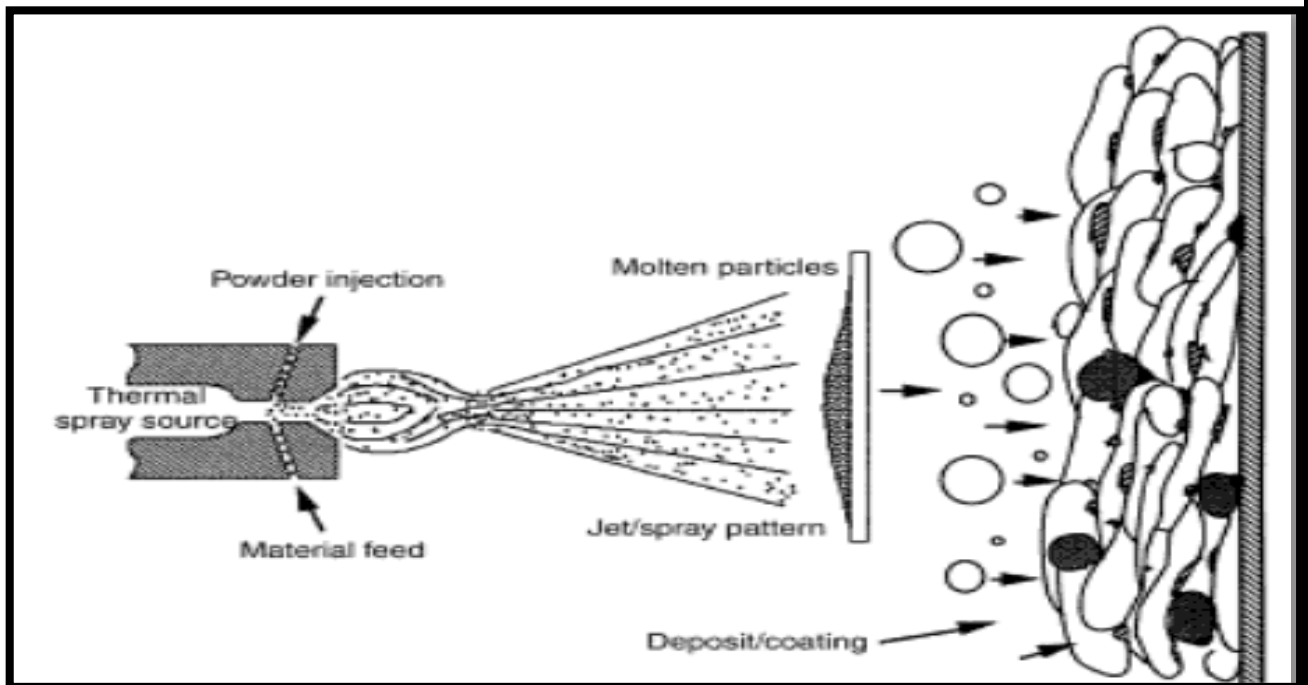
Thermal spraying is a process of depositing a superior material layer over a base metal or substrate either to improve the surface characteristics like corrosion resistance, wear resistance, surface fatigue or to get the desired dimension, size, surface appearance etc. Thermal spray coating processes are not only capable of applying coatings with excellent wear resistant properties, but also the range of materials capable of being sprayed so wide that applications for thermally sprayed wear resistant coatings are unlimited [53]. The thermal spray processes that have been used to deposit the coatings for the protection against the high-temperature corrosion are enlisted summarized below:

- Flame spraying with a powder or wire.
- Electric arc wire spraying.
- Plasma spraying.
- Spray and fused High Velocity Oxy-fuel (HVOF) spraying.
- Detonation Gun spraying.

4.1.1 THERMAL SPRAYING

Thermal spraying is one of the most versatile hard facing techniques available for the application of coating materials used to guard components from abrasive wear, adhesive wear, erosive wear or surface fatigue and corrosion (such as that

caused by oxidation or seawater) . Generally, any material which does not decompose, vaporize, sublime, or separate on heating, can be thermally sprayed. Consequently a large class of metallic and nonmetallic materials (metals, alloys, ceramics, cermets, and polymers) can be deposited by thermal spraying. The technique of thermal spraying has developed at a fast pace due to progress in the advancement of materials and modern coating tool. Plasma-sprayed ceramic coatings are used to protect metallic structural components from corrosion, wear and erosion, and to provide lubrication and thermal insulation [54].



(Fig.1 Typical thermal spray process and coating)

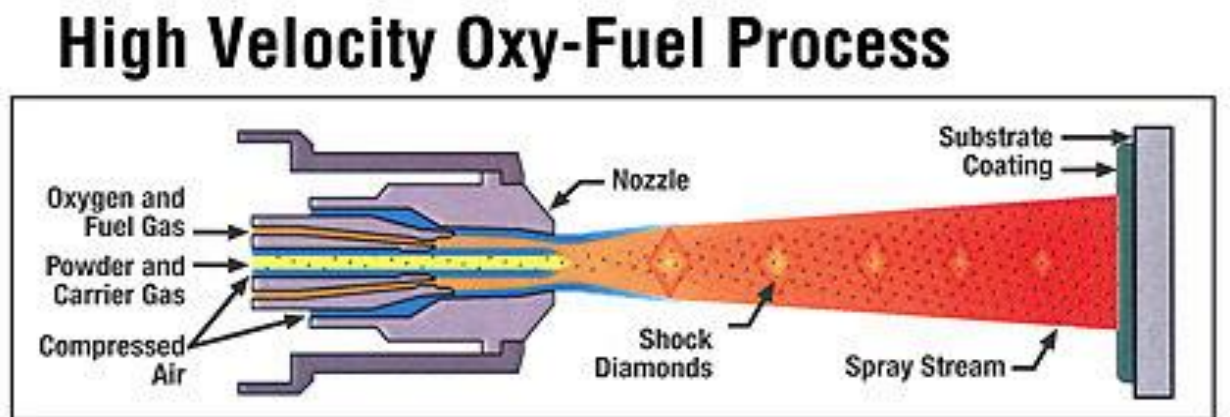
In particular, coatings made of Ni-20%Cr containing 12 wt% Ti (Ni-20%Cr-12 wt% Ti) are commonly used to improve the wear corrosion and erosion resistance of steel. In conservative plasma-spray processing of Ni20%Cr-12 wt% Ti coatings, powder particles are injected into a plasma jet, cause them to melt

into droplets that are propelled towards the substrate. Solidification of the droplets stream onto the substrate as “splats” results into the buildup of the coating, normally 100-300 μ m thick. In order to obtain chemical homogeneity in the coating, the processing is performed at “hot” plasma conditions which ensure complete melting of the powder particles. Plasma sprayed zirconium coatings as thermal barrier coatings have been applied to hot section components of gas engines to increase temperature capability Ni-base super alloys [55]. Conventional methods such as carburizing, nitriding, electroplating are being used over a century to protect tools, however, the development of the hard protective coatings in the narrower sense, started in the sixties with the discovery of chemical vapor deposition and physical vapor deposition techniques. In recent times, modern deposition techniques such as thermal spray and laser cladding have become more popular and can give large throughput in shortest possible time. Thermal spraying as a convenient way has been reported by several researchers. Thermal spraying offers an effective and economic way to make the coating without affecting any other properties of the component. Thermal spray coatings are produced by rapidly heating the feedstock material in a hot gaseous medium and simultaneously projecting it at a high velocity onto a prepared surface where it builds up to produce the desired coating [56]. Fig.1 shows the typical thermal spray process and coating.

4.1.2 HIGH VELOCITY OXY-FUEL (HVOF) SPRAYING

The high velocity oxy/air–fuel (HVOF/ HVAF) process is one of the most popular thermal spraying technologies and has been widely adopted by many industries due to its flexibility, cost effectiveness and superior quality of the coatings produced With the advent of this process, thermal sprayed coatings,

which previously had limited usefulness as corrosion protection coatings due to the presence of interconnected porosity in the structure, have now gained popularity and are being studied extensively for corrosion resistant properties. HVOF flame spraying has been an industrially established process since the mid 1980 s and has been widely adopted in many industries such as aerospace, automotive and other industries. HVOF spraying is a rapidly developing technology in combating high-temperature corrosion and is now challenging the vacuum plasma spraying technique (VPS), which is very expensive high hardness, high abrasive resistance, good wear resistance with a strong ability to provide high-temperature corrosion resistance.(capital costs approximately 2 million US\$). HVOF coatings have very low porosity.



