

**Sathyabama Institute of Science and Technology
(Deemed to be University)**

Submitted in partial fulfillment of the requirements for the award of Bachelor
of Engineering in Mechanical Engineering

By

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DEPARTMENT OF MECHANICAL ENGINEERING

SCHOOL OF MECHANICAL ENGINEERING

**SATHYABAMA INSTITUTE OF SCIENCE AND TECHNOLOGY
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DEPARTMENT OF MECHANICAL ENGINEERING

BONAFIDE CERTIFICATE

This is to certify that this Project Report is the bonafide work of NIRANJAN. M (Reg. No: 38150072) who carried out the project entitled “**Evaluation of Thermal Cyclic behavior on Thermal Barrier Coating on HASTELLOY X**” under my supervision from June 2021 to November 2021.

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DECLARATION

I, **NIRANJAN.M** hereby declare that the project report entitled “**Evaluation of Thermal Cyclic behavior on Thermal Barrier Coating on HASTELLOY X**” done by me under the guidance of **Dr. A. ANDERSON M.E.,Ph.D.**, is submitted in partial fulfillment of the requirements for the award of Bachelor of Engineering Degree in Mechanical Engineering.

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ABSTRACT

Thermal barrier coatings (TBCs) enable the engines to operate at higher temperatures within raising the base metal temperatures using cooling systems inside the hot section components and thus, enhance the operating efficiency of the engines.

TBCs perform the important function of insulating components, such as gas turbine and aeroengine parts, operating at elevated temperature.

TBCs provides a temperature reduction of up to 300 K in the surface of the superalloy component.

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INTRODUCTION

The demand for improved performance in high temperature mechanical systems has led to increasingly harsh operating environments, particularly for the components in advanced gas turbine engines. Future improvements in gas turbine performance will require even higher operating efficiencies, longer operating lifetimes, and reduced emissions. Achieving these requirements will necessitate still further increases in the gas inlet temperatures and, consequently, the development of structural materials inherently capable of higher temperature performance. Advanced cooling schemes coupled with thermal barrier coatings (TBCs) can enable the current families of superalloy components to meet the materials needs for the engines of tomorrow.

Thermal barrier coating systems are currently capable of providing metal temperature reductions of up to about 140°C, whereas potential benefits are estimated to be greater than 170°C. The use of TBCs in combination with cooling schemes has enabled the operation of gas turbine engines having combustion gas temperatures in excess of 250°C above the melting temperature of the superalloy component (e.g., early stage turbine blades and vanes). Moreover, the use of TBCs at lower operating temperatures reduces the metal temperature, which in turn increases the service life of the component. In fact, current engine design primarily relies on the lifetime extension benefits of TBCs and does not fully exploit the significant performance improvements TBCs are capable of providing. This is because current, state-of-the-art TBCs are not considered “prime reliant” to the extent that they can be used with assurance that failure will not occur.

This limitation derives from a number of issues, including the following:

- 1) TBCs do not provide self-renewing protection. When they spall the thermal protection is lost.
- 2) TBC service life is subject to scatter that to date has not been adequately taken into account.

3) There are currently no effective methods (e.g., nondestructive evaluation) that can act as quality control and/or monitor for TBCs.

4) Life prediction for TBCs is not as accurate as is needed

1.1 CONSTITUENTS OF TBC

Thermal barrier coatings (TBC) are applied to metallic surfaces, such as gas turbines or aero-engine parts, operating at elevated temperatures. These coatings serve to insulate components from large and prolonged heat loads by utilizing thermally insulating materials which can sustain an appreciable temperature difference between the load-bearing alloys and the coating surface. In doing so, these coatings can allow for higher operating temperatures while limiting the thermal exposure of structural components, extending part life by reducing oxidation and thermal fatigue. In conjunction with active film cooling, TBCs permit working fluid temperatures higher than the melting point of the metal airfoil in some turbine applications.

These are produced by a process in which molten or softened particles are applied to impact onto a substrate. Modern TBCs are required not only to limit heat transfer through the coating but also to protect engine components from oxidation and hot corrosion. By attaching an adherent layer of a low thermal conductivity material to the surface of an internally cooled gas turbine blade, a temperature drop can be induced across the thickness of the layer. This results in reduction of the component surface temperature to which it is applied. This temperature drop reduces the oxidation rate of the bond coat applied to metal components, and so delays failure by oxidation. The temperature acting on hot section of gas turbine goes up to about 1300°C during engine operation. However, metallic materials cannot be used at these temperatures due to harsh effect of the high temperature. Therefore, a Thermal Barrier Coating (TBC) is needed to satisfy effective protection to the metallic component.

The first part of a TBC system is metallic substrate. Ni-based superalloys (Inconel) are the most widely used metallic materials in parts like turbine blade and combustion chamber due to their resistance to high temperature conditions. Therefore, the substrate material of the TBC system is generally Inconel alloys. The bond coat layer is the second part of the TBC system. The basic properties expected from the bond coating layer are as follows

The bond coat should provide good oxidation resistance to metallic substrate.

The bond coat should provide good adherence between the metallic substrate and top coat.

The bond coat should tolerate the thermal expansion mismatch between the metallic substrate and top coat.

The third part of the TBC system is a thermally grown oxide (TGO, predominately alpha-alumina) layer between the top coat and bond coat. A very thin TGO layer forms on the bond coat during coating process due to oxidation of the bond coat at the process temperatures, but it grows while the TBC system in gas turbine is operating at high temperatures. This layer has importance because failure of the TBCs mostly happens at the interface between TGO layer and top coat layer when the thickness of TGO layer reaches a critical value. At elevated temperatures ($>950^{\circ}\text{C}$), Al in the bond coat layer diffuses toward the bond coat. On the other hand, oxygen penetrates through the ceramic top coat layer and reacted with the Al. As a result, a TGO layer forms between the bond and the coating.

The final layer is the top coat. This ceramic layer creates the largest thermal gradient of the TBC and keeps the lower layers at a lower temperature than the surface.

The basic properties expected from the top coating material are:

- The coating material should have high melting temperature to resist to the high temperature of gas plasma.

- It should have low thermal conductivity to provide good insulation to the metallic substrate.
- It should have high thermal expansion coefficient to match with the metallic bond coat and substrate's thermal expansion coefficient.
- Its phase structure should stay stable from room temperature to operating temperature.
- It should adhere well to the metallic substrate.
- It should have low sintering rate.
- It should have high resistance to erosion, corrosion, and oxidation

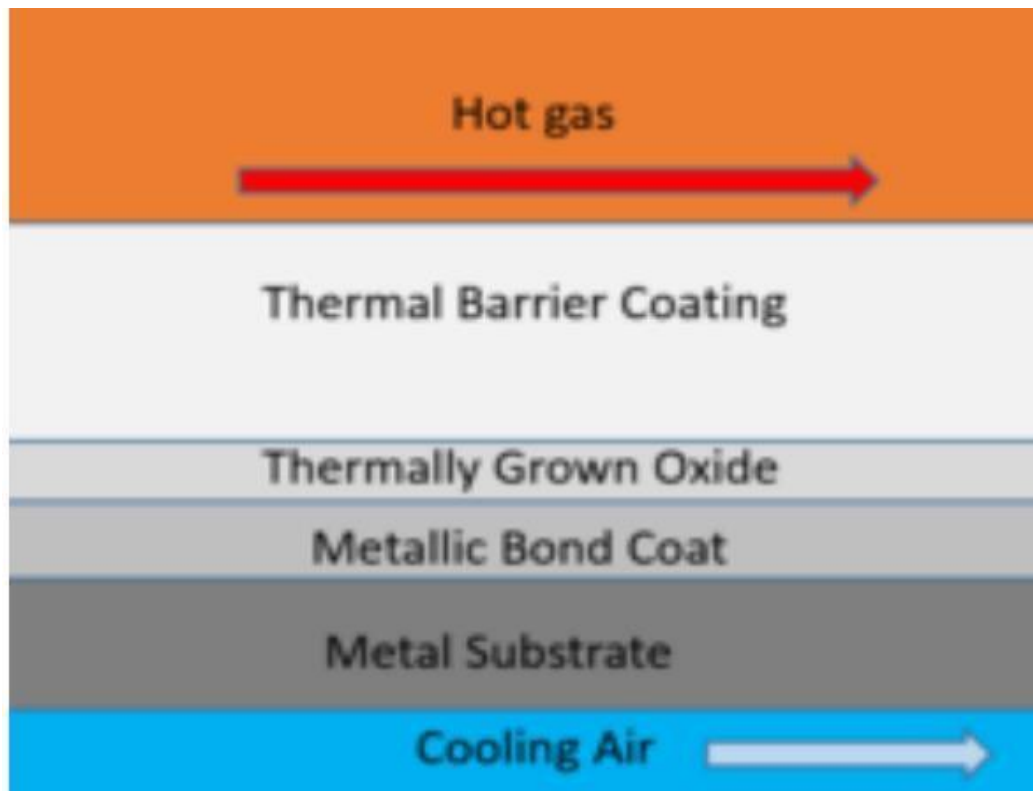


Fig 1.1 Structure of Thermal barrier coatings

Some of the requirements for the coating materials are as follows,

- High thermal cyclic life
- High sintering resistance
- CMAS attack resistance
- High erosion resistance
- High oxygen penetration resistance
- High coefficient of thermal expansion
- High fracture toughness

1.2 APPLICATION

Interest in increasing the efficiency of gas turbines for aviation applications has prompted research into higher combustion temperatures. Turbine efficiency is strongly correlated with combustion temperature. Higher temperature combustion improves the thermodynamic efficiency of the machine, giving a more favourable ratio of work generated in relation to waste heat. Thermal barrier coatings are commonly used to protect nickel-based superalloys from both melting and thermal cycling in aviation turbines. Combined with cool air flow, TBCs increase the allowable gas temperature above that of the superalloy melting point.

To avoid the difficulties associated with the melting point of superalloys, many researchers are investigating ceramic-matrix composites (CMCs) as high temperature alternatives. Generally, these are made from fiber-reinforced SiC. Rotating parts are especially good candidates for the material change due to the enormous fatigue that they endure. Not only do CMCs have better thermal properties, but they are also lighter meaning that less fuel would be needed to produce the same thrust for the lighter aircraft. The material change is, however, not without consequences. At high temperatures, these CMCs are reactive with water and form gaseous silicon hydroxide compounds that corrode the CMC. Even more advanced environmental barrier coatings are required to protect these CMCs from water vapor as well as other environmental degradants.

