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Study of Refractory Materials Usage in Aerospace Engines Technology

Thesis Submitted in Partial Fulfillment of the Requirements for the
Degree of Bachelor of Engineering. (BEng Honor)

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الآية

قال سبحانه: ﴿ أَلَمْ يَرَوْا إِلَى الطَّيْرِ مُسَخَّرَاتٍ فِي جَوْ السَّمَاءِ مَا يُمْسِكُهُنَّ إِلَّا اللَّهُ إِنَّ فِي ذَلِكَ لَآيَاتٍ لِّقَوْمٍ يُؤْمِنُونَ ﴾ سورة النحل {79}.

Abstract

When engine parts are subjected to a high temperature, their life time and performance will reduce due to the defects result from that high temperature.

This report shows the definition of refractory materials, its properties and the effect of using them in rockets engines (nozzles) and aircrafts engines (turbine blades).

A turbine blade studied by using ANSYS 16.0 software in order to show the effect of thermal barrier coating which expose noticeable reduction in the temperature penetrating the blade's layers, hence the thermal barrier coating increase the durability of the blade by decreasing the temperature subjected to the basic blade material.

Supersonic turbine blade materials percentage displayed by using X-Ray florescent test.

التجريد

عند تعريض اجزاء المحرك لدرجات حرارة عالية يقل العمر التشغيلي لها و اداؤها نتيجة للتشوهات الناشئة في الاجزاء نتيجة لتعرضها للحرارة العالية .

هذا التقرير يوضح تعريف المواد الحرارية ، خصائصها و أثر استخدامها في محركات الصواريخ و محركات الطائرات .

لتوضيح اثر طلاء العزل الحراري مما أظهر نقصان ANSYS 16.0 تمت دراسة ريشه توربينية باستخدام برنامج ملحوظ في الحرارة المخترقة لطبقات الريشة ولذلك العزل الحراري يزيد تحميلية الريشة و ذلك بتقليل درجة الحرارة المسلطه علي المادة الاساسية للريشه. كما تم عمل اختبار الاشعة تحت البنفسجية على ريشة توربينة لتوضيح نسب المواد المكونة لها.

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Dedication

To Our fathers the men whom learning
us the life

To the our dear mothers who looks after
us when we were kids

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List of abbreviation

AD	Apparent Density
APS	Air Plasma Sparing
ASM	American Society for Metals
ASTM	American Society for Testing and Material
BD	Bulk Density
CMC	Ceramic Matrix Composite
CVD	Chemical Vapor Deposition
EB-PVD	Electron Beam Physical Vapor Deposition
HMOR	Hot Modulus of Rupture
LPPS	Low Pressure Plasma Sparing
MOR	Modules of Rupture
NASA	National Aeronautics and Space Administration
PCE	Pyrometric Cone Equivalent
PIM	Powder Injection Molding
P/M	Powder Metallurgy
TBC	Thermal Barrier Coating
TEUL	Thermal Expansion Under Load
TGO	Thermal Growth Oxidation

1 Chapter One: Introduction

1.1 Overview

Refractory materials are material having high melting points, with properties that make them suitable to act as heat-resisting barriers between high and low temperature zones.

Rocket nozzles and turbine blades and many aerospace engine's parts are subjected to very high temperature that leads to shortage its life time.

Refractory materials provide thermal resistance up to 1500°C or more so it can increase the parts and structure life time and make the operation more efficiently.

Using refractory materials at rocket nozzles and turbine blades give the engine more space to operate better and give more thrust.

1.2 Problem Statement

The high temperature subjected to the engine parts like rocket nozzles and turbine blades leads to thermal stresses, creep, erosion or other defects that leads to reduce its quality and its operation time.

1.3 Proposed solution

Use refractory materials at the parts that subjected to a high temperature

1.4 Aims and Objectives

1.4.1 Aim

To play a good role in improving engines materials and performance.

1.4.2 Objectives

- Study the usage of refractory materials on rockets engines
- Study the usage of refractory materials on aircraft engines
- Study the effect of thermal barrier coating on turbine blades

1.5 Methodology

Date collected from journals, scientific papers and relative reports to write the literature review, then the utilization of refractory materials have been presented as fabricating materials on rockets nozzles and as coating material in turbine blades.

Supersonic turbine blade materials percentage displayed by X-Ray florescent test using X-Ray florescent gun (X-MET 5000).

A turbine blade with thermal barrier coating and other one without thermal barrier coating have been drawn using CATIA V5 software and then transformed to ANSYS 16.0 software to make the thermal analysis and a comparison have been done between the two blades to show the effect of adding the coat layer to the blade and then the result submitted in graph and that results was discussed and marked conclusion and reach to objectives report.

1.6 Outlines of research

Chapter one was an introduction and the literature review was represented in chapter two then in chapter three the usage of refractory materials in aerospace engines was showed then the case study , result and discussion represented in chapter four and five respectively and the last chapter contained the conclusion and recommendations

2 Chapter Two: Literature Review

2.1 CERAMIC

The word ceramic is derived from the Greek word (koromiko's).

The term covers inorganic non-metallic materials which are formed by the action of heat. Up until the 1950s or so the most important of these were the traditional clays, made into pottery, bricks, tiles and the like, along with cement and glass. Clay based ceramic are described in the article on pottery.

A material of ceramic and metal is known as (cermet).

The American Society for Testing and Material (ASTM) define ceramic article as:

'An article having a glazed or unglazed body of crystalline or partly crystalline structure or of glass, which body is produced from essentially inorganic, non-metallic substances and either is formed and simultaneously or subsequently matured by the action of the heat'

This is done either by the action of heat, or at lower temperatures using precipitation reactions from high purity chemical solutions. The term includes the purification of raw materials, the study and production of the chemical compounds concerned, there is the science and technology of creating objects from inorganic, non-metallic materials. Formation into components and the study of their structure, composition and properties. [1]

Ceramic materials may have a crystalline or partly crystalline structure, with long-range order on atomic scale. Glass ceramics may have an amorphous or glassy structure, with limited or short-range atomic order. They are either formed from a molten mass that solidifies on cooling, formed and matured by the action of heat, or chemically synthesized at low temperatures using, for example, hydrothermal or sol-gel synthesis.