(Fig.2 Schematic typical across section of high velocity oxy- fuel spray coating)

High-velocity oxygen-fuel (HVOF) is another form of thermal spray. This coating system mixes a fuel source (e.g., kerosene, hydrogen, methane) and oxygen gas in a combustion chamber and ignites the mixture. The material to be

coated is inserted into the flame and accelerated towards the substrate. Compared to plasma spray processes, HVOF has a lower process temperature, which is fuel dependant, but a significantly higher in particle velocity (\gg Mach 1). Figure 2 shows gun used in HVOF spraying. This increased particle velocity allows for higher density coatings as well as residual compressive stresses in the coating [57]. Powder generation for thermal spray applications can be performed by a variety of methods, including high pressure gas atomization (HPGA), cast and crush methods, water granulation, and centrifugal disintegration. For Ni-based alloys, powder yields via HPGA are typically low, approaching 30 to 40% for size fractions used in thermal spray; moreover the deposition efficiency in thermal spray is rarely above 65%. These compounding yields lead to prohibitive cost issues with certain alloying elements, such as Pt, that must be circumvented.

4.1.2.1 The characteristic advantages of HVOF–sprayed coatings are:

- 1) High density;
- 2) Strong adhesion to substrates;
- 3) High cohesive strength;
- 4) Strongly limited reactions and phase transformations; and
- 5) High compressive residual stresses are possible which are beneficial concerning the life–time of coated components under dynamical load.

4.1.2.2 MECHANISM OF HVOF COATING

HVOF process is based on a combination of thermal and kinetic energy transfer, i.e., the melting and acceleration of powder particles, to deposit the desired coating. A schematic of HVOF–spray process has been shown in Fig.[2]. The HVOF system consists of a spray gun, powder feed unit, flow meter unit, and an

air and gas supply unit. The powder feed unit comprises a hopper assembly, air vibrator, feed rate meter and control cabinet. The desired powder is fed from the powder feed unit by means of a carrier gas to the gun, where combustion occurs. The amount of powder required for deposition may be regulated using the powder feed-rate meter. In the combustion zone, powder particles, typically in the size range 10–63 μm , are injected into a high temperature; high speed gas jet within a specially designed gun. The jet is produced through the combustion of a fuel with oxygen at high pressures and flow rates within the gun. The powder particles typically attain velocities of 300–800 ms^{-1} at the substrate to be coated whilst reaching temperatures which allow these particles to be molten or semi molten prior to impact. By scanning the gun across the substrate, a coating layer of low porosity is built up from the impact, bonding and solidification of successive particles. In HVOF spraying, a fuel such as hydrogen, oxygen, ethylene or kerosene is burned with oxygen into a combustion chamber of a gun, in which the coating material in powder form is fed [58]. Supersonic gases expel as a spray the heated powders, which in contact with the component substrate, produces coatings with low porosity and high adherence. The hypersonic velocity of the flame shortens the time of interaction between the powder and flame, while the low temperature (3000 K) of flame limits the grain growth and decomposition of coating. Due to the high impact velocity of particles the coating shows a high adhesive strength, high cohesive strength of individual splats, high density and low porosity. The HVOF coatings have lenticular or lamellar grain structure, resulting from rapid solidification of small globules, which flatten upon striking a colder surface at high velocities as demonstrated.

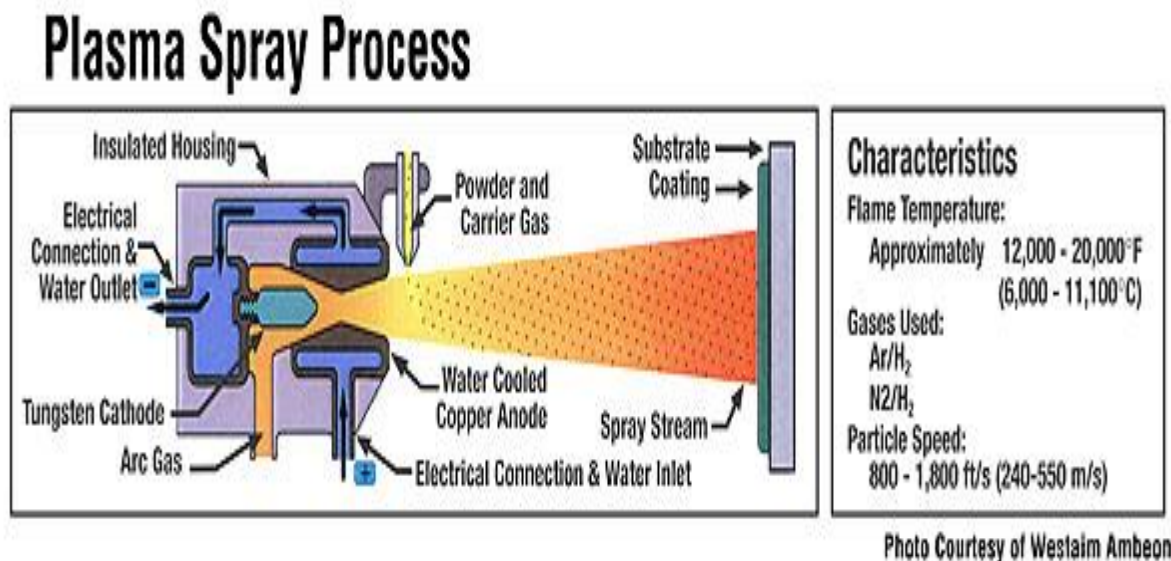
4.1.2.3 PROPERTIES OF HVOF COATINGS

HVOF spraying is able to make coatings with following features:-

- High hardness
- Lower capital cost and ease of use compared to other processes
- Low oxidation during spraying
- Enables metals and alloys with high melting point up to about 2000°C to be deposited.
- High density
- Good surface finish
- Less effect of the environment during the spray process
- High abrasive resistance
- Good wear resistance
- Excellent corrosion protection
- Homogeneous
- Strong adhesion to substrates
- High cohesive strength
- Limited reactions and phase transformations
- Lower flame temperature compared with plasma spraying
- High compressive residual stress possible
- More uniform and efficient particle heating due to high turbulence
- Reduced mixing with ambient air once jet and particle leave the gun
- Thicker coatings than with plasma and arc spraying can be produced
- Lower ultimate particle temperatures compared to other processes
- Process can be automated

4.1.3. PLASMA SPRAYING

is the gun is Thermal spray is a versatile tool in the coating industry due to the variety of materials that can be applied (metals, ceramics, polymers) with little to no compositional change, as well as a significantly high application rate. Atmosphere Plasma Spray (APS) and Low Pressure Plasma Spray (LPPS) are very similar in operation. Both APS and LPPS use a high amperage source to generate gas plasma (e.g., argon, helium, nitrogen) between a water-cooled Cu anode and a Thoriated-W cathode. Powder is then fed into the plasma and accelerated towards the substrate as illustrated in Figure 18. The major difference between APS and LPPS is that LPPS is placed inside a chamber where the atmosphere can be controlled in both pressure and composition [59].



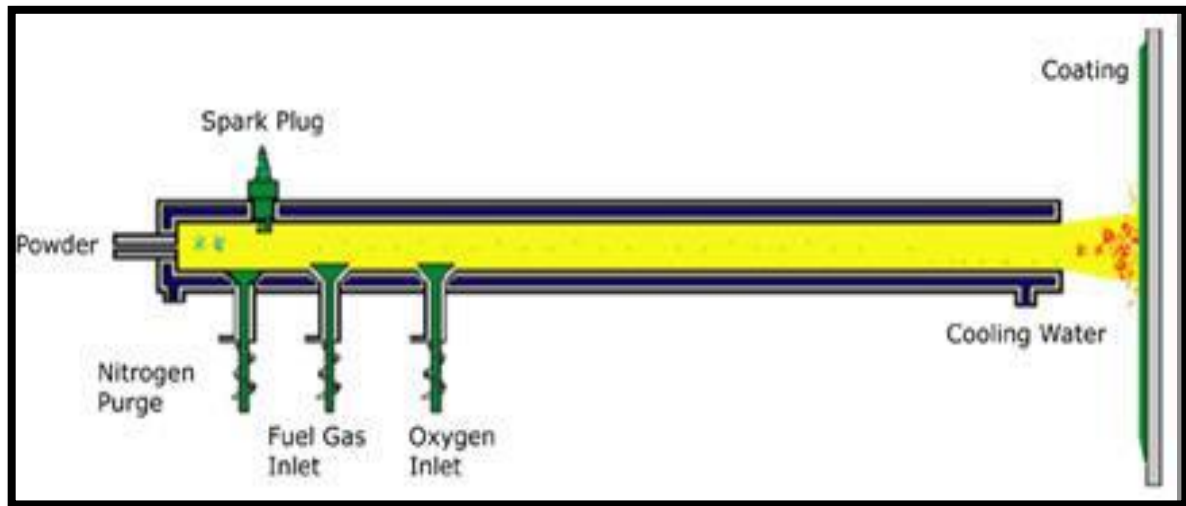
(Fig.3 APS torch diagram)

The plasma spray process is shown on the Figure [3]. When the plasma jet is formed, a powder through nozzles carried by the "carrier" gas is injected into it. Accelerated and melted powder particles leave the plasma jet in the form of molten particle stream. The molten particles bombard the substrate surface where

they cool forming a coating. Also particles may be cooled and collected in the form of spheres. Every molten particle has a high thrust which leads to high bond strength of the coat. The temperature of the substrate remains below 100°C. Thickness of the coat varies between 0.3 and 1 mm, but it may be also up to 5 mm. The basic function of the plasma jet is to heat the powder particles to the melting point and to accelerate them to the highest possible speed.