For instance, as the gas temperatures increase towards 1400 K-1500 K, sand particles begin to melt and react with coatings. The melted sand is generally a mixture of calcium oxide, magnesium oxide, aluminum oxide, and silicon oxide (commonly referred to as CMAS). Many research groups are investigating the harmful effects of CMAS on turbine coatings and how to prevent damage. CMAS is a large barrier to increasing the combustion temperature of gas turbine engines and will need to be solved before turbines see a large increase in efficiency from temperature increase

1.3. MATERIA

LS

Many materials are widely used as a substrate for testing and coating purposes. There are a range of different materials that can be used as a quality coating using plasma spraying. Most materials are available in the suitable powder form such as metals, ceramics and alloys, and can be individually selected depending on the substrate.

a) Mild steel

Low carbon steel has 0.04–0.3% carbon content and is the most common grade of carbon steel. Mild steel is also considered low carbon steel as it is defined as having a low carbon content of 0.05–0.25%. Mild steel is ductile, highly formable, and can be used for automobile body parts, plates, and wire products. At the higher end of the low carbon content range, and with the addition of manganese of up to 1.5%, mechanical properties are suitable for stampings, forgings, seamless tubes, and boiler plates



Fig 1.2 Mild Steel

b) Stainless steel

Stainless Steel can be up to three times stronger than aluminum, although it is also heavier. Its strength, hardness and resistance to heat make it ideal for use on the skin surface of the aircraft and in the landing gear and it typically comprises around 11-13 percent of the materials used in an aircraft. The durability of steel is its most important characteristic in aero plane manufacture and although it is heavier than other materials like aluminum it is often used for hinges, cable and fasteners where its strength is key.



Fig 1.3 Stainless steel

c) Aluminum

Aluminum is a highly popular material in the manufacture of aircraft due to the combination of low density and high strength properties, making it ideal for mass-produced commercial aircraft. Aircraft manufacturers prefer to use high-strength Aluminum alloys (primarily alloy 7075) to strengthen Aluminum aircraft structures. Alloy 7075 has copper, magnesium and zinc added for extra strength. Aluminum typically comprises around 80 percent of an aircraft's weight (unloaded) and because it is highly resistant to corrosion, it can be left unpainted.

At high temperatures, however, Aluminum can lose strength so it is not used on the skin surface of an aircraft



Fig 1.4 Picture of Aluminum alloy

Materials used in gas turbine engines.

Nickel alloys are popular in aerospace industry to make turbine blades, discs and other critical jet engine parts because they provide excellent adhesion, corrosion protection, hardness, wear and erosion resistance, is appropriate for applications where stress needs to be minimized and are structurally tough and have fantastic creep resistance properties. In aircraft engines, which operate at very high temperatures and stresses, special nickel-based alloys are used owing to their ability to retain their strength at elevated temperatures. In addition to this, nickel alloys are used in the exhaust valves, thermostat rods, tanks and piping for liquefied gas storage.

HASTELLOY X

Hastelloy x is a wrought nickel base alloy with excellent high temperature strength and oxidation resistance. All of the product forms excellent in terms of forming and welding

. Although HASTELLOY X is primarily noted for heat and oxidation resistance it also has good resistance to chloride stress – corrosion cracking and has good resistance

to carburization , excellent resistance to reducing or carburizing atmosphere. Alloy X is one of the most widely used nickel base superalloys for gas turbine engine components.

AMS 5754 has no yield or tensile strength requirement , but it does require a harness maximum and stress rupture minimums. Strong and Oxidation Resistant to 2200 Deg.F(1200 Deg.C) – Hastelloy X a solid solution is strengthened grade has good strength and oxidation resistance up to 2200 Deg.F

NIMONIC

Nimonic is a registered trademark of special Metals Corporation of that refers to a family of nickel -based high-temperature low creep superalloys. Nimonic alloys typically consist of more than 50% nickel and 20% chromium with additives such as titanium and aluminum

The main use is in gas turbine components and extremely high performance reciprocating internal combustion engines. The Nimonic family of alloys was first developed in the 1940s by research teams at the Wiggin works in Hereford, England in support of the development of the Whittle jet engine

d) Nickel Alloys

1.3.1 SUBSTRATE CHOSEN FOR STUDY

Inconel 718 is a nickel-based alloy that is designed for very high yield strength. It has creep rupture properties at temperatures up to 1300°F and is known for being weldable. It has a tensile strength of 13.3Ksi. Inconel 718 has a good resistance to oxidation and corrosion at high temperatures as well. When heated, it forms a thick, stable oxide layer, protecting the surface it is coated on from any attack.

It is used in the manufacturing of jet engines and high-speed airframe parts.

It also finds several applications in rocket engines and cryogenic environments due to its good toughness at low temperature (preserving parts from a brittle fracture).



Fig 1.5 Inconel 718

1.3.3. TYPES OF TBCs

There are a range of different materials that can be used as a quality coating using plasma spraying. Most materials are available in the suitable powder form such as metals, ceramics and alloys, and can be individually selected depending on the substrate.

a) Mullite

Mullite is a compound of alumina and silica, with the formula $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$. It has a low density, along with good mechanical properties, high thermal stability, low thermal conductivity, and is corrosion and oxidation resistant. However, it suffers from crystallization and volume contraction above 800°C , which leads to cracking and delamination. Therefore, this material is suitable as a zirconia alternative for applications such as diesel engines,

where surface temperatures are relatively low and temperature variations across the coating may be large



Fig 1.6 Mullite powder

b) Alumina

Only α -phase Al_2O_3 is stable among aluminum oxides. With a high hardness and chemical inertness, but high thermal conductivity and low thermal expansion coefficient, alumina is often used as an addition to an existing TBC coating. By incorporating alumina in YSZ TBC, oxidation and corrosion resistance can be improved, as well as hardness and bond strength without significant change in the elastic modulus or toughness. One challenge with alumina is applying the coating through plasma spraying, which tends to create a variety of unstable phases, such as γ -alumina. When these phases eventually transform into the stable α -phase through thermal cycling, a significant volume change of $\sim 15\%$ (γ to α) follows, which can lead to microcrack formation in the coating.



Fig 1.7 Alumina powder

c) CeO_2 + YSZ

CeO_2 (Ceria) has a higher thermal expansion coefficient and lower thermal conductivity than YSZ. Adding ceria into a YSZ coating can significantly improve the TBC performance, especially in thermal shock resistance. This is most likely due to less bond coat stress due to better insulation and a better net thermal expansion coefficient. Some negative effects of the addition of ceria include the decrease of hardness and accelerated rate of sintering of the coating (less porous).



Fig 1.8 Mixture of CeO_2 + YSZ

d) Rare-earth zirconates

$\text{La}_2\text{Zr}_2\text{O}_7$, also referred to as LZ, is an example of a rare-earth zirconate that shows potential for use as a TBC. This material is phase stable up to its melting point and can largely tolerate vacancies on any of its sublattices. Along with the ability for sitesubstitution with other elements, this means that thermal properties could potentially be tailored. Although it also has very low thermal conductivity compared to YSZ, it also has a low thermal expansion coefficient and low toughness.

e) Rare earth oxides

The mixture of rare earth oxides is readily available, cheap, and may have promise as effective TBCs. The coatings of rare earth oxides (ex: La_2O_3 , Nb_2O_5 , Pr_2O_3 , CeO_2 as main phases) have lower thermal conductivity and higher thermal expansion coefficients when compared to YSZ. The main challenge to overcome is the polymorphic nature of most rare earth oxides at elevated temperatures, as phase instability tends to negatively impact thermal shock resistance.

1.3.4. MATERIALS CHOSEN FOR STUDY

f) YSZ

YSZ is the most widely studied and used TBC because it provides excellent performance in applications such as diesel engines and gas turbines. Additionally, it was one of the few refractory oxides that could be deposited as thick films using the then-known technology of plasma spraying. As for properties, it has low thermal conductivity, high thermal expansion coefficient, and low thermal shock resistance. However, it has a fairly low operating limit of 1200°C due to phase instability, and can corrode due to its oxygen transparency.

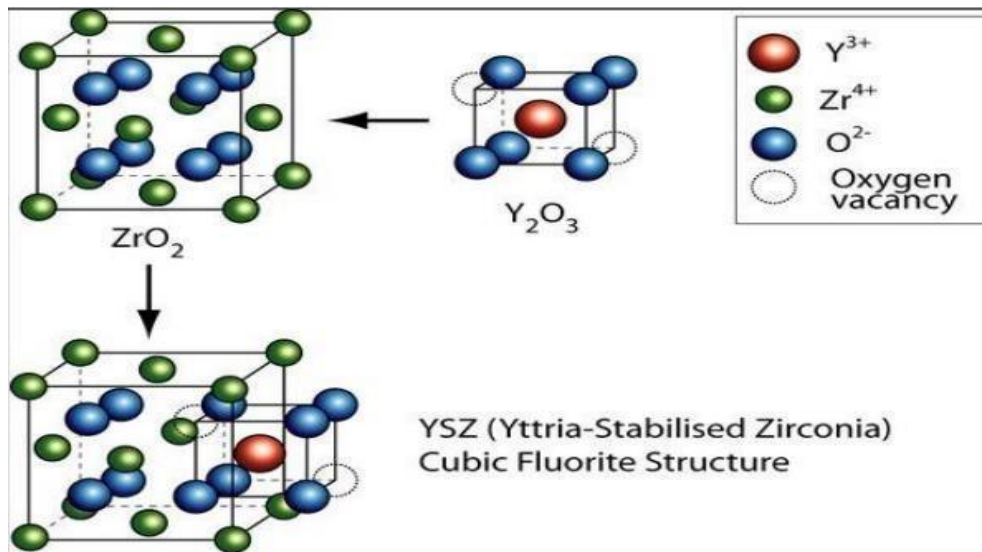


Fig 1.9 Yttria-Stabilized Zirconia Crystal Structure

It has the exceptional combination of desired properties, such as

- High melting point (2700 °C)
- A relatively low thermal conductivity (2.6 W/mK)
- High coefficient of thermal expansion (CTE, $11 \times 10^{-6} \text{ K}^{-1}$)
- High fracture toughness ($\sim 3 \text{ MPa} \cdot \text{m}^{1/2}$)

f) Gadolinium Zirconate

Gadolinium zirconate with pyrochlore or defect fluorite-type structure is a new and promising alternative ceramic top coating material to YSZ. The most important features that make it advantageous are given below:

1. GZ has higher thermal stability at elevated temperatures ($>1200^\circ\text{C}$) than YSZ. Therefore, it can be used at temperatures above 1200°C .