The special character of ceramic materials gives rise to many applications in materials engineering, electrical engineering, chemical engineering and mechanical engineering. As ceramics are heat resistant, they can be used for many tasks that materials like metal and polymers are unsuitable for. Ceramic materials are used in a

wide range of industries, including mining, aerospace, medicine, refinery, food and chemical industries, packaging science, electronics, industrial and transmission electricity, and guided light wave transmission.

2.1.1 CLASSIFICATION OF TECHNICAL CERMIC:

1-Oxides:

(Alumina, zirconia)

2-Non-oxides:

(Carbides, borides, nitrides, silicide)

3-compsite:

(Particulate, reinforced combination of oxides and non-oxides.)[1]

2.1.2 Engineering Ceramics

Ceramic		Applications
Alumina	Al_2O_3	Cutting tools, dies, wear resistant parts and coatings, oxidation barriers, bearing surfaces, high temperature components, turbine parts, hip implants, body amour, radiation shielding.
silicon Carbide	SiC	
silicon Nitride	Si_3N_4	
zirconia	ZrO_2	
Boron Nitride	BN	

Table 1. Types of engineering ceramics

2.1.3 CERAMIC PROPERTIES

The properties of ceramic materials, like all materials, are dictated by the types of atoms present, the types of bonding between the atoms, and the way the atoms are packed together. This is known as the atomic scale structure. Most ceramics are made up of two

or more elements. This is called a compound. For example, alumina (Al_2O_3) is a compound made up of aluminum atoms and oxygen atoms.

The atoms in ceramic materials are held together by a chemical bond. The two most common chemical bonds for ceramic materials are covalent and ionic. For metals, the chemical bond is called the metallic bond. The bonding of atoms together is much stronger in covalent and ionic bonding than in metallic. That is why, generally speaking, metals are ductile and ceramics are brittle. Due to ceramic materials wide range of properties, they are used for a multitude of applications. [1]

In general, most ceramics are:

- a. Hard,
- b. Wear-resistant,
- c. Refractory,
- d. Thermal insulators,
- e. Electrical insulators,
- f. Nonmagnetic,
- g. Oxidation resistant,
- h. Prone to thermal shock, and
- i. Chemically stable.

2.1.4 Properties of ceramic materials

- 1- Higher endurance to high temperatures.
- 2- High resistance to deformation in plastic case exposure to flatten,
- 3- The resistance to aging and environmental conditions.
- 4- Poor conductors of electricity and heat.
- 5- Resistance redox processes.
- 6- Resistance to thermal stress.
- 7- Lacking property ductility which features material.

2.1.5 The important properties of ceramics

1- Weight

In spacecraft weight is an important factor of economic and technical aspects of the ceramic materials are used

2- Durability

Satellites are designed to take longer, ranging from (10 to 30)year in this property of properties available in ceramic materials as shown in the trials that creep rate is very small comparing with metals .

3- Thermal shock resistances

Exposed turbine engines used in aircraft for thermal transfer regular where a short time and this is what makes it imperative need to configure full knowledge of all the coefficients of thermal expansion.

2.1.6 Strength of ceramics

A material's strength is dependent on its microstructure. The engineering processes to which a material is subjected can alter this microstructure. The varieties of strengthening mechanisms that alter the strength of a material include the mechanism of grain boundary strengthening. Thus, although yield strength is maximized with decreasing grain size, ultimately very small grain sizes make the material brittle. Considered in tandem with the fact that the yield strength is the parameter that predicts plastic deformation in the material, one can make informed decisions on how to increase the strength of a material depending on its microstructural properties and the desired end effect.

Theoretically, a material could be made infinitely strong if the grains are made infinitely small. This is unfortunately, impossible because the lower limit of grain size is a single unit cell of the material. Even then, if the grains of a material are the size of a single unit cell, then the material is in fact amorphous, not crystalline. Since there is no long range order and dislocations cannot be defined in an amorphous material.

It has been observed experimentally that the microstructure with the highest yield strength is a grain size of about 10 nanometers, because grains smaller than this undergo another yielding mechanism, grain boundary sliding producing engineering materials with this ideal grain size is difficult because of the limitations of initial particle sizes inherent to Nano Materials and nanotechnology.

2.1.7 Examples for applications for advanced ceramics in the aerospace industry

Ceramics are increasingly being used in commercial and military aircraft, and have been used in space shuttles for many years.

Electrical applications

Advanced ceramics underpin the electronics industry and the average aircraft is packed full of electronics. Gradually, these electrical components, such as sensors, antennas, capacitors and resistors, are getting smaller and smaller and more capable. Therefore, this is a major area of development for advanced ceramics.

As far back as the 1990's, the design team of Concorde, the world's then only supersonic airliner, selected a glass ceramic, MACOR®, developed by Corning Incorporated, as it needed a lightweight and electrically insulating technical material for use in the engine control and management system. MACOR® was initially developed by Corning as it wanted a material that is stable at high temperatures and could be machined like plastic.

Structural applications

Structural ceramics, crystalline inorganic non-metals, are used in aerospace as Thermal Barrier Coatings (TBCs) in the hot part of the engine. Or, it is used in composites either as reinforcement and/or as matrix such as CMCs – ceramic matrix composites. Being lightweight and tough tends to be a main driver for using a ceramic composite. From here, engineers need to assess how a composite will perform at an elevated temperature in an air atmosphere and what impact erosion will have on the system and at what rate.

Ceramics are lighter than most metals and stable at temperatures, substantially above high grade technical plastics. As a result of this and other properties, structural ceramic applications include thermal protection systems in rocket exhaust cones, insulating tiles for the space shuttle, missile nose cones and engine components.

Looking for a performing material, the United States' Space Shuttle Orbiter program team decided to use the MACOR® Machinable Glass Ceramic at all hinge points, windows, and doors on the reusable Space Shuttle Orbiter. Also, large pieces of the Corning glass ceramic have been used in a NASA spaceborne gamma radiation detector.[1]

Turbine Applications

Using technical ceramics for various parts of the engine have been looked at for the past 30-40 years. Currently, there is quite a lot of activity in developing silicon carbide (SiC/SiC composites) for use in jet engine turbines, mainly concentrated on the turbine blades. The main driver is fuel efficiency as engineers seek to run the jet engine without the need for cooling channels that currently stop the metal alloy blades from melting. If the blades were made of ceramic composites, which could deal with 1,500-1,600° Celsius, the engine could run at higher temperatures. Therefore, the energy efficiency would increase using less fuel and the airplane could fly further or more efficiently.