4.1.4. DETONATION GUN SPRAYING

D-gun spray process is a thermal spray coating process, which gives an extremely good adhesive strength, low porosity and coating surface with compressive residual stresses. A precisely measured quantity of the combustion mixture consisting of oxygen and acetylene is fed through a tubular barrel closed at one end. In order to prevent the possible back firing a blanket of nitrogen gas is allowed to cover the gas inlets. Simultaneously, a predetermined quantity of the coating powder is fed into the combustion chamber. The gas mixture inside the chamber is ignited by a simple spark plug. The combustion of the gas mixture generates high pressure shock waves (detonation wave), which then propagate through the gas stream. Depending upon the ratio of the combustion gases, the temperature of the hot gas stream can go up to 4000 deg C and the velocity of the shock wave can reach 3500m/sec. The hot gases generated in the detonation chamber travel down the barrel at a high velocity and in the process heat the particles to a plasticizing stage (only skin melting of particle) and also accelerate the particles to a velocity of 1200m/sec. These particles then come out of the barrel and impact the component held by the manipulator to form a coating [60].



(Fig.4 Schematic typical across section of detonation gun spray coating)

The high kinetic energy of the hot powder particles on impact with the substrate result in a build up of a very dense and strong coating. The coating thickness developed on the work piece per shot depends on the ratio of combustion gases, powder particle size, carrier gas flow rate, frequency and distance between the barrel end and the substrate. Depending on the required coating thickness and the type of coating material the detonation spraying cycle can be repeated at the rate of 1-10 shots per second. The chamber is finally flushed with nitrogen again to remove all the remaining “hot” powder particles from the chamber as these can otherwise detonate the explosive mixture in an irregular fashion and render the whole process uncontrollable. With this, one detonation cycle is completed above procedure is repeated at a particular frequency until the required thickness of coating is deposited. The chamber is finally flushed with nitrogen again to remove all the remaining “hot” powder particles from the chamber as these can otherwise detonate the explosive mixture in an irregular fashion and render the whole process uncontrollable. With this, one detonation cycle is completed

above procedure is repeated at a particular frequency until the required thickness of coating is deposited [61].

4.1.4.1. STUDIES RELATED TO DETONATION GUN SPRAYED COATINGS

Sova *et al.* [62] studied the development of multi material coatings by cold spray and gas detonation spraying. The basic objective was the development of multifunctional multi material protective coatings using cold spraying (CS) and computer controlled detonation spraying (CCDS). As far as CS was concerned, the separate injection of each powder into different zones of the carrier gas stream was applied. Cu–Al, Cu–SiC, Al–Al₂O₃, Cu–Al₂O₃, Al–SiC, Al–Ti and Ti–SiC coatings were successfully sprayed. As to CCDS, powders were sprayed with a recently developed apparatus that was characterized by a high-precision gas supply system and a fine dosed twin powder feeding system. Computer control provided a flexible programmed readjustment of the detonation gases energy impact on powder thus allowing selecting the optimal for each component spraying parameters to form composite and multilayered coatings. Several powders were sprayed to obtain composite coatings, specifically, among others, WC Co–Cr+Al₂O₃, Cu+ Al₂O₃ and Al₂O₃+ZrO₂.

Sundararajan *et al.* [63] evaluated the tribological performance of 200 µm thick TiMo(CN)–28Co and TiMo(CN)–36NiCo coatings obtained by using the detonation spray coating system. Towards the above purpose, the detonation spray coating conditions were optimized to obtain the best coating properties (low porosity, high wear resistance) by varying two of the important coating process variables, i.e., oxygen to fuel ratio and gas volume. In both the coatings it was observed that the best tribological performance and also the lowest

porosity were obtained. However, the coatings with the highest hardness did not exhibit the best tribological performance. A comparison of the tribological performance of the optimized TiMo(CN) type coatings with that of optimized WC–Co coatings revealed that the abrasion resistance of TiMo(CN) type coatings is comparable to that of WC–Co coatings. However, the erosion and sliding wear resistance of TiMo(CN) type coatings were considerably lower than that of WC–Co coatings. Microstructure characterization of D-gun sprayed Fe–Al intermetallic coatings was done by Senderowski *et al.* [64]. Intermetallic Fe–Al type coatings about 100 μm thick were deposited on a plain carbon steel substrate by D-gun spraying technique. The 40–75 μm size fraction of the feedstock powder was obtained by self-propagating high-temperature synthesis and sieved prior to D-gun spraying. This powder contained a mixture of Fe–Al type intermetallic phases conventionally appointed Fe_xAl_y . The Fe–Al coatings were analysed by transmission electron microscopy, selected area electron diffraction, and semi-quantitative energy-dispersive X-ray analysis in micro-areas. Particular attention was paid to the substructure of the individual grains in the coating zone abutting the steel substrate. The Fe–Al coatings have a multi-layer composite structure. The results explain the formation mechanism of the coating microstructure. The powder particles, which were heterogeneous in chemical composition and structure, were heated, highly softened or even partially melted and oxidised while flying from the gun barrel to the substrate. After impacting the substrate or previously deposited material and being shot peened by the following powder particles, they were rapidly cooled and plastically deformed, creating overlapping splats. In the zone adjacent to the substrate, alternating FeAl and Fe_2Al_5 intermetallic phases formed columnar crystals. The columnar crystal areas were separated by elongated amorphous

oxide layers. Areas of mixed equiaxed subgrains of FeAl and Fe₃Al phases, fine grains of Fe-rich Fe(Al) solid solution, and micro- and nano-pores were also present. Formation and corrosion behavior of Fe-based amorphous metallic coatings prepared by detonation gun spraying was studied by ZHOU *et al.* [65]. Amorphous metallic coatings with a composition of Fe₄₈Cr₁₅Mo₁₄C₁₅B₆Y₂ were prepared by detonation gun spraying process. Microstructural studies show that the coatings present a densely layered structure typical of thermally sprayed deposits with the porosity below 2%. Both crystallization and oxidation occurred obviously during spraying process, so that the amorphous fraction of the coatings decreased to 54% compared with fully amorphous alloy ribbons of the same component. Corrosion behavior of the amorphous coatings was investigated by electrochemical measurement. The results show that the coatings exhibit extremely wide passive region and low passive current density in 3.5% NaCl (mass fraction) and 1 mol/L HCl solutions, which illustrates excellent ability to resist localized corrosion. Kamal *et al.* [66] evaluated the cyclic hot corrosion behaviour of detonation gun sprayed Cr 25%NiCr coatings on nickel- and iron-based superalloys. Cr₃C₂-NiCr cermet coatings were deposited on two Ni-based superalloys, namely superalloy 75, superalloy 718 and one Fe-based superalloy superalloy 800H by detonation-gun thermal spray process. The cyclic hot-corrosion studies were conducted on uncoated as well as D-gun coated superalloys in the presence of mixture of 75 wt.% Na₂SO₄+25wt.% K₂SO₄ film at 900 °C for 100 cycles. Thermogravimetric technique was used to establish the kinetics of hot corrosion of uncoated and coated superalloys. X-ray diffraction, FE-SEM/EDAX and X-ray mapping techniques were used to analyze the corrosion products for rendering an insight into the corrosion mechanisms. It was observed that Cr₃C₂-NiCr coated superalloys showed better hotcorrosion