2. GZ has lower thermal conductivity (1.3 W/mK^{-1} at 1100°C) than YSZ (1.8 W/mK^{-1} at 1100°C). Thus, GZ provides better thermal insulation to the metallic substrate than YSZ.
3. GZ has more superior hot corrosion resistance than YSZ. Thanks to this feature, elements emitted due to fuel pollution are less harmful to the GZ- based TBC.
4. GZ has more resistance to the CMAS attack than YSZ. Because the CMAS powders (particles such as dust, volcanic ash, rock, etc.) entering to turbine melt at about 900°C and try to penetrate through the coating surface. Porosities of the TBC are filled with CMAS, and thus strain incompatibility of the TBC is limited. This molten CMAS cannot penetrate to GZ-based TBC due to the sealing layer formed on the surface of the GZ-based TBC.



Fig 1.10 Gadolinium zirconate

1.4. COATING METHODS

Based on the energy source, thermal spray methods can be divided into a few main groups:

1. Plasma spray methods (APS, VPS, LPPS)
2. Combustion Flame Spray Methods (FPS, FWS)
3. High velocity oxy/air - Fuel methods (HVOF/HVAF)
4. Arc spray methods
5. Cold gas methods (CGS)

a) Plasma spray:

Uses a plasma-forming gas (typically argon or nitrogen) as both the heat source and propelling agent for the coating material. A high voltage arc struck between an anode and cathode within the gun ionizes the gas, which is then forced through a convergent/divergent nozzle. As the gas exits the nozzle, it reverts to its natural state, liberating large amounts of heat. Powdered coating material is injected into the hot gas stream, where it is melted and projected at high velocity onto a prepared substrate.

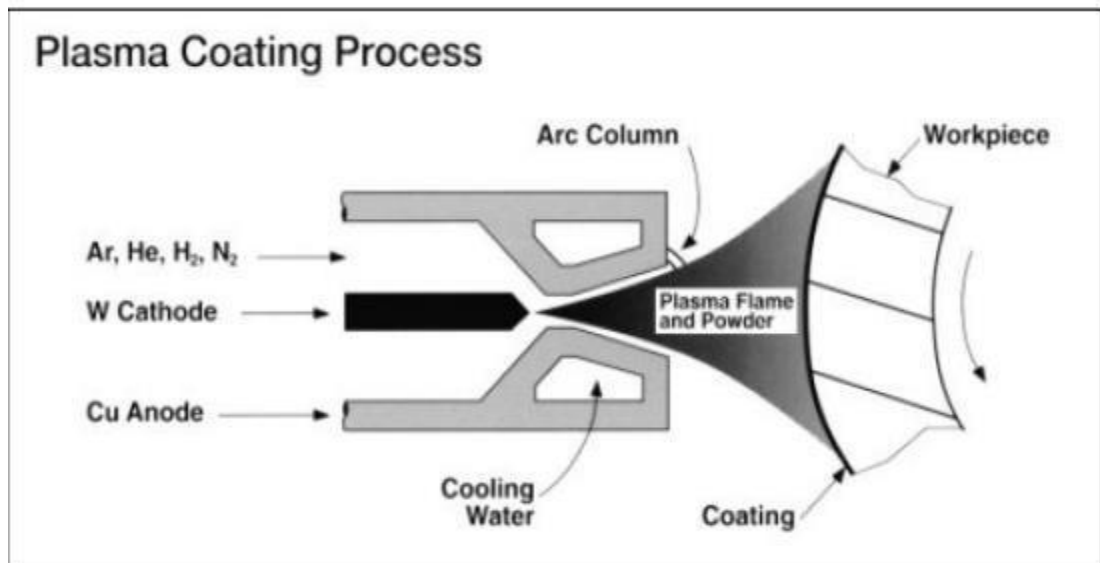


Fig 1.11 Plasma coating process

Advantages:

Coatings are dense and strongly bonded to the substrate. In general, they have higher integrity and perform better than coatings applied by other thermal-spray processes.

b) Wire flame spray:

Applies coatings of any metal that can be drawn into a wire. It has a melting point below that of a combustion flame. Drive rolls feed the wire through a flame-spray gun to its nozzle where the wire is melted in an oxygen/fuel-gas (oxy fuel) flame after which compressed air atomizes the metal and projects it onto the prepared surface.

Advantages: Best choice for all-purpose spraying. Coatings can be applied rapidly and at low cost.

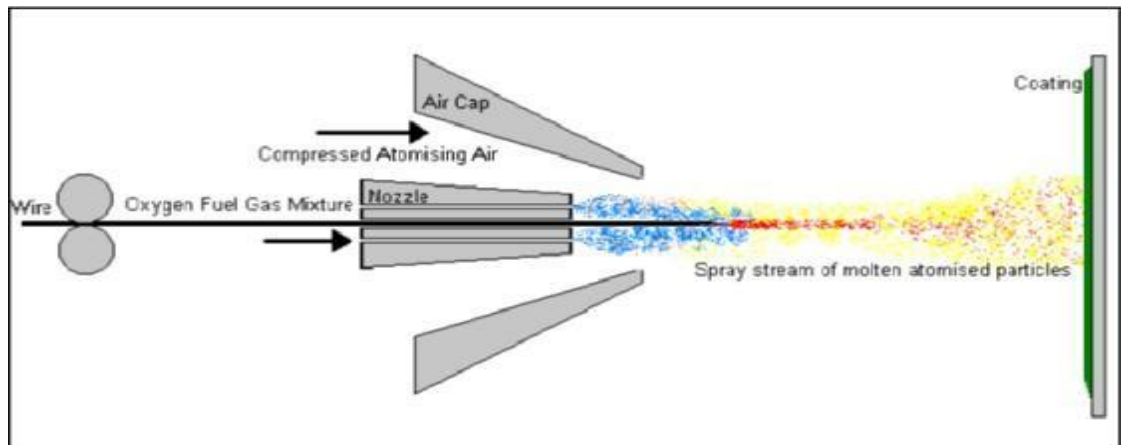


Fig 1.12 Wire flame spray process

c) Electric-arc spray:

It applies metal coatings in wire form. Push/pull motors feed two electrically charged wires through the spray gun. When their tips touch at the gun head, an arc is created which melts the wires at temperatures above 3,980 °C after which compressed air atomizes the molten metal and projects it onto a prepared surface.

Advantages: It can spray up to a large area and can also apply thick coatings. Its built-in flexibility permits tailoring of coating characteristics, such as hardness and surface texture

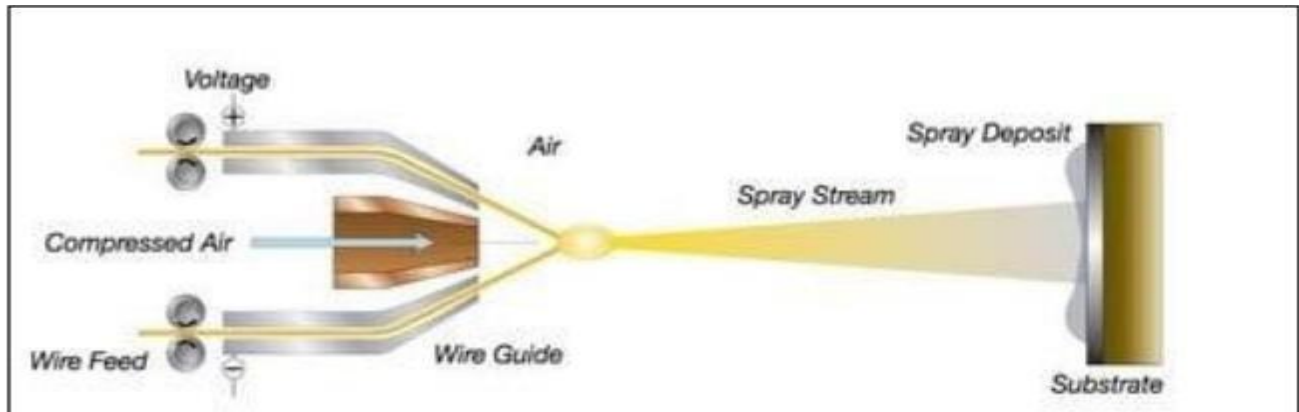


Fig 1.13 Electric-arc spray process

d) High-Velocity Oxy-fuel (HVOF):

It uses high-velocity combustion of mixtures of oxygen and a fuel gas to heat and propel semi-molten-to-molten powdered materials. The sprayed particles impact the substrate with extremely high kinetic energy and with negligible oxidation of the coating material.

Advantages: The HVOF method produces coatings that have the highest bond strength and lowest porosity. Coatings also have low internal stresses, which allow thick layers to be deposited, and fine as sprayed surface finishes. HVOF is well suited to producing high-quality tungsten and chromium-carbide coatings.

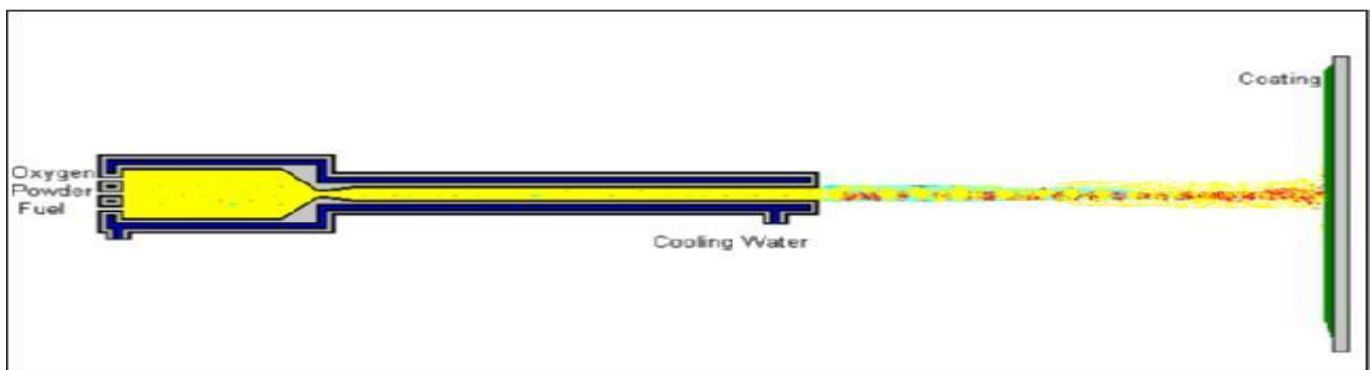


Fig 1.14 High-Velocity Oxy-fuel process

e) EB-PVD:

In the EB-PVD process, the source material is heated with an electron beam, vapors are produced, and the evaporated atoms condense on the substrate. Crystal nuclei form on favored sites and grow laterally and in thickness to form individual columns that provide in-plane compliance. A TGO layer often forms on the bond coat in these TBC systems and increases the residual stress. Further, brittleness of the top coat increases with the sintering of the coating. Consequently, the adhesion of the bond coat to the top coat becomes weak at high temperatures. Therefore, the TGO layer is very detrimental for TBC performance.