To conclude, ceramics are integral to aeronautics and aerospace. They are ubiquitous in the electrical systems and facilitate the drive towards more powerful, yet smaller electrical devices. Structural ceramics are increasing in popularity and deployment. They also offer huge potential for transforming aircraft engine capabilities that could dramatically influence the aeronautics of the future.[1]

2.2 REFRACTORIES

2.2.1 Introduction to refractories

Refractories are material having high melting points, with properties that make them suitable to act as heat-resisting barriers between high and low temperature zones.

The refractory materials can be used in hot sections in satellite, space shuttle, rockets, subsonic and supersonic aircrafts.

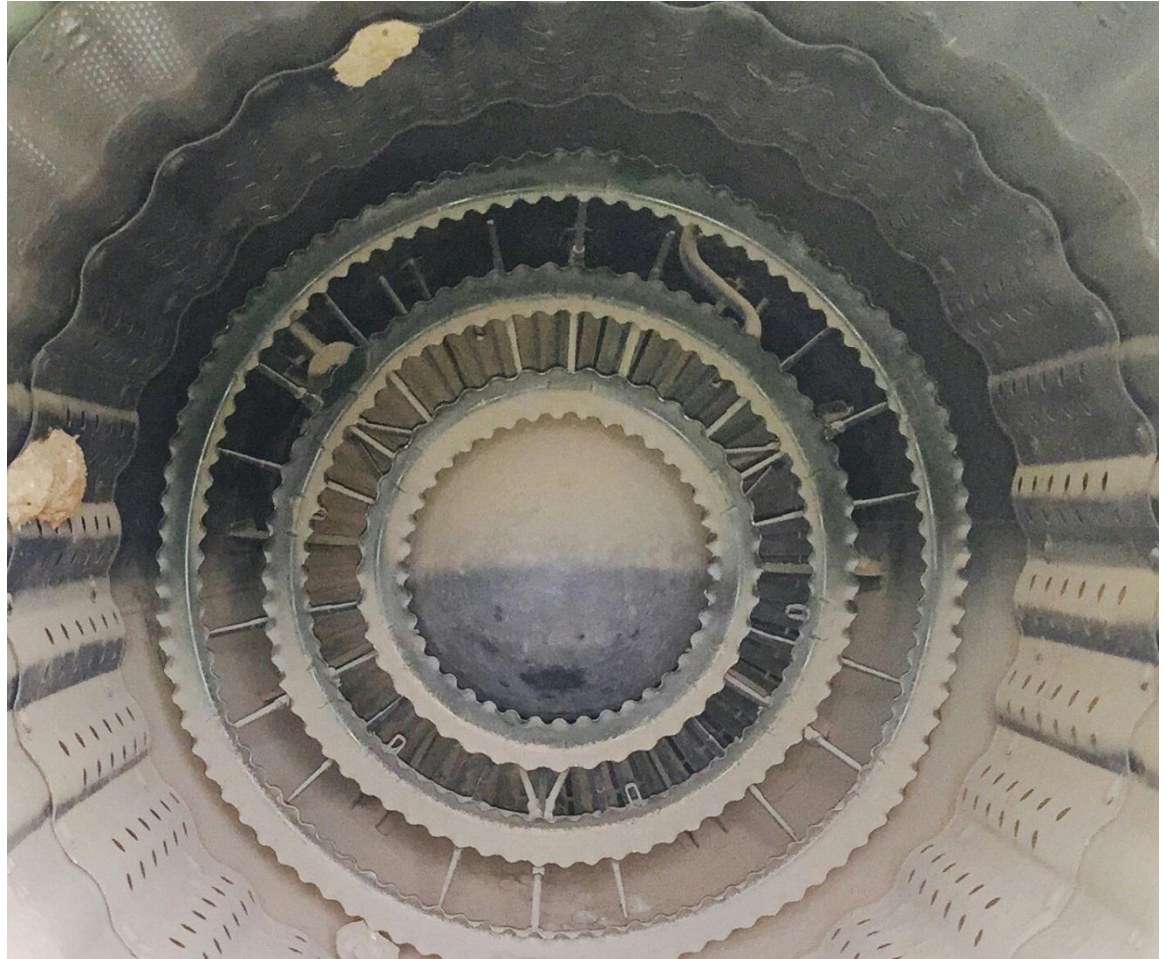


Figure 1.MIG-21 afterburner

Refractories are useful in constructing application-specific high temperature areas/surfaces.

The value of refractories is judged not merely by the cost of the material itself, but by the nature of job and/or its performance in a particular situation. Specifically, the performance of a refractory depends on its qualities and quantities in three phases—solid, glass/liquid, and pores—which govern the ultimate property of a refractory material.

A 'green bond' is developed by mixing various sizes of similar refractory material having some strengths and property, which are changed during firing/heat treatment in the course of service. The qualities of refractories are thus dependent on their chemical, physical, mineralogical and thermal properties.[2]

Refractory materials are generally tailor-made on the basis of:

- a. Process parameters like temperature profile, mode of operation, chemical environment, etc.
- b. Expected quality characteristics
- c. Best techniques for engineering and application, so that the final physical, chemical, mechanical, and thermal properties are compatible to the application

Refractory materials are used in two different forms, namely, shaped and unshaped products.

2.2.2 Shaped refractories

The most familiar form of refractory materials is the rectangular brick shape. However, refractories are presently available in a variety of shapes and sizes for convenience in construction.

2.2.3 Unshaped refractories

There is a class of refractory materials which can form joint-less lining. This class of refractory materials is called monolithic. All unshaped refractory materials have this ability to form joint-less lining, and hence they are grouped as monolithic.

1. Unshaped refractories are manufactured in powder form as granular material and known as castables, ramming masses, gunning mix, plastic masses, etc.
2. Castables are mixed with water before casting.
3. Ramming masses are first mixed with water or any other liquid to the required quality, and then rammed either manually or pneumatically with a heavy rammer.
4. Gunning masses are passed through a machine in which the powder material is put under pressure and conveyed pneumatically through a hose. The material gets

mixed up with water before it exits the hose nozzle, and sticks to the surface on which it is applied to form a lining.