resistance than the uncoated superalloys in the presence of 75 wt.% NaSO₄+25wt.%K₂SO₄ film as a result of the formation of continuous and protective oxides of chromium, nickel and their spinel, as evident from the XRD analysis. Murthy *et al.* [67] analyzed the abrasive wear behaviour of WC–CoCr and Cr₃C₂–20(NiCr) deposited by HVOF and detonation spray processes. The abrasion tests were done using a threebody solid particle rubber wheel test rig using silica grits as the abrasive medium. Authors found that the DS coating performs slightly better than the HVOF coating possibly due to the higher residual compressive stresses induced by the former process and WC-based coating has higher wear resistance in comparison to Cr₃C₂ -based coating. Also, the thermally sprayed carbide-based coatings have excellent wear resistance with respect to the hard chrome coatings. Zhang *et al.* [68] investigated 10500C isothermal oxidation behavior of detonation gun sprayed NiCrAlY coating. NiCrAlY coating was deposited on a single crystal Ni-base superalloy by detonation gun spraying. By means of XRD, SEM and EDS, isothermal oxidation behavior of the coatings at 1050 °C were studied. The results showed that detonation gun sprayed NiCrAlY coatings held a favorable oxidation resistance. Their oxidation kinetics at 1050 °C obeyed the parabolic law. α -Ni-Cr scale was formed on the coating surface and kept almost intact afteroxidation for 300 h. Internal oxidation led to the formation of Ni-Cr at the coating/substrate interface, and needlelike (Al, N) compounds appeared in the undersurface area of the substrate. A research on detonation gun coating with Fe-SiC composite powders mechanically activated was done by Jia *et al.* [69]. The Fe–SiC composite powder prepared by the mechanical activation process has been used for coating on materials with the detonation gun (D-gun) machine in order to develop a new way for coating. Authors found that the coating layer has fine,

homogeneous dense structure and good wear resistance. The results of SEM and X-ray diffraction (XRD) show that some reactions happened between Fe and SiC during the D-gun coating, the Fe–Si compounds formed and SiC strength the coating layer. It was proved that the technology combined mechanical alloying with D-gun coating is a new method for surface modification. Ahmed and Hadfield [70] investigated the rolling contact fatigue performance of detonation gun coated elements. A modified four ball machine which simulates a rolling element bearing was used to examine the coating performance and failure modes in a conventional steel ball bearing and hybrid ceramic bearing configurations. Tungsten carbide (WC-15% Co) and Nickel chromium (Ni-Cr) were thermally sprayed using a super D-Gun (SDG2040) on M-50 bearing steel substrate in the geometrical shape of a cone. A coated cone replaced the upper ball that contacts with three lower balls. The rolling contact fatigue (RCF) tests were performed under immersed lubricated conditions using two different lubricants. Fatigue failure modes were observed using a scanning electron microscope. Microhardness measurements of the coating and the substrate and elastohydrodynamic fluid film thickness results are included. Authors found the requirement for significant optimization of the coating before use in rolling element bearing applications. The coating was fractured in a delamination mode. Authors found that an optimization in coating process is required before these coatings can be used for rolling contact applications. WC-Co coatings performed better than Ni-Cr coatings in rolling contact.

4.1.5. PHYSICAL VAPOR DEPOSITION (PVD) PROCESS

In physical vapor deposition (PVD) process, the coating is deposited in vacuum by condensation from a flux of neutral or ionized atoms of metals. Several PVD

techniques are available for deposition of hard coatings. Among them, cathodic arc vapor (plasma or arc ion plating) deposition, magnetron sputtering (or sputter ion plating), and combined magnetron and arc processes are most widely used techniques to deposit titanium-aluminum based coatings. PVD process is carried out in high vacuum at temperature between 150 and 500°C. The high purity solid coating material (metals such as titanium, chromium & aluminum) is either evaporated by heat or by bombardment with ions (sputtering) [71]. At the same time, a reactive gas (e.g. nitrogen or a gas containing carbon) is introduced; it forms a compound with the metal vapors and is deposited on the tools or components as a thin, highly adherent coating. In order to obtain a uniform coating thickness, the parts are rotated at uniform speed about several axes. The PVD techniques are widely used nowadays for improvement of the mechanical and other properties, of a broad range of engineering materials. Employing the PVD techniques for the deposition of coatings (namely multilayer coatings) ensures high corrosion and wear resistance. Besides, the ceramic nitrides, carbides present interesting colours which allow them to be used in decorative components (e.g., golden or a polished brass-like) [72].

In. S. Choi et.al. [73] have studied the corrosion behavior of TiAlN coatings prepared by PVD in a hydrofluoric gas atmosphere. TiAlN coating has one of the highest working temperature (800oC) due to the surface being covered with a stable and passive aluminum oxide layer. When TiAlN is exposed to a HF gas atmosphere in working conditions, it reacts with HF and forms aluminum fluoride (AlF₃), which is chemically very stable to various corrosives such as acid, alkaline, alcohol and even HF. The process was quite successful and the coating exhibit better corrosion resistance. Sugehis Liscano et al. [74] have studied corrosion performance of duplex treatments based on plasma nitriding

and PAPVD (Plasma Assisted physical vapour deposition) TiAlN coatings. The plasma nitrided substrates were coated commercially with BALINIT FUTURA NANO (TiAlN) coatings (Balzers, Inc., USA). The nanograined TiAlN coating has shown better results than the conventional counterpart. R. Rodríguez-Baracaldo et. al. [75] have studied the high temperature wear resistance of (TiAl)N PVD coating on untreated and gas nitrided AISI H13 steel with different heat treatments. The coated specimens have shown better wear resistance as compared to the uncoated specimens. W. Kalss et al. [76] have studied some Ti and Al based coating and reported that the TiAl-based nitrides such as TiAlN and AlTiN were stable against oxidation up to temperatures about 800°C. The coating with best oxidation resistance was AlCrN. Even at 1100°C only a thin layer of about 150nm in thickness could be observed. These coatings exhibit good thermal conductivity and better wear resistance. All coatings were deposited by a standard Balzers RCS cathodic arc coating machine.

4.1.6. CHEMICAL VAPOR DEPOSITION (CVD) PROCESS

Chemical Vapor Deposition (CVD) process is a versatile process that can be used to deposit nearly any metal as well as non metal such as carbon or silicon [77]. The first step is the production of metal vapours. Several chemical reactions can be used: thermal decomposition, pyrolysis, reduction, oxidation, nitridation etc. The main reaction is carried out in a separate reactor. The vapors thus formed are transferred to the coating chamber where the sample is mounted and maintained at high temperature. One of the limitations of the CVD is the high substrate temperature, which in many cases changes the microstructure of the substrate, and another is the size of specimens, often smaller parts are used due to limitation of chamber size. S. Tsipas et. al. [78] have studied Al–Mn

CVD-FBR protective coatings for hot corrosion application. In this study, new Al–Mn protective coatings were deposited by CVD-FBR on two ferritic steels (P-92 and HCM12). The CVD-FBR has been shown to be a powerful and effective technique to obtain Mn-containing aluminide coatings on ferritic steels. These coatings could be potential candidates for steam oxidation protection of ferritic steels. F.J. P´ereza et. al. [79] have studied adhesion properties of aluminide coatings deposited via CVD in fluidised bed reactors_CVD-FBR/on AISI 304 stainless steel. The CVD-FBR technique has been shown to be a very interesting surface modification technology because aluminum diffusion coatings can be produced at lower temperatures and shorter times than by conventional pack cementation. Overall, the heat-treated aluminum coated AISI 304 specimens may find an application due to the combination of their toughness and the potential good corrosion properties.

4.1.7. NANOSTRUCTURED COATINGS

Nanostructured coatings composed of crystalline/amorphous nanophase mixture have recently attracted increasing interests in fundamental research and industrial applications, because of the possibilities of synthesizing a surface protection layer with unique physicalchemical properties that are often not attained in the bulk materials. Nanostructured materials as a new class of engineering materials with enhanced properties and structural length scale between 1 and 100 nm. Nanostructured ceramic coatings produced by Plasma sprayed processes are being developed for a wide variety of applications that required resistance to wear, erosion, corrosion, cracking and spallation, with improved properties. Pavitra Bansal et al [80] compared conventional] and the nano Ni-20Cr – 12wt% Ti plasma sprayed ceramic coatings on steel substrate. These new

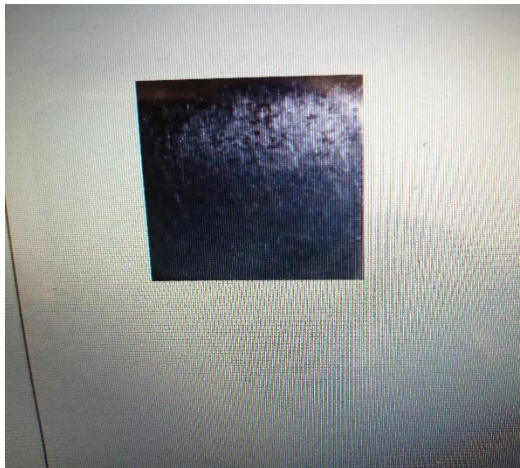
coatings (referred to as “nano”, since they are derived from nanocrystalline powders) have improved abrasive wear-resistance and have a bond strength , as measured using the ASTM “pull” test, two times greater than that of the conventional plasma sprayed coatings, making the “nano” coatings technologically attractive . Nano-materials are in their infancy of development but already show many processing and properties advantages over conventional coarse counterparts. Leon L.Shaw et al [81] studied the dependency of microstructure and properties of nanostructure and properties of nanostructured coatings on plasma spray conditions. Ni-20Cr – 12wt% Ti coatings formed via a plasma spray approach using reconstituted Nano sized Ni-Cr and Ti powder. Wear test suggest that the coating produced from Nano powder feedstock could have better wear resistance than the coatings produced using commercial coarse-grained powders. Chuanxian Ding et al. [82] have investigated the plasma sprayed nanostructured zirconia coatings for wear resistance. The plasma sprayed nanostructured zirconia coatings reported possess a higher wear resistance then their conventional counter parts. The higher wear resistance of the nanostructured coatings is attributed to their optimized microstructure and improved micro-hardness.