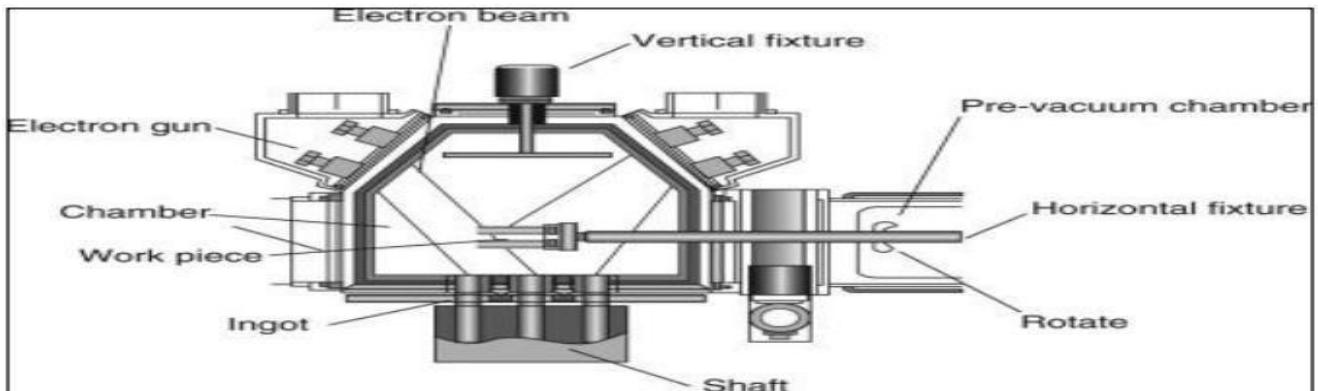


Fig 1.15 EB-PVD apparatus

f) Cold gas:

The Cold Spray or cold gas-dynamic spraying process is the next progressive step in the development of high kinetic energy coating processes. Similar in principle to the other thermal spray methods, it follows the trend of increasing particle spray velocity and reducing particle temperature as with the HVOF/HVAF processes, but to a more extreme level. It basically uses the energy stored in high pressure compressed gas to propel fine powder particles at very high velocities (500 - 1500 m/s). As with the other processes a fine balance between particle size, density, temperature and velocity are important criteria to achieve the desired coating.

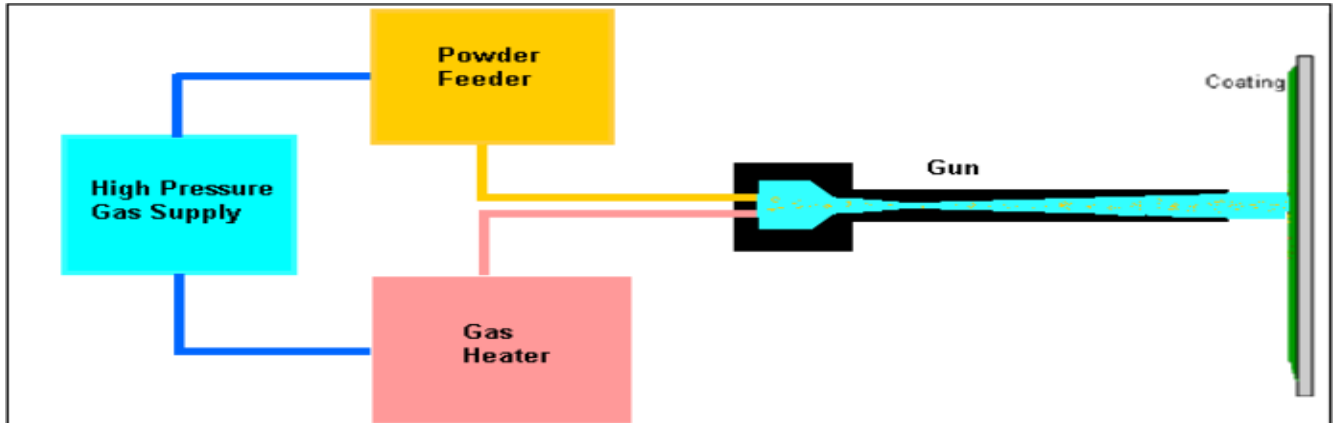


Fig 1.16 Cold gas process

1.4.1 COATING METHOD USED FOR THE STUDY

Atmospheric Plasma spray coating involves the plasma generator which consists of a circular anode, usually of copper, and a cathode of thoriated tungsten. The cathode is made of graphite in a water-stabilized torch. The electric arc discharge supported by a generator through the connectors heats up the working gases, which expand in the atmosphere forming a jet. The powder, suspended in a carrier gas, is injected into the jet. The particles of the powder after being melted and accelerated in the jet impact the substrate and form the coating.

Plasma spraying is relatively straight forward in concept but rather complex in function. The gun operates on direct current, which sustains a stable non-transferred electric arc between a thoriated tungsten cathode and annular water-cooled copper anode. A plasma gas generally, argon, complemented by a few percent of an enthalpy enhancing gas, such as hydrogen is introduced at the back of the gun interior. The gas in the form of swirling in a vortex passes out through the front exit of the anode nozzle. The electric arc from the cathode to the anode completes the circuit, generally on the outer face of the anode, forming an exiting plasma flame which axially rotates due to the vortex momentum of the plasma gas. The temperature of the plasma just outside of the nozzle exit is effectively in excess of 15,000 K for a typical dc torch operating at 40 kW. The plasma temperature drops off rapidly from the exit of the anode, and therefore the powder to be processed is introduced at the hottest part of the flame

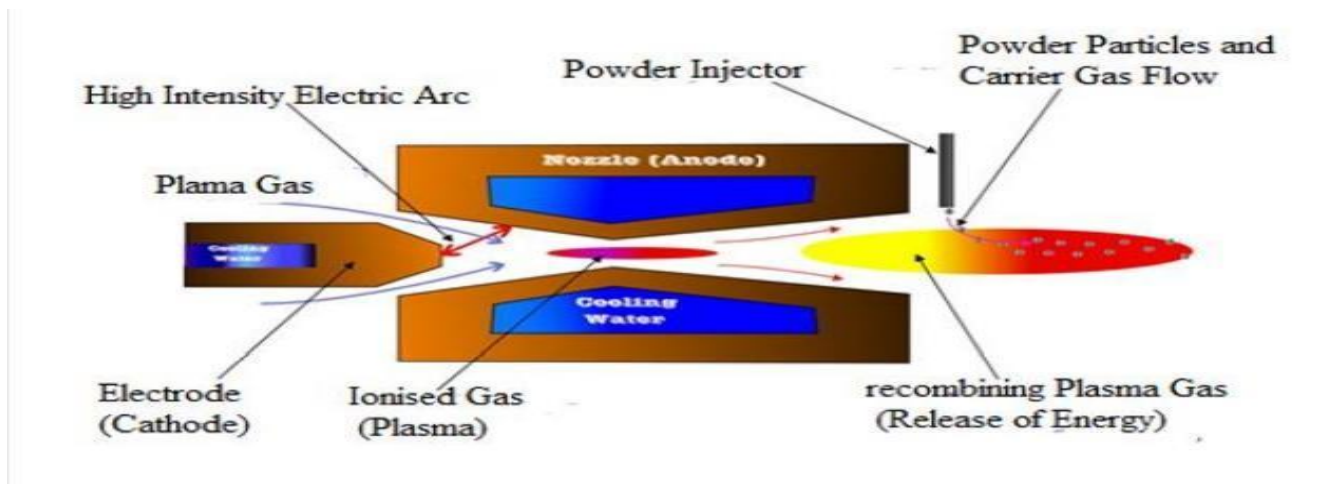


Fig 1.17 Atmospheric Plasma Spray technique

1.5. METHODS OF COATING'S CHARACTERIZATION

The coatings are characterized thoroughly by using many techniques. The simplest way of controlling the coating's quality is careful observation of its surface. The properties of coatings determine their behaviour during service. The best possible test is the one made under conditions simulating 'real-service' conditions. However, such a test is expensive and sprayed coatings are most frequently characterized by testing their physical or chemical properties.

1.5.1 Thermal Cyclic Test

Thermal Shock Resistance (TSR), also called thermal stress resistance, describes the capacity of a brittle material to resist rapid temperature variations without failure. The TSR depends on the conditions of heating (steady- state flow, transient heating, heating by convection or radiation, etc.) and may be expressed as the maximum allowable temperature difference in the body. In practice, TSR is tested for the system of a coating onto a substrate. Most of the tests simulate the conditions of the service of the coatings. A typical thermal cycling furnace test rig is used to test coated turbine blades. Thermal Cyclic Fatigue Test was conducted by Furnace cycle test. In Furnace Cycle Test each thermal cycle consists of a 10-minute heat up to the steady-state temperature, a 45-minute soak at the steady-state temperature and a 5-minute forced air cool down. The chosen steady state temperature was 1150°C. The peel off determines the starting of the damage.



Fig 1.18 Thermal cyclic fatigue test chamber

1.5.2 Hot Corrosion Test

Hot corrosion is a mechanism of "high temperature corrosion", which includes high temperature oxidation, sulfidation and carbonization. Hot Corrosion can be classified as hot corrosion by sulfates, Hot Corrosion by Vanadium, and Hot Corrosion by Lead. Two types of sulfate-induced hot corrosion are generally distinguished. They are Type I and Type II. Type I takes place above the melting point of sodium sulfate and Type II occurs below the melting point of sodium sulfate but in the presence of small amounts of SO_3 .

In Type I, the protective oxide scale is dissolved by the molten salt. Sulfur is released from the salt and diffuses into the metal substrate forming discrete grey/blue colored aluminum or chromium sulfides so that, after the salt layer has been removed, the steel cannot rebuild a new protective oxide layer. Alkali sulfates are formed from sulfur trioxide and sodium-containing compounds. As the formation of vanadate's is preferred, sulfates are formed only if the amount of alkali metals is higher than the corresponding amount of vanadium. The same kind of attack has been observed for potassium and magnesium sulfate.