5. Plastic masses comprise ready-mix material that is applied manually in the furnace to form a lining.[2]

2.2.4 Classification

The primary constituents of any refractory may be a single compound like alumina, silica or mullite, or a combination of these materials. Their melting points are as follows:

1. Silica (SiO_2) — 1723 °C
2. Alumina (Al_2O_3) — 2050 °C
3. Mullite (71.8% Al_2O_3 , 28.2% SiO_2) — 1996 °C

Relatively small amounts of oxides of sodium (Na_2O) and potassium (K_2O), and other minerals containing calcium (CaO), magnesium (MgO), titanium (TiO_2), and iron oxide, promote liquid-phase formation at low temperatures. Hence, the presence of these oxides in refractories must be limited to trace amounts to avoid formation of low temperature liquid phase.

Refractories in which the predominant constituents are alumina, silica or a combination thereof may be placed in the following categories:

1. Fireclay refractory
2. High alumina refractory
3. Silica refractory
4. Mullite refractory

2.2.4.1 Fireclay refractory

Fireclays are hydrated aluminum silicates that occur naturally. They are sufficiently pure to serve as raw materials for refractories. The principal mineral in fireclays is kaolinite. While other clay minerals may be present, the formula $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ can usually represent, the clay fraction. As kaolinite is heated to high temperatures when used to make refractories, it loses its water; theoretically, 45.9% alumina and 54.1% silica remain.

Plastic and semi-plastic fireclays, as their names indicate, develop varying degrees of plasticity when they are mixed with water. This is an important factor in the manufacture of fireclay bricks, because the plastic fireclays facilitate the forming process and act as a bonding phase for the raw and calcined flint clays, and they have greater variation in their impurity content.

2.2.4.2 Silica refractories

Silica bricks are made from raw materials that are essentially quartz. During the initial firing, alpha-quartz is first converted to beta-quartz, accompanied by an abrupt expansion at 573 °C. Slow rates of heating are required through this temperature range to prevent cracking, as the volume change is about 0.9%. Since the final firing temperature is somewhat over 1426 °C, the brick as it is put into service consists of cristobalite particles (properties of cristobalite are not affected by temperature fluctuation, provided the temperature does not drop below 600 °C), with possibly some having residual unconverted quartz cores.

2.2.4.3 High-Alumina Refractories

High-alumina bricks serve as a multi-purpose refractory material for severe environments. They are used extensively in the steel industry for such applications as hot metal cars, electric furnace roofs, piers and muffles for a variety of furnaces, and numerous applications where strength at high temperature is an essential requirement. The aluminum and glass industries use high-alumina refractories to keep the melt in the molten state.

Most high-alumina refractories are classified according to their alumina content, which could range from 50%-99%. They are designated as 50%, 60%, 70%, 80%, 85% and 90% alumina. Two classes of high-alumina refractories are distinguished by a microstructure that is essentially a single, crystalline phase. These are: (1) mullite refractories and (2) corundum refractories.

2.2.4.3.1 Mullite refractories

Mullite is about 72% alumina with 28% silica. The manufacturing procedures are designed to maximize the formation of the compound mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$). A refractory with 71.8% alumina and 28.2% silica will be composed of only mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) if fired at equilibrium conditions. However, the extent to which well-developed mullite crystalline form occurs in a refractory depends on the purity of the raw materials used and the manufacturing processes, particularly firing. Therefore, all high-alumina bricks with around 70% alumina may have a well-developed mullite phase. Mullite refractories have excellent volume stability and strength at high temperatures. They are highly suitable material for electric furnace roofs, blast furnaces and blast furnace stoves, hot metal cars, and the superstructure of glass tank furnaces.

2.2.4.3.2 Corundum refractories

The 99% alumina class of refractories is called corundum. These refractories comprise single-phase, polycrystalline, alpha-alumina.[2]

2.2.5 Properties of refractory materials

The quality of a refractory and its suitability for a particular application primarily depends on its physical, chemical and mineralogical properties. It may be possible to assess the quality of a refractory on the basis of a single property or a group of properties. The most common properties that are considered in selecting the optimum refractory lining configuration are listed below.

- i. Apparent porosity
- ii. Bulk density
- iii. Modulus of rupture (MOR)
- iv. Hot modulus of rupture (HMOR)
- v. Cold crushing strength
- vi. Pyrometric cone equivalent (PCE)
- vii. Thermal expansion
- viii. Thermal expansion under load (TEUL) and creep
- ix. Thermal conductivity

Both shaped and unshaped refractories are available in the market under different brand names with special features and for different applications. The analytical data on these products are generally provided in the company product brochures. However, purchasers are advised to get refractory samples analyzed once in a while to verify/cross check the supplier's claims as well as assess the quality of the procured refractory on their characteristics, consistency and variation in composition due to imperfect manufacturing.[2]

2.2.5.1 Apparent porosity

The apparent porosity is a measure of the effective open pore space in a refractory into which molten metal, slag, fluxes, vapors, etc. can penetrate and thereby contribute to eventual degradation of the structure. The porosity of any product is expressed as the average percentage of open pore space in the overall refractory volume.

2.2.5.2 Bulk density

The bulk density is generally considered in conjunction with apparent porosity. It is a measure of the weight of a given volume of refractory. For many refractories, the bulk density provides a general indication of the product quality. While evaluating a refractory brand or comparing several products of equivalent type (except insulating types), it is considered that the refractory with higher bulk density (generally concurrent with lower porosity) will be better in quality. The structure of a refractory having higher bulk density will be denser, resulting in better resistance to chemical attack, decreased metal penetration, better abrasion resistance and other related benefits.

2.2.5.3 Modulus of Rupture (MOR)

The modulus of rupture (MOR) is the flexural breaking strength of a refractory. MOR is measured at room temperature and expressed in pounds per square inch or kilograms per square centimeter.