CHAPTER 5. MATERIAL OF EXPERIMENTAL METHOD

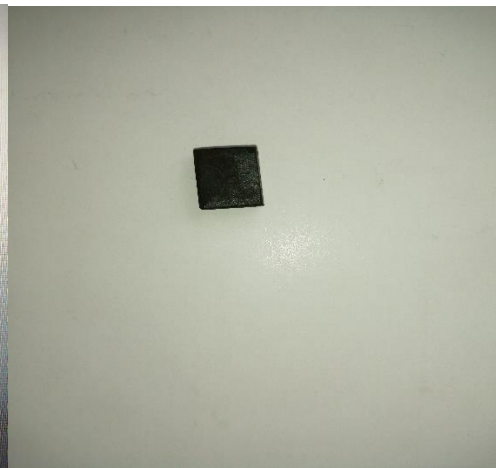
5.1. SUBSTRATE MATERIAL

The substrate material used in the current investigation is of SS-304 coated with Ni-Cr and Ti powder. The substrate is selected to study the oxidation behavior in the [gas_turbine](#) blades, seals, and combustors, as well as [turbocharger](#) rotors and seals, electric submersible well pump motor shafts, high temperature fasteners, chemical processing and [pressurevessels](#), [heatexchanger](#) tubing, steam generators and core components in nuclear [pressurized_water_reactors](#) etc. To reduce the oxidation losses surface coating was done by Detonation-gun thermal spray coating. The nominal composition of substrate material is C-0.08%, Cr-17.5-20%, Ni-8-11%, Mn-2%, Si- 1%, P-0.045, S-0.03%, Fe-balance.

Before oxidation & Hot corrosion:



(Fig.5 uncoated SS-304)



(Fig.6 Coated SS-304)

After Oxidation:

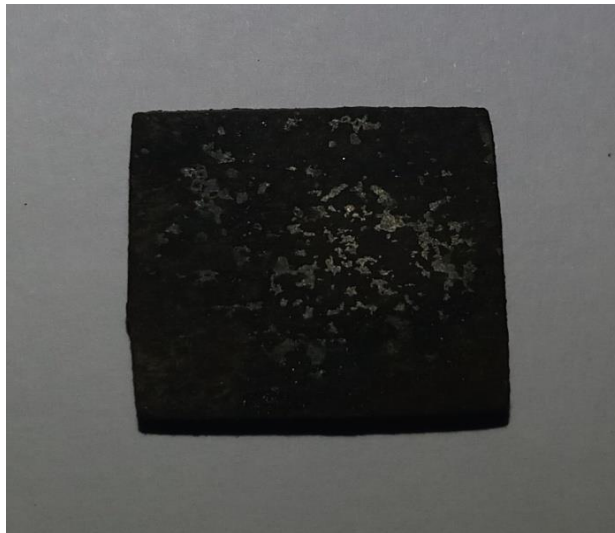


(Fig.7 uncoated ss-304)

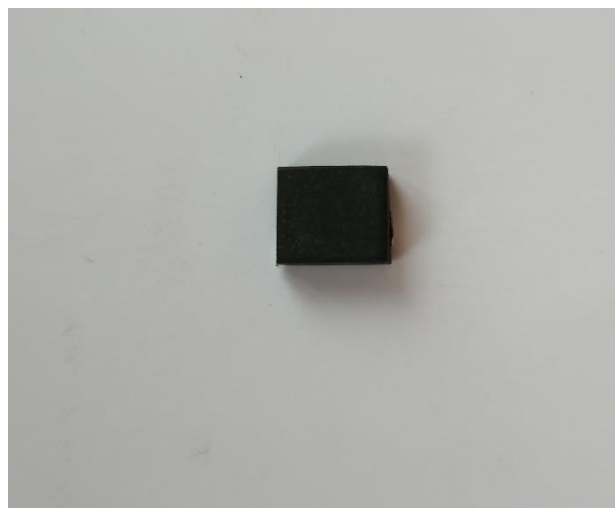


(Fig.8 coated SS-304)

After Hot Corrosion:



(Fig.9 uncoated ss-304)



(Fig.10 Coated SS-304)

5.2. SUBSTRATE PREPARATION

The specimens with dimensions of approximately (15×10×5)mm³. The specimens were polished using emery papers of 220, 400, 600 grit sizes and subsequently on 1/0, 2/0, 3/0 and 4/0 grades. Final polishing was carried out on a cloth polishing wheel machine with 1 μm alumina powder suspension. Subsequently the specimens were properly washed with water and cleaned with acetone and dried, then they were accurately weighed and measured to determine the total surface area exposed to the oxidative environment, before the application of the coatings by D-gun spray process. Commercially available Ni-Cr and Ti coating powder was deposited on the Inconel-600 by this process at SVX powder M surface engineering Pvt., Limited, Noida India.

Table 1. Nominal Chemical Composition (wt. %) of Stainless steel SS-304

Composition %	C	Cr	Ni	Mn	Si	P	S	Fe
SS-304	<0.08	17.5-20	8-11	< 2	<1	<0.045	<0.03	Balance

5.3. EXPERIMENT PROCEDURE

- ❖ The silicon wire tube furnace was used (fitted with a temperature indicator of Electromek Model-1551P, India) to an accuracy of ±5°C.

- ❖ The coated specimen and uncoated specimen were polished using polishing machining ($1\mu\text{m}$ accuracy).
- ❖ Dimension of the specimen were noted down using digital vernier caliper.
- ❖ The specimen were thoroughly cleaned, washed with acetone and dried in hot air to remove moisture.
- ❖ The specimen were then heated in an oven up to 250°C , which helps in uniform application of salt mixture.
- ❖ Salt mixture sample containing $50\%\text{Na}_2\text{SO}_4$ - $50\%\text{NaCl}$ dissolved in distilled water was coated on the warm polished specimen using a brush (thickness between 3.0 - 5.0 mg/cm^2).
- ❖ The Alumina boats and the salt coated specimen were dried in the oven at 150°C for 30 minutes duration-weighed precisely.
- ❖ These specimen kept in aluminum boat were preheated to maintain the weight constant for high temperature cyclic corrosion studies (preheated at constant temperature of 1200°C for 10hr duration).
- ❖ The boat containing the specimen was introduced into hot zone in furnace whose temperature was set at 800°C .
- ❖ Holding time inside the furnace was maintained for 1 hour duration and then afterwards the boat with the specimen was taken out and cooled to room temperature in still air.
- ❖ The boat with specimen was weighed precisely again using an Electronic balance (sensitivity of 10^{-3} gm, model CB-120, contech, Mumbai, India) was used to conduct the thermo gravimetric studies (this constitutes one cycle of corrosion study).
- ❖ Weight change method has been considered for the analysis.

- ❖ At the end of each cycle, Visual observations were made to study the color change, the luster, formation of oxide scale...etc.
- ❖ The above study (cyclic hot corrosion studies) was carried out for 50 cycles.

5.4. DEVELOPMENT OF COATING

The materials used as coatings must ensure an effective protection against oxidation as well as have a high thermal conductivity (heat-exchangers) in order to provide good service behavior and an effective and economical maintenance layout. Various thermal spray processes, such as Detonation-gun, Plasma and High velocity oxy-fuel (HVOF) spraying methods are mostly used to apply coating to impart a wear resistance against abrasion and erosion in corrosive environment at high temperature. The coatings properties are influenced not only by the properties of the powders used but also significantly by the spray process and spray parameters. Thermal spraying as a convenient way has been reported by several researchers. Thermal spraying offers an effective and economic way to make the coating without affecting any other properties of the component. Thermal spray coatings are produced by rapidly heating the feedstock material in a hot gaseous medium and simultaneously projecting it at a high velocity onto a prepared surface where it builds up to produce the desired coating. Thermal spraying has been widely considered to apply protective coatings on the Inconel to counteract the corrosion problems. In current studies, Ni-Cr and Ti coating has been sprayed on SS-304 at 800⁰C by Detonation Gun (D-Gun) sprayed technique. A commercially available Ni-Cr and Ti powders having particle size 30-50 μ m size (M/S H.C. Starc company, Germany) were deposited on substrate by D-gun process at SVX Powder M Surface Engineering Pvt. Ltd, New Delhi (India). Samples were grit-blasted before the D-gun spraying. All the process

parameters, including the spray distance (165mm) were kept constant throughout the coating process. The coating was deposited on all six surfaces of the specimen.