Vanadium is present in petroleum, especially from Canada, western United States, Venezuela and the Caribbean region, in the form of porphyrine complexes. These complexes get concentrated on the higher-boiling fractions, which are the base of heavy residual fuel oils. Residues of sodium, primarily from sodium chloride and spent oil treatment chemicals, are also present. More than 100 ppm of sodium and vanadium will yield ash capable of causing fuel ash corrosion.

Most fuels contain small traces of vanadium. The vanadium is oxidized to different vanadate's. Furthermore, the presence of vanadium accelerates the diffusion of oxygen through the fused salt layer to the metal substrate; vanadate's can be present in semiconducting or ionic form, where the semiconducting form has significantly higher corrosivity as the oxygen is transported via oxygen vacancies. Ionic form in contrast transports oxygen by diffusion of the vanadate's, which is significantly slower. The semiconducting form is rich on vanadium pentoxide.

At high temperatures or lower availability of oxygen, refractory oxides such as vanadium dioxide and vanadium trioxide were formed. These do not promote corrosion. However, vanadium pentoxide is formed at high temperatures. Various composition ratios of vanadate's are formed with sodium oxide. Vanadate's of composition approximating $\text{Na}_2\text{O} \cdot 6\text{V}_2\text{O}_5$ have the highest corrosion rates at the temperatures between 593°C and 816°C; at lower temperatures the vanadate is in solid state, at higher temperatures vanadate's with higher proportion of vanadium provide higher corrosion rates.

The solubility of the passivation layer oxides in the molten vanadate's depends on the composition of the oxide layer.

Iron (III) oxide is readily soluble in vanadate's between $\text{Na}_2\text{O} \cdot 6\text{V}_2\text{O}_5$ and $6\text{Na}_2\text{O} \cdot \text{V}_2\text{O}_5$, at temperatures below 705°C which amounts equal to the mass of the vanadate. This composition range is common for ashes, which aggravates the problem. Chromium (III) oxide, nickel (II) oxide, and cobalt (II) oxide are less soluble in vanadate's; they convert the vanadate's to less corrosive ionic form and their vanadate's are tightly adherent, refractory and acting as oxygen barriers.

The corrosion rate by vanadate's can be lowered by lowering the amount of excess air for combustion (thus forming preferentially the refractory oxides), refractory coatings of the exposed surfaces, or use of high-chromium alloys.

Lead can form a low melting slag capable of fluxing protective oxide scales. Electrochemistry contributes an understanding of the mechanism that is basic to the corrosion of all metallic objects. Metallurgy provides knowledge of the characteristics of metals and their alloys as well as the methods of combining the various metals and working on them into the desired shapes.

a) Burner Rig Test

In gas turbine, burner rig test has been developed to rank the coatings. The figure shows the ducted burner rig hot corrosion test. The essential features are the combustion chamber, means to ingest the salt and the specimen holder that is rotated and often periodically removed from the hot gas stream to induce thermal stress. The specimens are usually about 10 to 11 cm in length and about 1cm in diameter. In the burner rig test, the specimens are periodically removed from the test to measure weight changes or thickness and to be examined visually. Upon conclusion of the test the specimens are sectioned, metallographically prepared and examined using optical metallography and scanning electron microscope. It is also important to note that the testing in burner rigs is expensive. Furthermore, the construction and operation of burner rigs requires experienced designers and operators.

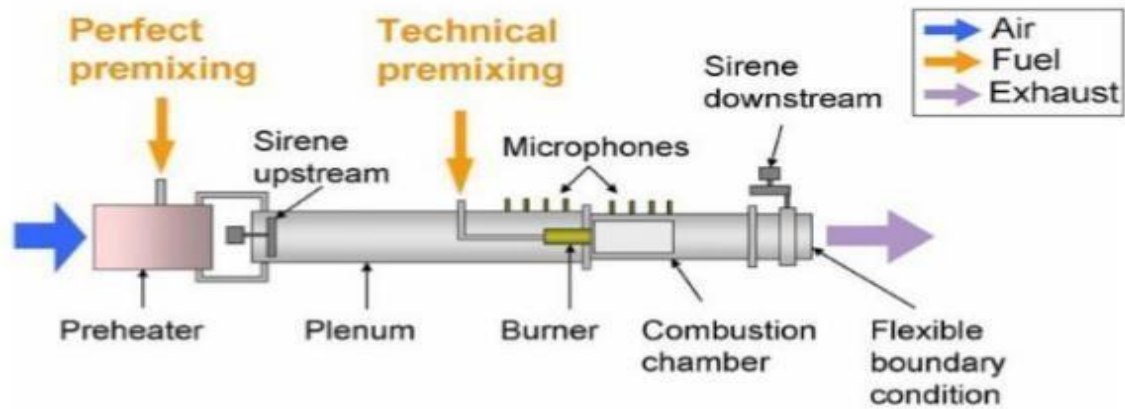


Fig 1.19 Burner rig apparatus

b. Immersion test

In Immersion test, coupons are placed in deep melts. This type of test is usually used for deep melts. Immersion testing which was the first laboratory test method is not considered reliable for gas turbine environment

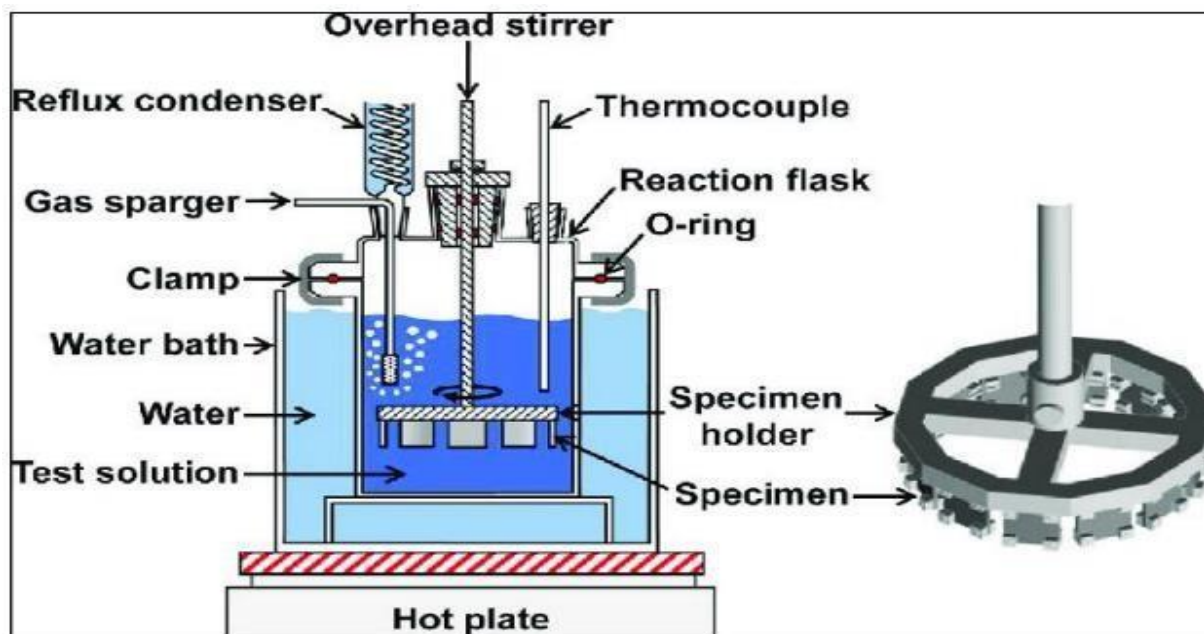


Fig 1.20 Immersion test apparatus

ssified into many types depending on the mechanism responsible for removal of material from the surface. The following classification of mechanical wear suggests few distinct mechanisms for the removal of material from sliding metal surfaces.

Adhesive wear arises primarily from adhesion between the sliding surfaces. Erosive wear can be attributed to the action of numerous small particles, which impinge on a surface, such as sand blasting. Fretting wear is a process in which surfaces slip by a very small amplitude relative to each other thereby resulting in an oscillatory movement. Abrasive wear is a process in which a hard, sharp indenter is pressed into the surface of a softer work piece and plows a groove thereby resulting in the removal of material from the softer surface.

lubrication. Many, probably more than several hundreds, different wear testing arrangements and procedures are used in laboratories around the world and described in technical literature. However big difference of one arrangement as compared with another, a wear tester will always involve two components loaded against and relatively moving each other. The movement can be driven by a motor or by an electro-magnetic device. For convenient purpose, the material or component being investigated is normally referred to as specimen, the other termed as counter face.

CHAPTER 2

LITERATURE SURVEY

Dapeng Zhou et al., designed and deposited double-layered and triple layered APS YSZ/SPS GZO TBCs. Microstructures, thermal cycling performances and CMAS attack resistance of both TBCs systems were investigated. During thermal cycling test, both TBCs systems exhibited an extremely longer lifetime than conventional single-layered APS YSZ TBCs. This probably can be attributed to the high strain tolerance microstructures of TBCs and the better sintering resistance of GZO.

Yasin Ozgurluk et al., exposed YSZ, Gd₂Zr₂O₇, YSZ/Gd₂Zr₂O₇ TBC systems to 45 wt.% Na₂SO₄ and 55 wt.% V₂O₅ molten salt mixtures at 1000 °C temperature. TBC samples were investigated and compared using scanning electron microscope (SEM), energy dispersive spectroscopy (EDS) analysis and X-ray diffractometer (XRD). The hot corrosion failure mechanisms of YSZ, Gd₂Zr₂O₇ and YSZ/Gd₂Zr₂O₇ TBCs in the molten salts were evaluated. Hot corrosion molten salts severely damaged the column morphology of the EB-PVD method, reducing the thermal insulation properties and strain tolerance of TBCs.

Satyapal Mahade et al., In this work, compared the erosion resistance at room temperature of standard 8YSZ single-layer TBC along with GZ/YSZ multi-layered TBCs that were deposited by suspension plasma spray process. Single-layer 8YSZ had a higher erosion resistance than GZ/YSZ multi-layered TBCs despite of its higher porosity content and slightly lower hardness among the as-sprayed TBCs. A denser GZ top layer in the case of triple-layer TBC helped in slightly improving the erosion resistance compared to the GZ/YSZ double-layer TBC.