2.2.5.4 Hot modulus of rupture (HMOR)

The hot modulus of rupture (HMOR) is the flexural breaking strength of a refractory at a chosen elevated temperature or over a range of temperatures. The structural integrity and general abrasion characteristics of a refractory can be estimated

from HMOR, making it an essential property to determine the suitability of a refractory in a certain temperature profile for a certain set of application conditions.

2.2.5.5 Cold crushing strength

The cold crushing strength is the capacity of a refractory to provide resistance to a compressive load at room temperature. It is the load, in pounds per square inch or kilograms per square centimeter, at which the refractory breaks.

2.2.5.6 Pyrometric cone equivalent (PCE)

The pyrometric cone equivalent (PCE) is a measure of the refractoriness and state of maturity of the material composition of a refractory product after firing. It represents the state at which a refractory mixture/composition starts becoming soft and deforms within a particular temperature range, depending upon the heating pattern in the firing stage.

Representative PCE values for selected refractories include cones 33-34 for super duty fireclay, cones 29-31 for medium duty fireclay and cones 36-37 for a 60% alumina product. The cone values reported for refractories are based on a defined standard time-temperature relationship, so different heating rates will result in different PCE values. PCE can be useful for quality control purposes to detect variations in batch chemistry that result from changes or errors in the raw material formulation.

2.2.5.7 Thermal expansion

Thermal expansion is the intrinsic characteristic of refractory products to expand on heating and contract on cooling. The dimensional changes of a refractory due to thermal expansion are commonly expressed in permanent linear change (%) and the coefficient of thermal expansion (length per unit length). [2]

2.2.5.8 Thermal expansion under load (TEUL) and creep

Dimensional changes take place in a refractory under a compressive load at elevated temperature. The dimensional change could be linear on increasing the temperature is known as thermal expansion under load (TEUL). The dimensional changes due to extended period of holding/soaking of a refractory at pre-selected temperature is

nonlinear, and leads to plastic deformation known as creep. More specifically, creep is the heat-activated plastic deformation of a body under stress as a function of time. TEUL and creep are typically determined in sequence in the same test, using the same sample.

2.2.5.9 Thermal conductivity

The thermal conductivity is defined as the quantity of heat that will flow through a unit area in a direction normal to the surface area in a defined time with a known temperature gradient under steady state conditions across the area. It indicates the general heat flow characteristics of refractories. The heat flow potential is higher with higher thermal conductivity value, and vice versa. High thermal conductivity refractories are required for some applications where good heat transfer is essential, such as coke oven walls, regenerators, muffles, and water-cooled furnace walls. However, refractories with lower thermal conductivity are preferred in industrial applications, as they help in conserving heat energy.

The thermal conductivity of refractories is dependent on factors such as chemical and mineralogical composition, temperature, porosity, extent of sintering, and furnace environment. Porosity is a significant factor in heat flow through refractories. The thermal conductivity of a refractory decreases on increasing its porosity.[2]

2.2.6 Quality assessment of refractory materials

The critical properties of a refractory should be analyzed for generic assessment of its quality, and to compare the analytical results with the quantitative values of the properties of the refractory that are supplied by the manufacturer.

2.2.6.1 Physical Analysis

All refractory materials contain pores of varying quantity. The majority of the physical properties, that is, density, strength, expansion, and thermal conductivity of materials, are directly influenced by the quantity and quality of these pores. Two types of pores—closed and open—are observed in a refractory. Pores which do not have any connection with the atmosphere are known as closed pores, while those that have access to the atmosphere are known as open pores. These are normally expressed in terms of percentage of total volume and could be calculated from the mass and volume of any

refractory material. The mass of a refractory could be measured either in solid state (W_{ss}) or in powder state (W_{ps}). Similarly, its volume too could be measured either in solid state (V_{ss}), which includes the volume of pores, or in powder state (V_{ps}), which does not include the volume of pores. It is also possible to measure the volume of pores (V_{pore}) present in a solid state of refractory material. ,, - pore.,

By analyzing porosity alone, it is possible to assess refractory quality. Porosity is defined as the ratio of volume of vacant spaces/pores (V_{pore}) to the total volume of material (V_{ss}) expressed in percentage. Therefore, porosity (%) = V_{pore} / V_{ss} in percentage.

Specific or true density is defined as the ratio of the weight of the material in powder state (W_{ps}) to its volume (V_{ps}) in the same state. The material is powdered to some definite size so that there are no pores available in the material.

Therefore, true density (TD, in grams/cubic centimeter) = mass (W_{ps}) in grams/volume of solid (V_{ps}) in cm^3 .

Bulk density (BD) is determined for refractory material having open and closed pores. It is the ratio of mass in solid state (W_s) to bulk volume (V_s) of a refractory.

Thereafter, the volume of open pores can be found out by some easy method (for instance, by filling the open pore areas with water or other liquid and measuring the volume of water/liquid, which gives the volume of open pores) to calculate the apparent density (AD) of the refractory. The apparent density (AD) is defined as the ratio of mass in solid state (W_s) to the resultant volume, which is obtained by adding the volume of solid (V_s) with the volume of closed pores (V_{pore}). AD is expressed in grams/ cubic centimeter.

Therefore, $AD = W_{ss} / (V_{ss} + V_{pore})$ grams/ cm^3

The quantities of total pores, open pores and closed pores can be determined using three density data: i.e., true density, bulk density, and apparent density. These values for any refractory could be easily obtained and are necessary for assessing its quality and expected performance. [2]

2.2.6.2 Chemical and mineralogical analysis

Refractories are identified by their major chemical constituents, which govern their quality and properties. It is essential to carry out complete chemical analysis of refractory materials for its quality assessment. As a thumb rule, it is known that the higher the alumina content, the better is the property. However, it is obvious that while the major chemical constituents of a refractory do play the most important role in determining its ability to perform, the minor constituents—mainly impurities also play a very important role in its performance.

Refractory materials are normally oxides having a tendency to react with one another at high temperature to form different compounds with different crystal structures. The mineralogical formation and crystal structures of the same chemical constituents will vary depending upon the extent of heat treatment/thermal exposure the material receives in manufacturing or in operating conditions. The crystal structure that forms will decide the performance of the refractory, as the resistance to corrosion/erosion behavior largely depends on it. Therefore, it is essential to know the microstructure of the refractory along with its chemical constituents.