5.5. COATING PROCESS PARAMETER

Table.3.Parameter used in detonation gun spray coating

1. Parameter	Ni-20Cr and Ti
2. Pressure of working gases	MPa
2.1 Oxygen	0.2
2.2 Acetylene	0.14
2.3 Nitrogen	0.4
2.4 Air	0.4
3. Consumption of working gases per shot	M ³
3.1 Oxygen	27.15 ⁻⁵
3.2 Acetylene	23.10 ⁻⁵
3.3 Nitrogen	5.10 ⁻⁴
3.4 Air	5.10 ⁻⁴
4. Consumption of powder per shot	0.05-0.02 g/shot
5. Water consumption rate	15-25litter/minute
6. Firing rate	1-10 Hz
7. Diameter of acceleration portion of barrel or coating coverage	0.022m
8. Coating thickness per shot	5-25micro meter
9. Coating capacity at the rate of 7 micro/shot	0.75m ² /h

10. System control	Manual semi /auto
11. Over all dimensions	Meter
11.1 Gun	1.80 x 1.1
11.2 Control console	102x0.5x1.5
12. Power supply for main	
12.1 Frequency	50-60Hz
12.2 Voltage	430V
12.3Power	450VA
13. Sound pressure level	150Db
14. Relative humidity of ambient	50%

5.6. CHARACTERIZATION OF AS-SPRAYED COATINGS

The visual inspection of as-sprayed coatings was done. The Surface Roughness of the as sprayed coated samples was measured with the help of surface roughness tester (Surftest, SJ- 210,Mitutoyo) . In each coated specimen on four fields on the surface were used to obtain the value of surface roughness (μm). Metallurgical microscope (Letiz India pvt. Ltd.) was used to measure the porosity of the as-sprayed coatings. Three fields on the surface of each coated specimens were used to obtain the value of porosity. (SEM) scanning electron microscopy (From IIT, KANPUR) analysis was done to characterize the surface morphology of the coating.

5.7. OXIDATION AND MOLTEN SALT CORROSION TEST

Hot corrosion studies were conducted at 800°C in laboratory using Silicon wire tube furnace having PID temperature controller (make Digitech, India). The bare

samples were subjected to mirror polishing including cloth polish. Dimensions were accurately measured by digital vernier (make Mototoyo, Japan) to calculate area of sample. Finally specimens were cleaned i.e. degreased by ethanol and kept in alumina boat. Prior to experiment alumina boat was kept in oven for 5hr at 250°C in oven and then kept in furnace at 800°C for 2hr to expel all the moisture. After this samples of SS-304 were kept in alumina boat and then inserted in the tubular furnace for 1 hr at a temperature of 800°C and then they were removed and cooled further for 20 minutes to room temperature and their weights were measured. In case of hot corrosion in the given salt environment of 50%Na₂SO₄+50%NaCl for as sprayed samples each cycle consisted of 1 hr heating at 800°C followed by 20 min. cooling at room temperature. The salt coating of uniform thickness with 3–5mg/cm² of 50%Na₂So₄+50%NaCl was applied with camel hairbrush on the preheated samples (250°C). After the salt application the samples were kept in an oven for 2½ hr at 250°C and then cyclic oxidation test was carried out on samples. The samples were subjected to weight change measurements after visual observation at the end of each cycle. Weight was taken with help of Electronic Balance Model CB-120 (Contech, Mumbai, India) with a sensitivity of 0.001 gms. Burnt oxide layer which were spalled out in boat were also taken into consideration i.e. the weight was taken along with the boat. This cycle was repeated for 50 times i.e. 50 cycles were made for each sample. Corroded samples from air and salt environment were analyzed by SEM.



Figure. Tube furnace



Figure. Heavy duty transformers



Figure. Ceramic boat with specimen



Figure. Electronic weight balance machine

CHAPTER 6

6. EXPERIMENTAL RESULTS AND DISCUSSION

6.1. OXIDATION KINETICS

The weight gain plots for the substrate without coating and with coatings have been shown in Fig. 11,12 in the presence of air at 800°C. On x-axis “number of cycles” and on y-axis “weight gain/area (mg/cm²)” was taken. In case of air oxidation behaviour of SS-304 in air was somewhat linear because the oxide layer formed on substrate used to peel off very easily and as compared to this oxidation rate of SS-304 coated sample was too less as compared to bare Inconel. Fig. 11,12 shows plot of (weight gain/area) vs. Number of cycles. In this plot every curve is associated with straight line of same colour. This straight line is trend line and it is used to calculate rate constant (K_P) which is given in Table 4. The kinetics of oxidation may be defined by evaluation by parabolic rate constant value K_p, which was found by the following rate equation: $(\Delta W/A)^2/t = K_p$ where $(\Delta W/A)$ was the weight change measurement per unit surface area and K_p the parabolic oxidation rate constant, t the cooling time. The square of weight gain data were plotted against the number of cycles as shown in fig. 11 & fig. 12. Every line or curve in graph is having its approximate equation which is given below.

For SS-304 air oxidized bare sample the approximated curve equation is,

$$y=1E-05x-3E-06$$

$$R^2 = 0.963$$

For SS-304 air oxidized Ni-20Cr and Ti coated sample the approximated curve equation is,

$$y=4E-06x+6E-05$$

$$R^2 = 0.897$$

6.2 HOT CORROSION KINETICS

The kinetics of hot corrosion may be define by evaluation by parabolic rate constant value K_p , which was found by the following rate equation: $(\Delta W/A)^2/t = K_p$ where $(\Delta W/A)$ was the weight change measurement per unit surface area and K_p the parabolic rate constant, t the cooling time. The square of weight change data were plotted against the number of cycles as shown in fig.11 & fig.12; the trend line graph is plotted in fig.11,12 that represent the linear line and the approximate equation on line or curve graph which is given below.

For SS-304 salt oxidized bare sample the approximated curve equation is,

$$y=3E-05x+2E-05$$

$$R^2 = 0.970$$

For SS-304 salt oxidized Ni-20Cr and Ti coated sample the approximated curve equation is,

$$y=7E-05x-5E-06$$

$$R^2 = 0.884$$

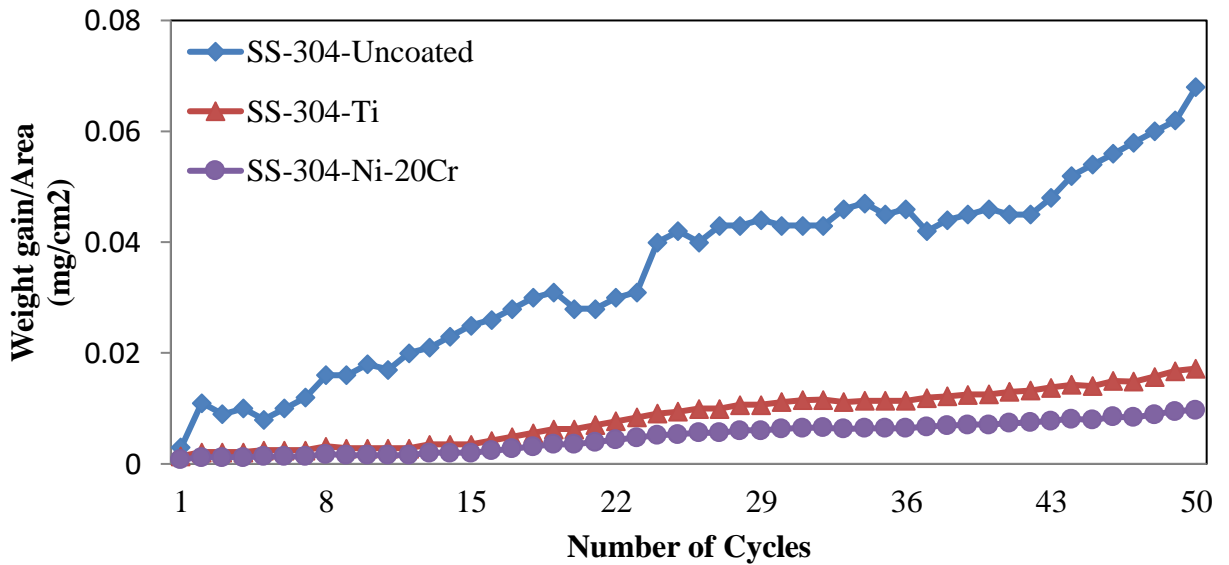


Fig11. Weight change/Area vs. number of cycles plot for coated and uncoated SS-304 subjected to cyclic oxidation and hot corrosion for 50 cycles in air and molten salt environment at 800°C.)