Mustafa Guven Gok et al., evaluated the production methods, design process, thermal and mechanical properties, failure mechanism, CMAS and hot corrosion resistance, and laser surface modification process of GZ-based TBCs.

It was found that it is possible to further improve the thermal conductivity and thermal failure properties of the GZ-based TBCs by using different coating architectures such as multilayer and functionally graded designs. GZ-based TBCs have a significant advantage in terms of its CMAS and hot corrosion resistance.

Satyapal Mahade et al., in their work found that although the failure modes under different thermal cyclic conditions differed for the investigated TBCs, durability was shown to be superior for 400GZ/100YSZ TBC. Further improvement in the durability of 400GZ/100YSZ TBC could be achieved by opting for a denser GZ microstructure (due to improved fracture toughness) as failure in BRT in this work was shown to be in the GZ layer close to the YSZ interface.

Mustafa Guven Gok et al., in their study inferred that thermal shock life time of the GZ/CYSZ coatings having multilayered and functionally graded designs was longer than single layered GZ TBC. This situation was attributed to the decreasing thermal stress in the MLED and FGed GZ/CYSZ coatings due to the

CYSZ having higher CTE than GZ. Results of the CMAS and hot corrosion tests showed that surfaces of YSZ and FG8 reacted differently with the CMAS + hot corrosion products.

Bobzin.K et al studied the friction and wear behavior of NiCoCrAlY and mixture of NiCoCrAlY and yttria partially stabilized zirconia. The wear behavior was tested by pin on disc method. The abrasion rating of the coating produced with the NiCoCrAlY + 5 wt.% YPSZ powder was half of the rating of the commercial

NiCoCrAlY coating. This showed that the ceramic mixed conventional coating has high wear resistance than the conventional NiCoCrAlY coatings.

Kristina Brinkiene et al studied the wear properties of plasma sprayed coatings. By the analysis of worn surfaces, the dominant wear mechanism for the plasma- sprayed coatings was abrasive wear. The higher wear resistance was specific to the plasma coatings with high zirconia content too

CHAPTER 3

AIM AND SCOPE OF THE PRESENT INVESTIGATION

3.1 AIM:

To determine the thermal and tribological behavior of double-layered YSZ/GZO samples coated using atmospheric plasma spraying (APS) technique in comparison with single layered YSZ and GZO samples.

3.2 OBJECTIVES OF STUDY

- To produce Yb₂O₃ doped Gd₂Zr₂O₇ thermal barrier coating in varied ratios on Hastelloy X nickel based super alloy
- To conduct hot corrosion test using Na₂SO₄+V₂O₅ molten salt test
- To analyse and the identify the effect of doping.

CHAPTER 4

Material and Methods

1. MATERIAL

- HASTELLOY X – material is used in aerospace industries in various parts of the gas turbines like turbine blades, vanes combustion chamber etc and hence it is selected as the substrate.
- NiCrAlY is selected for bond coat because of its good adherence b/w nickel super alloy substrate and ceramic top coat.
- Gd₂Zr₂O₇ is selected as the primary and ceramic top coat material and Yb₂O₃ is selected for dopant to improve the mechanical properties of the Gd₂Zr₂O₇ TBC
- HASTELLOY X was purchased locally from an Indian supplier.
- Ytterbium Oxide Yb₂O₃ was purchased from thermofisher scientific.
- Gadolinium Zirconate (Gd₂Zr₂O₇) was imported from china.

Methods

Substrate preparation.

The Hastelloy X substrate was cut into 20 mm dia discs using wire cut edm technique.

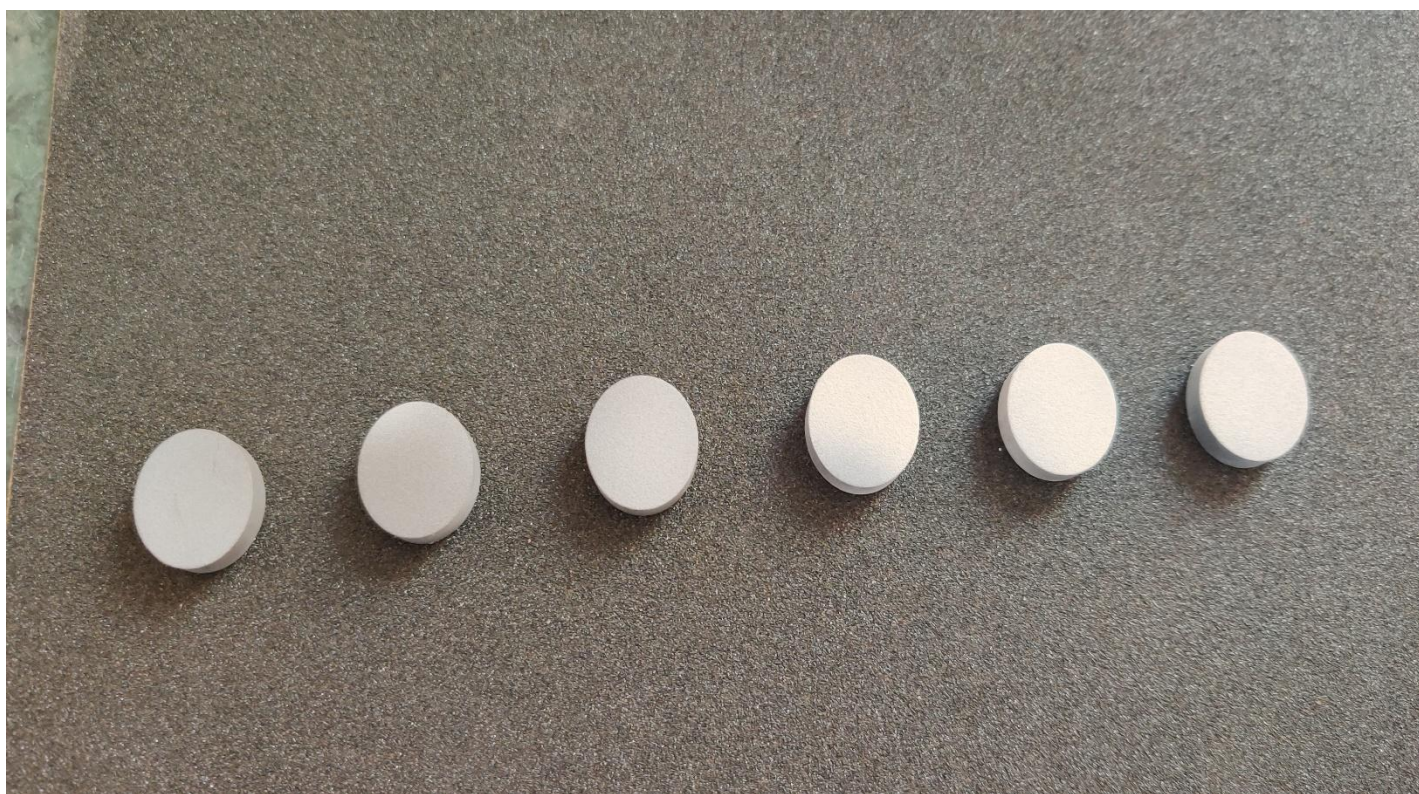


Figure 4.1 Cutting and Polishing

The samples were polished using silicon carbide emery papers of 100, 200, 300, 400, 600, 800 and 1000 grit sizes. The substrates were finally sand blasted using alumina particle at high velocity in

order to erode the top layer of the coating and thus making the surface suitable for depositing the bond coat

Doping the powder using ball

Gadolinium zirconate and ytterbium oxide were mixed together and 3 different materials prepared

- a) 9YbGZ was prepared by mixing 9wt% of Yb_2O_3 with 91 wt% of Gadolinium zirconate mixed together using a high energy ball mill.
- b) 12YbGZ was prepared by mixing 12wt% of Yb_2O_3 with 88 wt% of Gadolinium zirconate mixed together using a high energy ball mill.
- c) 15YbGZ was prepared by mixing 15wt% of Yb_2O_3 with 85 wt% of Gadolinium zirconate mixed together using a high energy ball mill.

Atmospheric plasma spray coating

All the substrates were deposited with the bond coat to a thickness of 120 microns approximately using atmospheric plasma spray coating. Ball milled 9YbGZ powder was deposited on bond coated substrate to produce 9YbGZ TBC as shown in figure.

And similarly 12YbGZ and 15YbGZ ball milled powder were deposited on top of bond coat to 250 to 300 microns to produce 12YbGZ and 15YbGZ as shown in the figure.