Quality assessment could be carried out of the refractory material by analyzing randomly selected samples from the lot for complete chemical composition, apparent porosity, bulk density, apparent density, HMOR, and mullite content. However, estimation of mullite percentage will require X-Ray analysis, for which facilities are not available everywhere. Hence, mullite percentage has to be estimated from other physical tests, and an occasional check of this parameter will suffice.[2]

3 Chapter Three: Usage of Refractory Materials in Aerospace Engines

3.1 Using the refractory materials in rockets engine's

3.1.1 Introduction



Figure 2. Rocket takeoff

Refractory materials mainly uses in the ultra-high temperature areas and the most subjected area to a high temperature on rockets are the nozzle throat area so there is many studies are done to develop a rocket nozzle that reduce the erosion rate using refractory materials.

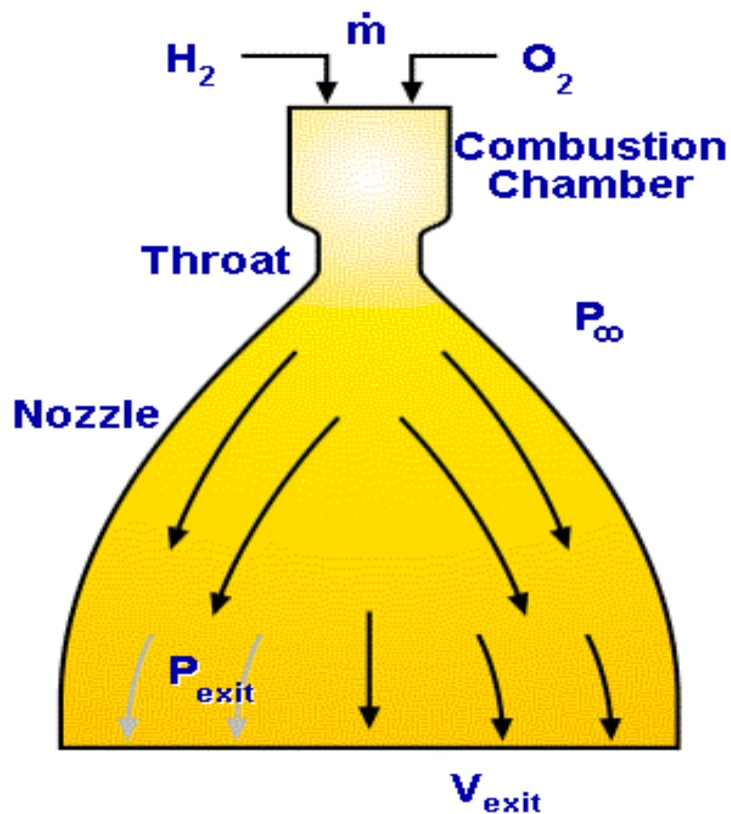


Figure 3. Simplified Drawn for Rocket Engine

Rocket nozzles are widely used for a mechanical part such as a tactical missile and weather and surveillance satellite. Such a rocket nozzle works in the high temperature, because the enormous amounts of exhaust gas containing a high temperature produced by combustion pass through throat-area which is the smallest cross-section area. Therefore, the material for a rocket nozzle must have good mechanical properties such as a high melting point, a good thermal shock resistance, and a low coefficient of thermal expansion to retain propulsion performance. In general, graphite and carbon-carbon composites have been widely used as nozzle materials to reduce the erosion rate of throat-area. However, the erosion rate of those materials is not enough to maintain propulsion.[3]

In this regard they have tried to employ different types of materials to reduce an increase of throat-area by erosion. A refractory metal is another representative material. Considering their thermal properties such as melting temperature, refractory metals are

possible candidate materials for a noneroding rocket nozzle in the ultra-high temperature and pressure. Refractory materials including niobium, tantalum, molybdenum and tungsten are the extraordinarily resistant materials against heat and wear. These materials have unique mechanical properties such as a high melting point, boiling point and density. Of all the refractory materials, rhenium has unique mechanical properties such that its melting temperature of 3180 °C exceeds all other metals except tungsten. Even though rhenium has a lower melting point than tungsten, rhenium has a better ductility at high temperature compared to other refractory materials. In addition, rhenium has the highest tensile strength among the refractory materials under high temperatures. Rhenium has a distinguishing mechanical property, the so-called rhenium effect. This mechanical property comes from its crystal structure i.e. rhenium has the closed-packed hexagonal structure, while other refractory metals have the body-centered cubic structure. Its hcp structure has a high solubility in transition metals having BCC and FCC structures. This characteristic enables rhenium to form an alloy e.g. W–Re (tungsten–rhenium alloy) and Mo–Re (molybdenum–rhenium alloy).[4]

These alloys increase mechanical properties such as tensile strength and plasticity, and enhance weld ability. In order to determine the optimum composition of Re-alloy, the phase change should be considered through the phase diagram. For instance, W–Re has the optimum solubility limitation of W with 26 wt. % Re to avoid the sigma (σ) phase which has a brittle mechanical property. There have been several studies for the refractory materials, especially related to the production method for rhenium alloys. As the most common method to form rhenium components, chemical vapor decomposition (CVD) and powder metallurgy (P/M) have been considered. Both methods are employed to fabricate the small or complex-shaped components. While CVD is considered as a clean method, it is not easy to produce the components in quantity. Although the P/M is suitable method for mass production, it is difficult to produce the required complex shape. In this regard, PIM (Powder Injection Molding) is an attractive method from the manufacturing point of view including shape complex and mass production. In manufacturing industries, the PIM process is a productive and cost-effective net-shaping process which combines advantages of both plastic injection molding and conventional powder metallurgy. This process has many advantages of shape complexity, tight

tolerances, and material selection of metals and ceramics. Once desired materials, mold geometries, and process parameters are decided, PIM is an appropriate process for mass production. The PIM process consists of four steps; (i) mixing — producing the pelletized feedstock of the powder and organic binders, (ii) molding — injecting the feedstock melt into the mold cavity, similar with thermoplastics; (iii) debinding — extracting or removing the organic binders out of injection molded part via solvents or the thermal energy, (iv) sintering — densifying the debound part from the low initial density to the high final density, close to the full density.[3, 5]

3.1.2 Erosion test

An erosion test have been done to show the properties of the nozzle that developed by the refractory materials.