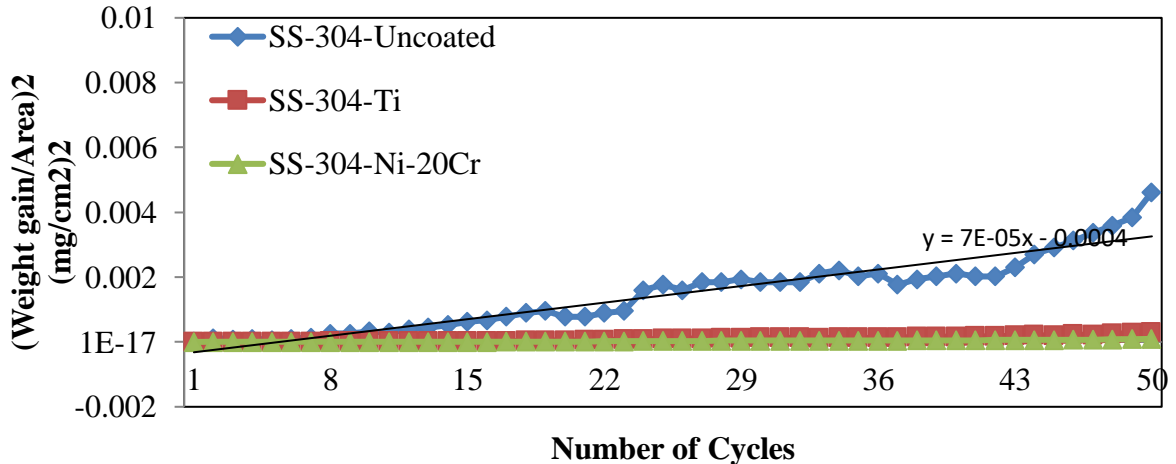


Figure12. Weight change/Area)² vs. number of cycles plot for coated and uncoated SS-304 subjected to cyclic oxidation and hot corrosion for 50 cycles in air and molten salt environment at 800°C.)

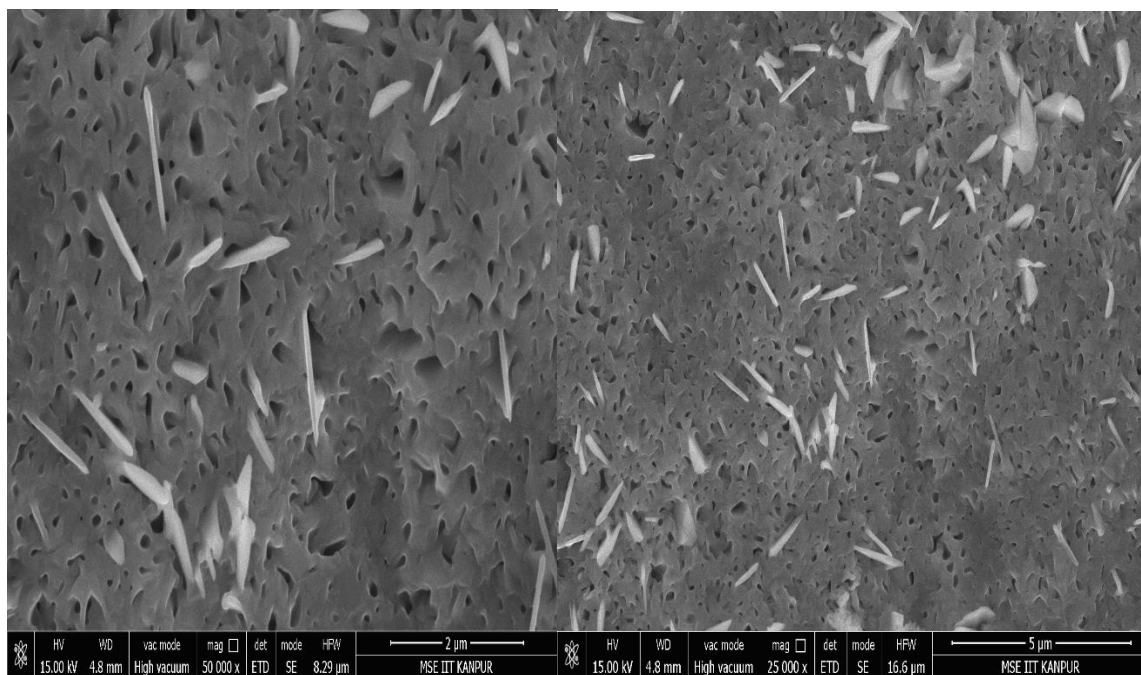
(Where X is number of cycle and Y is weight gain/area & these equation are calculated by using analysis mode of Origin software)

Table 4. Value of parabolic rate constant

Description	KP($10^{-6} \text{ g}^2 \text{ cm}^{-4} \text{ s}^{-1}$)
SS-304 bare air oxidized	0.001936×10^{-4}
SS-304 Ni-20Cr and Ti coated air oxidized	$0.000129579 \times 10^{-4}$
SS-304 bare salt oxidized	1.25534×10^{-4}
SS-304 Ni-20Cr and Ti coated salt oxidized	4.14577×10^{-4}

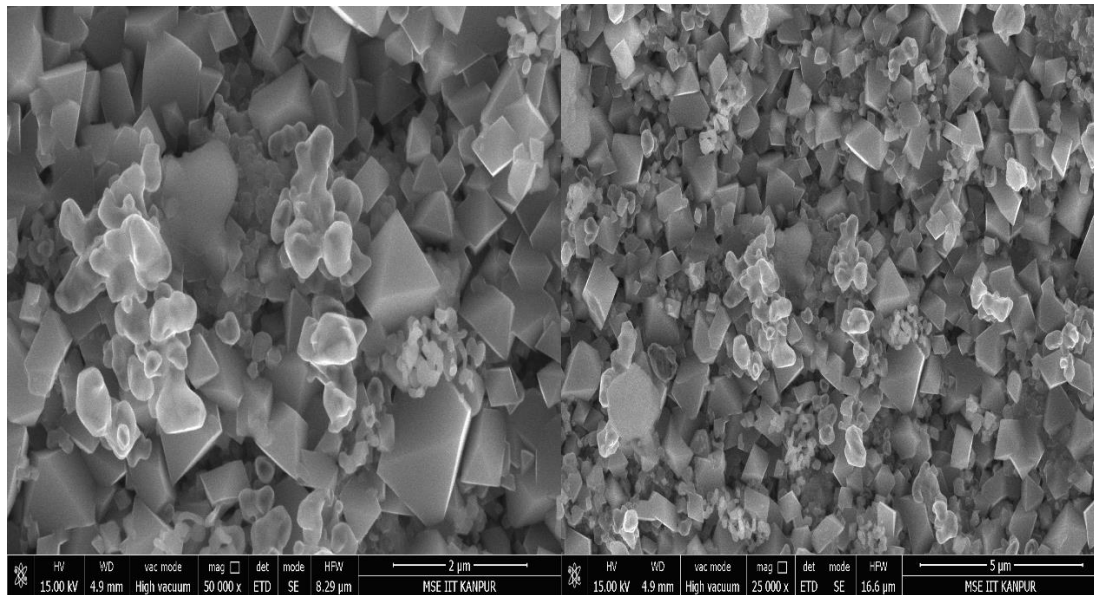
6.3 SCANNING ELECTRON MICROSCOPE (SEM) ANALYSIS

6.3.1. OXIDATION UNCOATED



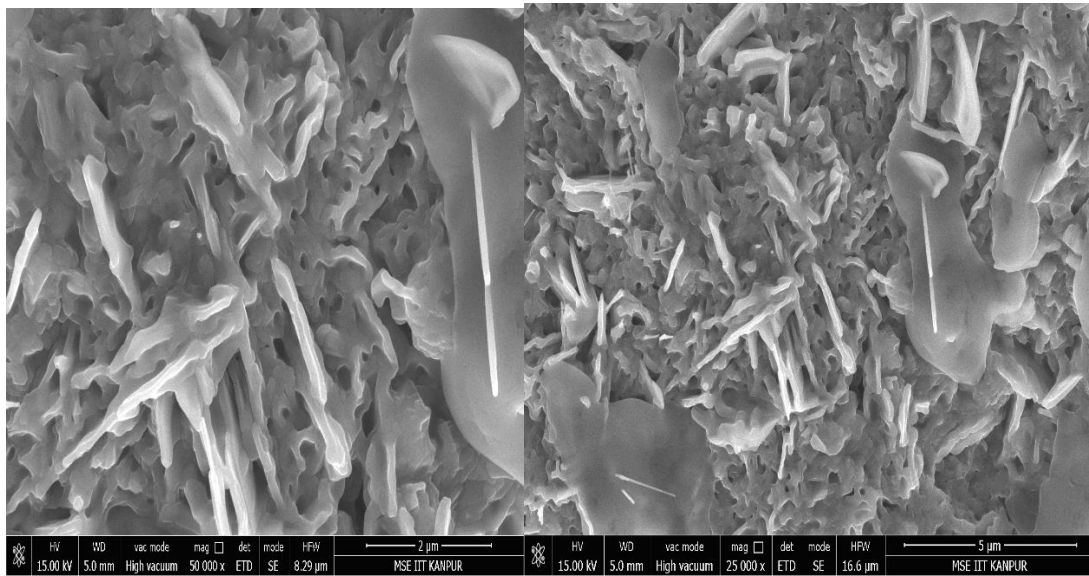
(Fig.13. Surface morphology and SEM analysis of uncoated SS-304 subjected to cyclic oxidation in air at 800°C.)