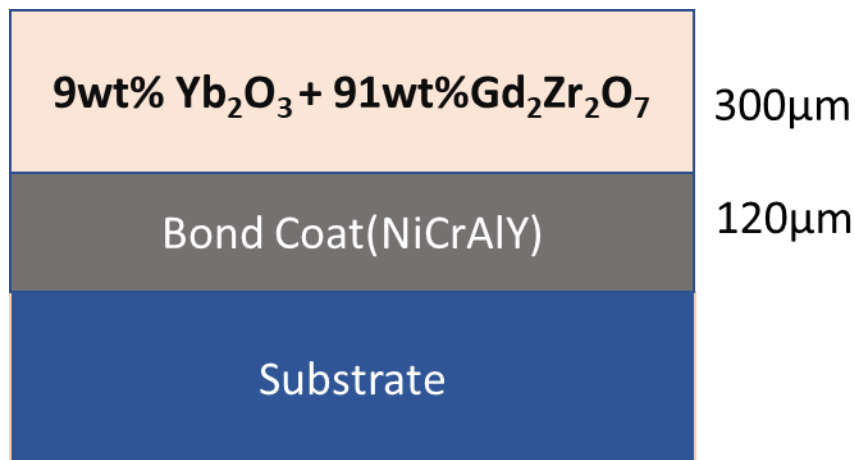


Figure 4.2 YbGZ TBC

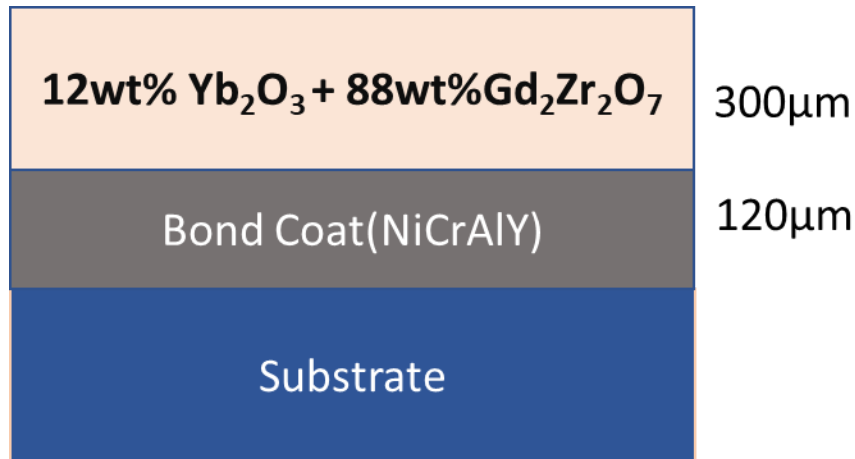


Figure 4.3 YbGZ TBC

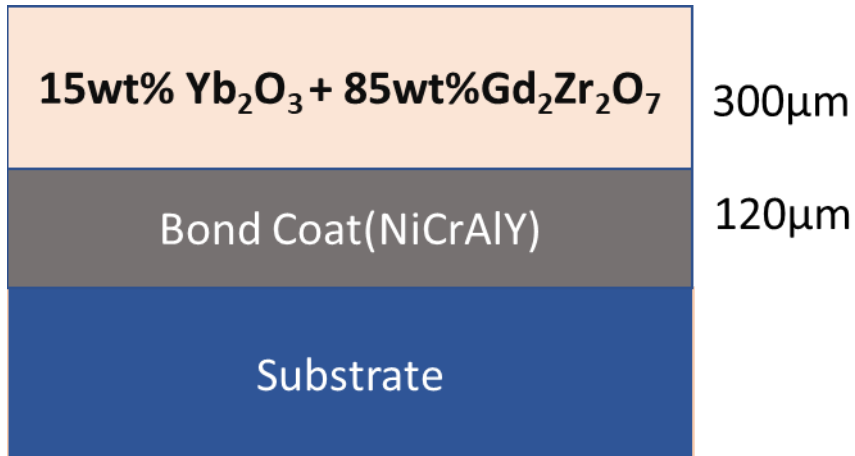


Figure 4.3.1 YbGZ TBC

TESTING

Isothermal oxidation test

The thermal stability of Yb_2O_3 doped GZ TBCs was performed by isothermal oxidation test (IOT) in the muffle furnace at 1423 K continuously. The sample was positioned separately over the crucible and placed in the furnace. The samples were thermally treated from room temperature to 1273 K with heating at heated to 1423 K at the rate of 5° min^{-1} and the 1423 K temperature was constantly maintained throughout the experiment. Constant temperature with prolonged dwelling periods was used to evaluate the thermal stability of the coating against sintering and oxidizing

environment. The furnace door was opened at a regular interval of 50 hours and the coating were visually inspected of any physical damage and furnace door closed immediately without allowing the loss in temperature of the furnace. Once a coating develops a crack or spallation the sample is removed from the furnace and phase change is analysed.

Thermal cyclic test

To assess the coating lifetime, thermal cycling test (TCT) was carried out by a programmable automated air furnace operated at 1423 K for a dwelling time of one hour followed by cooling down to room temperature by forced air flow for 5 min. The furnace consisted of two chambers. In the first chamber, the samples were pre-heated up to the testing temperature of 1423 K and samples were placed for 1 h, and then moved to the second chamber, where the samples were cooled down to room temperature by forced air flow. This heating and cooling periods are considered as one cycle and this cycle was repeated until 20% failure of the coating were observed. Failed coatings are removed from the furnace and failure was analysed.

Hot corrosion test

Most fuels contain small traces of vanadium. The vanadium is oxidized to different vanadates. Furthermore, the presence of vanadium accelerates the diffusion of oxygen through the fused salt layer to the metal substrate; vanadates can be present in semiconducting or ionic form, where the semiconducting form has significantly higher corrosivity as the oxygen is transported via oxygen vacancies. Ionic form in contrast transports oxygen by diffusion of the vanadates, which is significantly slower. The semiconducting form is rich on vanadium pentoxide. At high temperatures or lower availability of oxygen, refractory oxides such as vanadium dioxide and vanadium trioxide were formed. These do not promote corrosion. However, vanadium pentoxide is formed at high temperatures. Various composition ratios of vanadates are formed with sodium oxide. Vanadates of composition approximating $\text{Na}_2\text{O} \cdot 6\text{V}_2\text{O}_5$ have the highest corrosion rates at the temperatures between 593°C and 816°C; at lower temperatures the vanadate is in solid state, at higher temperatures vanadates with higher proportion of vanadium provide higher corrosion rates. ²² The solubility of the passivation layer oxides in the molten vanadates depends on the composition of the oxide layer. Iron (III) oxide is readily soluble in vanadates between $\text{Na}_2\text{O} \cdot 6\text{V}_2\text{O}_5$ and $6\text{Na}_2\text{O} \cdot \text{V}_2\text{O}_5$, at temperatures below 705 °C which amounts equal to the mass of the vanadate. This composition

range is common for ashes, which aggravates the problem. Chromium (III) oxide, nickel (II) oxide, and cobalt (II) oxide are less soluble in vanadates; they convert the vanadates to less corrosive ionic form and their vanadates are tightly adherent, refractory and acting as oxygen barriers. The corrosion rate by vanadates can be lowered by lowering the amount of excess air for combustion (thus forming preferentially the refractory oxides), refractory coatings of the exposed surfaces, or use of high-chromium alloys.

Hot corrosion test was carried out in presence of 55 wt % Na_2SO_4 - 45 wt % V_2O_5 at 1000 °C. 4 mg/cm² of Na_2SO_4 -60% V_2O_5 (eutectic mixture) salt was uniformly applied over the surface of the coatings. The samples were then dried at 200 °C and maintained at 1000 °C to isothermal HC test. The exposure temperature was maintained just below the lower critical temperature to test the coating at the extreme operating without altering the alloy properties. Samples were monitored regular for any signs of corrosion and failure and coating were subjected to the corrosion test until 20 % failure that is crack or spallation of the coating occurs.

CHAPTER 5

RESULTS AND DISCUSSIONS

Coating

All the substrates were deposited with NiCrAlY bond coat and then deposited with 9YbGZ , 12YbGZ and 15YbGZ ball milled powder using Air plasma spray coating technique to produce the Yb₂O₃ doped gadolinium zirconate TBC. The substrate thickness were measured before coating and labeled and tabulated. And the thickness after deposition of coating was measured tabulated. The difference gives is the coating thickness. All the substrates were coating to average thickness of 300 to 350 microns approximately. The coated samples then are subjected to thermal analysis.

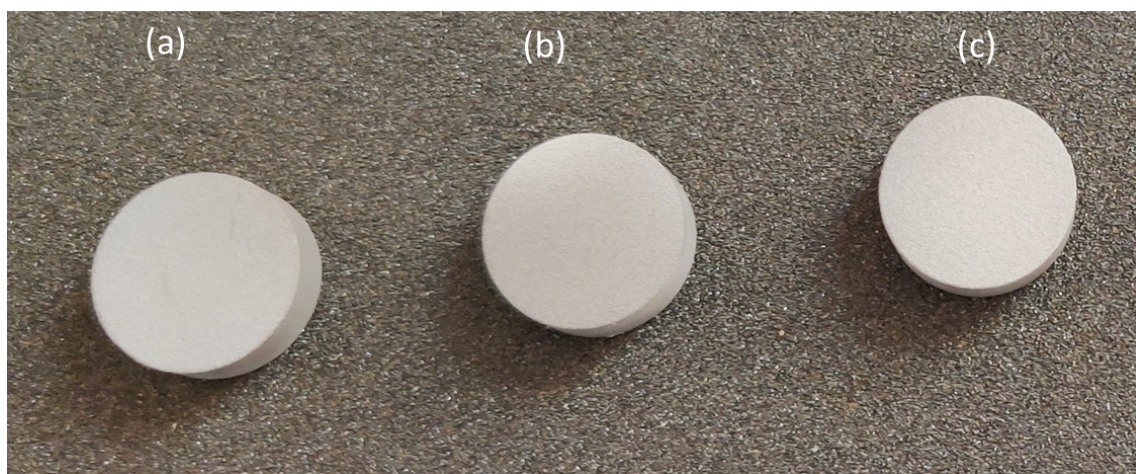


Figure 5.1 (a) 9YbGZ TBC (b) 12YbGZ TBC (c) 15YbGZ TBC

Isothermal oxidation test

The coated substrates were subjected to thermal oxidation in a furnace 1150 degrees Celsius for

500 hours. All the coatings did not show any sign of degradation until 300 hours. 9YbGZ TBC coating started developing a crack after 350 hours and more than 20 % failure of coating was observed after 360 hours. The other 12YbGZ TBC and 15YbGZ TBC did not show any sign of degradation until 350 hours more than 20 % failure of the coating was observed after 400 hours of isothermal oxidation test. And complete failure of the both 12YbGZ TBC and 15YbGZ TBC occurred after 450 hours. Top coat completely eroded after 450 hours of isothermal oxidation test.

Thermal cyclic fatigue test

The coated samples were placed in a muffle furnace preheated to 1150 degrees Celsius and the coatings are heated for 55 minutes and immediately removed from the furnace and cooled using pressurized air and brought to room temperature within 5 minutes this cycle was repeated until 20 percent failure of the coating was observed.

9YbGZ TBC coating was first coating show signs of failure the earliest the coating started developing crack along the circumference of the disc after 150 hours and after 160 cycles more than 20 % failure of the coating was observed. 12YbGZ TBC coating and 15YbGZ TBC coating did not show any sign of failure until 200 cycles.

After 240 cycles 12YbGZ TBC coating developed a swelling along the edge and also 15YbGZ TBC coating developed a crack along the after 250 hours and both coating developed more than 20 % spallation after 270 cycles.

Hot corrosion test

The Na_2SO_4 and V_2O_5 Molten salt hot corrosion test was performed on all the coatings. 55wt % Na_2SO_4 and 45 wt% of V_2O_5 were mixed together with small amount of distilled water to form a salt paste.

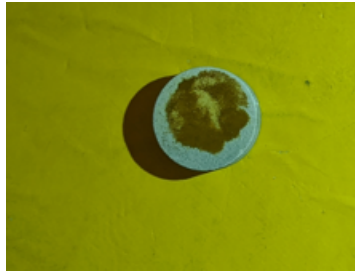


Figure 5.2 . Coating after applying salt paste

This was applied on the surface of the coating. And the samples were placed in the furnace and heated to 1273 K and observed for failure every 5 hours.