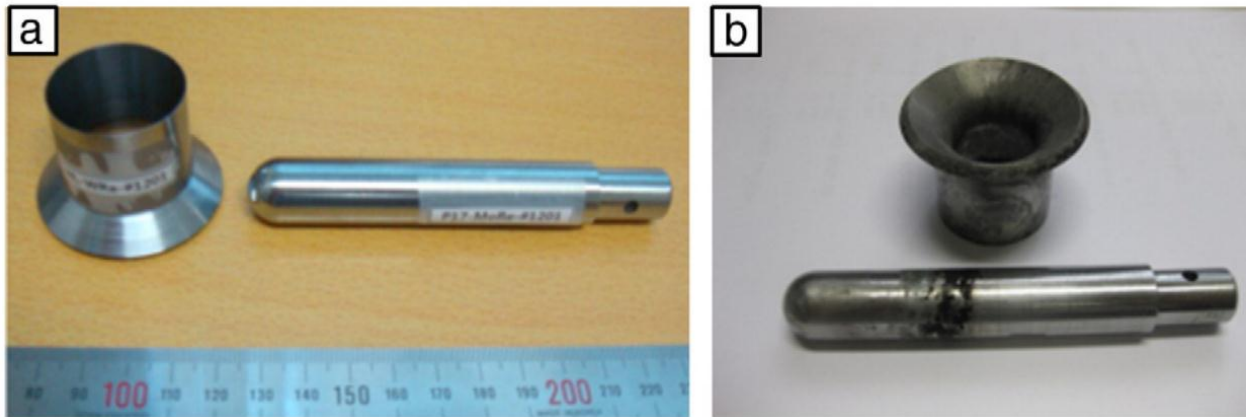


Figure 4. Rocket nozzle for eroding test (a) before erosion test, and (b) after erosion test.

Fig (4) Shows the rocket nozzle used in the erosion test. The tests were carried out under the two different pressure conditions. Even though there is no test standard for burning time of the erosion test, a lot of tests were carried out for less than 20 s. For instance, erosion measurement for 5 s burn times was performed by Don Mittendorf. In addition, ASM (American Society for Metals) international describes that “Rhenium-coated carbon has been evaluated for rocket engine exhaust nozzles that were required to operate for 20 s bursts”. Firstly, the test was carried out under the conditions of the incoming temperature of 3000 K and pressure of 2.76 ~ 9.65 MPa (400 ~ 1400 psi). The erosion rate obtained from the first test was 0 mm/s. i.e. there was no change in the diameter of the rocket nozzle. The second test was conducted under the relatively high pressure of average 10.34 MPa (1500 psi). The erosion rate of the second test was 0.009 mm/s. By comparison with the previously reported study, the measured erosion rates

were superior to the rocket nozzle made of pure W (erosion rate of pure W = 0.020–0.040 mm/s). Therefore, this rocket nozzle made of W–25 wt.% Re has outstanding erosion resistance, comparable with that of the pure W.[6]

After the erosion test, the hardness and microstructure for the cross-section of rocket nozzle were evaluated as shown in Fig (5).

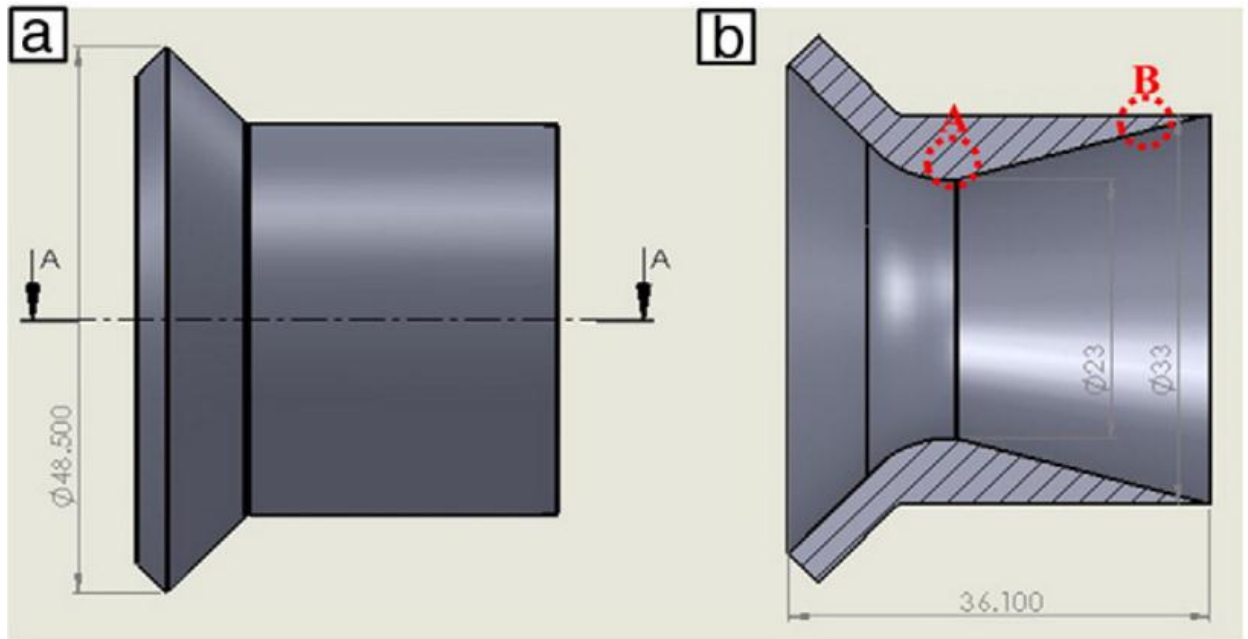


Figure 5. Measurement position of specimens for hardness (a) rocket nozzle configuration.