6.3.2. OXIDATION COATED



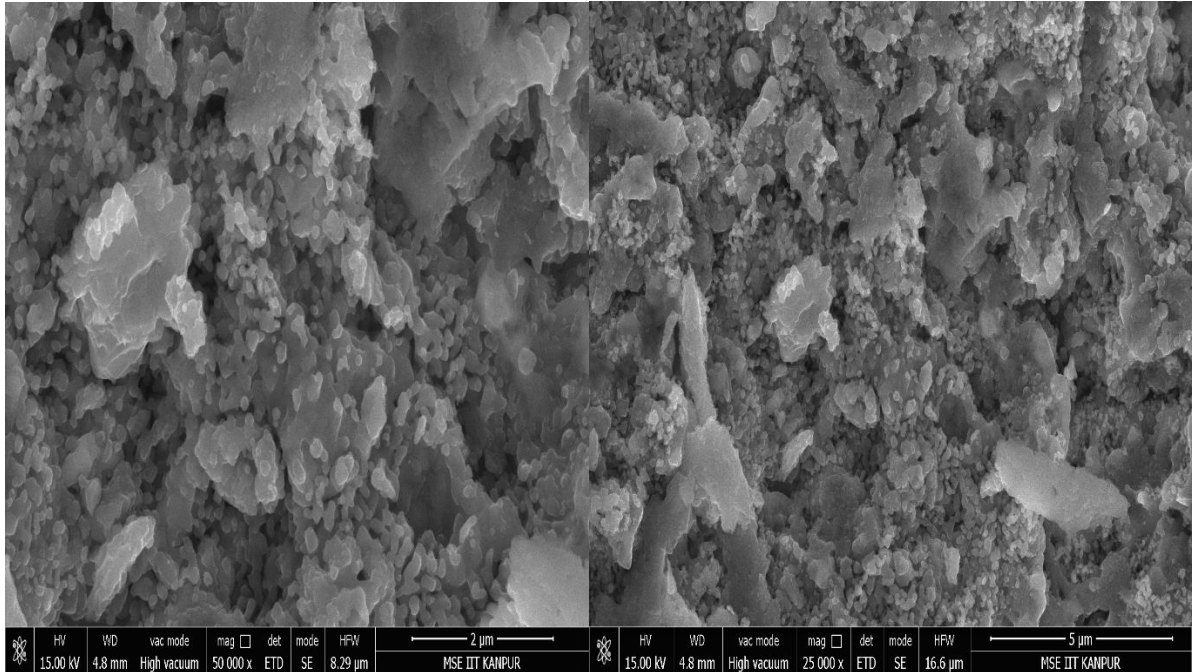
(Fig.14. Surface morphology and SEM analysis of D-Gun sprayed coated Ni-20Cr and Ti coating on SS-304 subjected to cyclic oxidation in air at 800°C)

6.3.3. CORROSION UNCOATED



(Fig.15. Surface morphology and SEM analysis of uncoated SS-304 subjected to cyclic oxidation and hot corrosion in air and molten salt 50%Na₂SO₄ + 50%NaCl at 800⁰C)

6.3.4. CORROSION COATED



(Fig.16. Surface morphology and SEM analysis of D-Gun sprayed coated Ni-20Cr and Ti coating on SS-304 subjected to cyclic oxidation and hot corrosion in air and molten salt 50%Na₂SO₄ + 50%NaCl at 800⁰C)

The FE-SEM micrograph of as-sprayed Ni-20Cr and Ti coating is shown in Fig.14 and Fig.16. The microstructure consists of irregular sized particles. There is also a presence of some superficial voids in the microstructure. The FE-SEM micrograph of as sprayed Ni-20Cr and Ti shows. The FE-SEM micrograph of as-sprayed Ni-20Cr and Ti shows elemental composition at some points as depicted in Fig.16 & Fig.18. There is also a presence of some superficial voids in the microstructure. The Ni-20Cr and Ti coated material sample shows iceberg structure which indicates that the sample coated with Ni-20Cr and Ti is porous but Ni-Cr and Ti coated sample shows newly 56 honeycomb like structure which has sufficient vacant sites for the absorption of oxygen. At temperature 800⁰C

surface morphology of uncoated SS-304 shows that scale forms on the surface of the uncoated SS-304 material was like flacks structure which has more porosity for absorption of oxygen.

CHAPTER 7

7. RESULT AND DISCUSSION

Degradation of metals and alloys due to hot corrosion has been acknowledged as a serious trouble for many high temperature aggressive environment applications. Alluminide coatings can be successfully deposited over the substrate material by HVOF, Detonation gun and Plasma Spray processes. Ni-20Cr and Ti coatings offer excellent corrosion and oxidation resistance, also having a high melting point and maintaining high resistance, strength and wear resistance at high temperature. It has been learnt from literature that detailed studies are needed to optimize the composition of cermets coatings for erosive-corrosive environments. The erosion resistance of cermets coatings increases with an increase in chromium carbide in the pre-sprayed powder. Researchers agree that carbide-based coatings provide excellent erosion protection, but disagree on the optimum amount of carbide for maximum erosion resistance. The thermal sprayed coatings consist of oxides and voids originating from spraying process that are found at the splat boundaries, through which the coatings were mainly attacked. Consequently, the need arises to employ denser coatings which degrade less due to their more. DETONATION Gun with liquid petroleum gas as the fuel gas has been used successfully used to deposit Ni-20Cr and Ti alloy coatings on boiler tube materials. Under the given spray parameters, seemingly dense laminar structured coating with thickness in the desired range of 200 to 400 μm . The cumulative weight gain for all the Detonation Gun coated SS-304 materials are significantly lower than that of uncoated specimen subjected to hot corrosion in 50%Na₂SO₄+50%NaCl molten salt environment

for 50 cycles at 800°C. Uncoated specimen suffered a higher corrosion rate and intense spalling of oxide scale was observed. The main constituent of oxide scale formed on all specimens is iron oxide. The acidic fluxing of the oxides by the molten salt mixture resulted in massive, porous oxide scale. All the coated specimen exhibit characteristic thick protective oxide scale, composed of oxides and spinel oxide of the active elements of the coating and imparted resistance to the hot corrosion in the given salt environment. The weight change curves for oxidation in both of the cases follow the parabolic law. Although different authors have made the efforts to understand the mechanism of hot corrosion using carbide based coatings in different aggressive environments in the laboratory but still long term exposure of these coatings in actual industrial environment needs to be studied for estimating the protection capabilities of these coatings. The FE-SEM micrograph of as-sprayed Ni-20Cr and Ti coating is shown in Fig.16 and Fig.18. The microstructure consists of irregular sized particles. There is also a presence of some superficial voids in the microstructure. The FE-SEM micrograph of as sprayed Ni-20Cr and Ti shows. The FE-SEM micrograph of as-sprayed Ni-20Cr and Ti shows elemental composition at some points as depicted in Fig.16 & Fig.18. There is also a presence of some superficial voids in the microstructure. The Ni-20Cr and Ti coated material sample shows iceberg structure which indicates that the sample coated with Ni-20Cr and Ti is porous but Ni-20Cr and Ti coated sample shows newly honeycomb like structure which has sufficient vacant sites for the absorption of oxygen. At temperature 800°C surface morphology of uncoated SS-304 shows that scale forms on the surface of the uncoated SS-304 material was like flacks structure which has more porosity for absorption of oxygen.

CHAPTER 8

8. REFERENCE

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