All the coating withstood the experiment for 30 hours without any sign failure due to corrosion. Top layer of the coating was deposited with the salt reacted with the molten and reactant products formed. They acts as a protective barrier and do not alloy any further corrosion to occur but in the isothermal condition the coating fail eventually after 40 hours one after other starting from 9YbGZ TBC followed by 12 9YbGZ TBC and finally 15YbGZ TBC in the span of 15 hours.

Conclusion

Yb_2O_3 was selected a dopant to improve the thermal cyclic and hot corrosion behavior of the gadolinium zirconate thermal barrier coating. The GZ was doped with 9%, 12% and 15% Yb_2O_3 using ball mill and the doped powder was deposited on NiCrAlY Bond coated Hastelloy X disc substrates of 20 mm dia to a overall thickness of 300 to 350 microns. The TBCs were subjected to isothermal oxidation test , thermal cyclic test and hot corrosion test and the conclusions are as follows.

- isothermal oxidation showed that the life of GZ was significant improved after doping. All the coating performed better than undoped GZ. And also with the increase in the dopant concentration the isothermal oxidation life is improved.
- Similarly in thermal cyclic fatigue test increase in the dopant concentration improves the cyclic life of the coating. Both the coating failed around the same number of cycles but the failure of 12YbGZ was much severe than 15YbGZ.
- All the doped coating have excellent hot corrosion resistance compared to undoped GZ. All three doped TBC failed in the 35th to 40th hours of testing. And failure of 15YbGZ was much less compared to 9YbGZ and 12YbGZ.

References

- [1] Anderson A., Ramachandran S., Corrosion Behaviour of partially stabilized Zirconia Coated Steel, National Journal on Advances in Building Sciences and Mechanics, Oct 2010, Vol.1, No.2, pp.40-42.
- [2] Anderson A., Ramachandran S, Hot corrosion behavior of Thermal barrier ceramic coatings on mild steel substrates, National Journal on Manufacturing Technology & Management, Sep.2012, Vol.1, No.2, pp.25-29. [IF-0.2534]
- [3] Bobzin K, Schlafer T, Richardt K, Bruhl M. (2008), "Friction and wear behaviour of NiCoCrAlY and mixture of NiCoCrAlY and yttria partially stabilized zirconia", Journal of thermal spray technology, Vol. 12, Issue 4, pp.576-596.
- [4] Brinkiene, Kristina & Kėželis, Romualdas & Čėsniėnė, Jūratė & Mėčius, Vladas & Žunda, Audrius. (2008). Characterization of Wear Properties of Plasma Sprayed Ceramic Coatings. 14.

[5] Canumalla, Ramachandra & Lee, Kang & Tewari, Surendra. (2003). Durability of TBCs with a Surface Environmental Barrier Layer Under Thermal Cycling in Air and in Molten Salt. *Surface and Coatings Technology*. 172. 150-157. 10.1016/S0257-8972(03)00260-3.

[6] Devarajan, Dinesh & Rani, Revati & Kumar, Niranjana & Panda, Kalpataru & A M, Kamalan kirubakaran & Parasuraman, Kuppusami & Baskaran, R.. (2019). Tribochemistry of TaN, TiAlN and TaAlN coatings under ambient atmosphere and high-vacuum sliding conditions. *Applied Surface Science*. 499. 143989. 10.1016/j.apsusc.2019.143989.

[7] Doleker, Kadir & Ozgurluk, Yasin & Ahlatci, Hayrettin & Karaoglanli, Abdullah. (2018). Isothermal Oxidation Behavior of Gadolinium Zirconate ($Gd_2Zr_2O_7$) Thermal Barrier Coatings (TBCs) produced by Electron Beam Physical Vapor Deposition (EB-PVD) technique. *Open Chemistry*. 16. 986-991. 10.1515/chem-2018-0112.

[8] Doleker, Kadir & Karaoglanli, Abdullah. (2016). Comparison of oxidation behavior of YSZ and $Gd_2Zr_2O_7$ thermal barrier coatings (TBCs). *Surface and Coatings Technology*. 318. 10.1016/j.surfcoat.2016.12.078.

[9] Doleker, Kadir & Odabas, Okan & Ozgurluk, Yasin & Asgarov, Khangardash & Karaoglanli, Abdullah. (2019). Effect of high temperature oxidation on Inconel 718 and Inconel 718/YSZ/ $Gd_2Zr_2O_7$. *Materials Research Express*. 6. 10.1088/2053-1591/ab26d8.

[10] Dudnik, E. & Lakiza, Sergii & Hrechanyuk, N. & Ruban, A. & Red'ko, V. & Hlabay, M. & Myloserdov, A (2018). The $Gd_2Zr_2O_7$ -Based Materials for Thermal

Barrier Coatings. Powder Metallurgy and Metal Ceramics. 57. 10.1007/s11106-018-9983z.

[11] Frommherz, Martin & Scholz, Alfred & Oechsner, M. & Bakan, Emine & Vaßen, Robert. (2015). Gadolinium zirconate/YSZ thermal barrier coatings: Mixed-mode interfacial fracture toughness and sintering behavior. Surface and Coatings Technology. 286. 10.1016/j.surfcoat.2015.12.012.

[12] Gök, Mustafa & Goller, Gultekin. (2019). State of the Art of Gadolinium Zirconate Based Thermal Barrier Coatings: Design, Processing and Characterization. 10.5772/intechopen.85451.

[13] Gök, Mustafa & Goller, Gultekin. (2017). Microstructural characterization of GZ/CYSZ thermal barrier coatings after thermal shock and CMAS+hot corrosion test. Journal of the European Ceramic Society. 37. 2501-2508. 10.1016/j.jeurceramsoc.2017.02.004.

[14] Golewski, Przemysław & Sadowski, Tomasz. (2019). The Influence of TBC Aging on Crack Propagation Due to Foreign Object Impact. Materials. 12. 1488. 10.3390/ma12091488.

[15] Gond, Dinesh & Puri, D & Prakash, satya. (2011). Hot Corrosion Behaviour of Yttria-Stabilised Zirconia as Plasma Sprayed Coated Boiler Steel in Air and Salt at 900°C under Cyclic Condition. Journal of Minerals and Materials Characterization and Engineering. 10. 10.4236/jmmce.2011.105035.

[16] G Purushotham, (2017) Performance Study of Yttria-stabilized Zirconia and Gadolinium Zirconate Coating for Nickel-base Alloy for Turbine Application, Indian Journal of Advances in Chemical Science 5(4).

- [17] Kaplan, Mustafa & Uyaner, Mesut & Avcu, Egemen & Yildiran Avcu, Yasemin & Karaoglanli, Abdullah. (2018). Solid particle erosion behavior of thermal barrier coatings produced by atmospheric plasma spray technique. *Mechanics of Advanced Materials and Structures*. 1-7. 10.1080/15376494.2018.1444221.
- [18] Karaoglanli, Abdullah & Doleker, Kadir & Ozgurluk, Yasin. (2019). Interface failure behavior of yttria stabilized zirconia (YSZ), La₂Zr₂O₇, Gd₂Zr₂O₇, YSZ/La₂Zr₂O₇ and YSZ/Gd₂Zr₂O₇ thermal barrier coatings (TBCs) in thermal cyclic exposure. *Materials Characterization*. 159. 110072. 10.1016/j.matchar.2019.110072.
- [19] Kokini, Klod & DeJonge, Jeffery & Rangaraj, Sudarshan & Beardsley, Brad. (2002). Thermal shock of functionally graded thermal barrier coatings with similar thermal resistance. *Surface and Coatings Technology*. 154. 223-231. 10.1016/S0257-8972(02)00031-2.
- [20] Mahade, S., Curry, N., Björklund, S. et al. Erosion Performance of Gadolinium Zirconate-Based Thermal Barrier Coatings Processed by Suspension Plasma Spray. *J Therm Spray Tech* 26, 108–115 (2017). <https://doi.org/10.1007/s11666-016-0479-4>
- [21] Mahade, Satyapal & Jonnalagadda, krishna praveen & Curry, Nicholas & Li, Xin-Hai & Bjorklund, Stefan & Markocsan, Nicolaie & Peng, Lin. (2017). Engineered architectures of gadolinium zirconate based thermal barrier coatings subjected to hot corrosion test. *Surface & Coatings Technology*. 328. 361-370. 10.1016/j.surfcoat.2017.09.005.
- [22] Mahade, Satyapal & Curry, Nicholas & Björklund, Stefan & Markocsan, Nicolaie

- & Joshi, S.V (2019). Durability of Gadolinium Zirconate/YSZ Double-Layered Thermal Barrier Coatings under Different Thermal Cyclic Test Conditions. *Materials*. 12. 10.3390/ma12142238.
- [23] Mudgal, Deepa & Singh, Surendra & Prakash, satya. (2012). High Temperature Cyclic Oxidation Behavior of Ni and Co Based Superalloys. *Journal of Minerals and Materials Characterization & Engineering*. 11. 211-219. 10.4236/jmmce.2012.113017.
- [24] Ozgurluk, Yasin & Doleker, Kadir & Karaoglanli, Abdullah. (2017). Hot corrosion behavior of YSZ, $Gd_2Zr_2O_7$ and YSZ/ $Gd_2Zr_2O_7$ thermal barrier coatings exposed to molten sulfate and vanadate salt. *Applied Surface Science*. 438. 10.1016/j.apsusc.2017.09.047.
- [25] Scrivani, Andrea & Rizzi, G. & Bardi, Ugo & Giolli, C. & Muniz-Miranda, Maurizio & Ciattini, S. & Fossati, A. & Borgioli, F (2007). Thermal Fatigue Behavior of Thick and Porous Thermal Barrier Coatings Systems. *Journal of Thermal Spray Technology*. 16. 816-821. 10.1007/s11666-007-9128-2.
- [26] Zhenghao Gan, Heong Wah N.G, (2004), "Cyclic thermal shock behaviour on plasma sprayed graded coatings", *Material science and engineering*, Vol.385, Issues 1-2, pp.314-324
- [27] Zhou, Dapeng & Mack, Daniel & Bakan, Emine & Mauer, Georg & Sebold, Doris & Guillon, Olivier & Vaßen, Robert. (2019). Thermal Cycling Performances of Multilayered Yttria Stabilized Zirconia/Gadolinium Zirconate Thermal Barrier Coatings. *Journal of the American Ceramic Society*. 10.1111/jace.16862.
- [28] Zhu, Dongming & Bansal, Narottam & Lee, Kang & Miller, Robert. (2001).

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Coating Materials.