The hardnesses were measured using a standard Vickers hardness unit with a load of 200 N (20 kgf) in the highest erosion area (A) and the thinnest area (B) in the cross-section of the nozzle. Indentations were made along the lines located 80 μm depth from the inner surface in the A and B areas. Considering that the hardness, after eroding test, has to be measured on the eroded surface, Vickers scale having the relatively small indenter than the indenter of Rockwell is more appropriate. For comparison to the previously reported study, the obtained Vickers hardness data was converted to Rockwell hardness unit. In order to have reliability, the error between each measurement method was evaluated by simultaneously measuring hardness at the same area. The average values (13 times measurements) measured by Rockwell and Vickers. The calculated error of 1.3% was in a reasonable range. The obtained Vickers hardness data was converted to Rockwell hardness unit as shown in Fig (6).

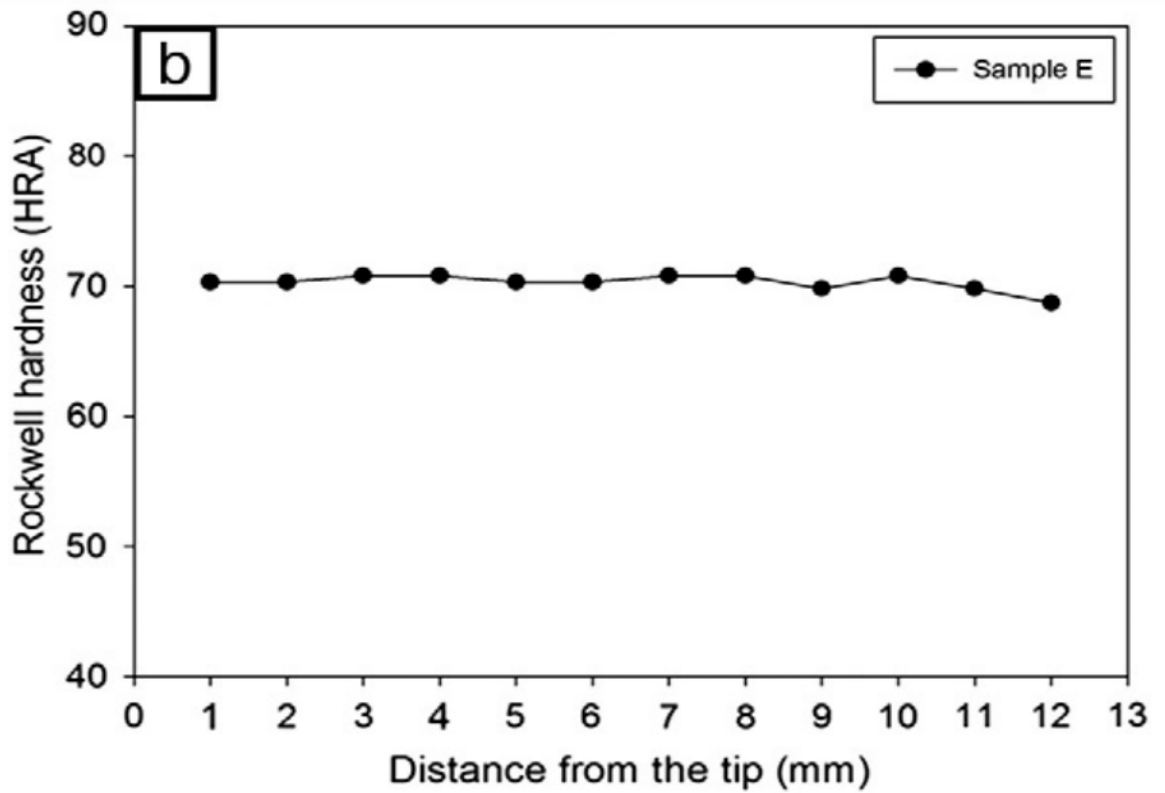
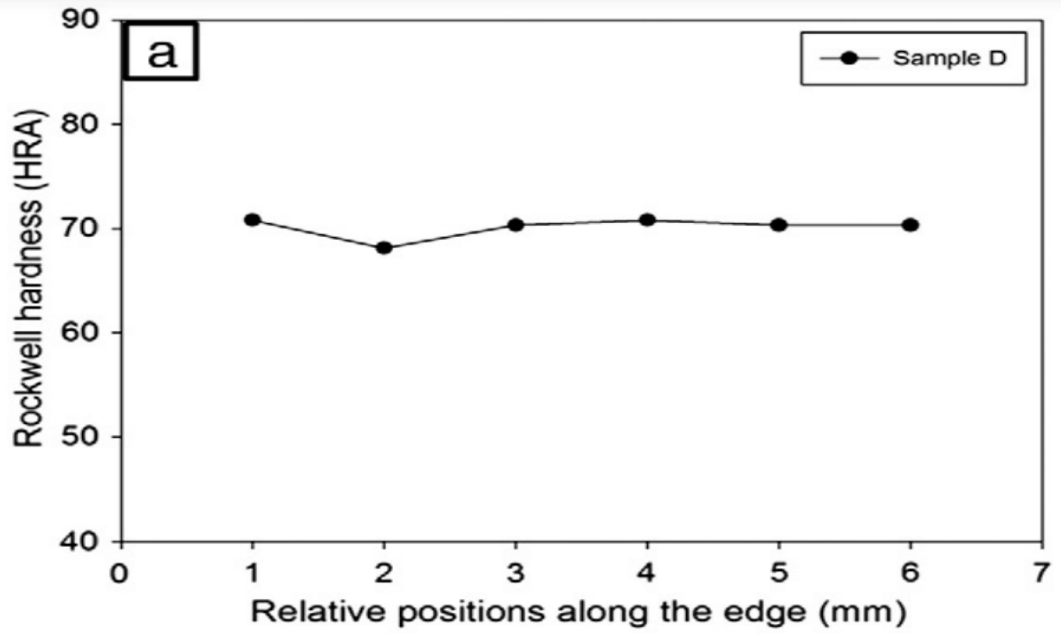


Figure 6. Hardness for rocket nozzle (a) at position of A, and (b) at position of B.

The hardness variations along the locations are very small. The average values of Rockwell hardness at position of A and B are 70.1 and 70.3, respectively. Compared with the hardness before the eroding test, the hardness remains nearly unchanged.[7]

3.2 Using the Refractory Materials in Aircraft's Engines

3.2.1 INTRODUCTION

In the next generation of power plant technology, both oxy fuel and hydrogen fuel may be utilized as the substitute for current combustion technology. Both future technologies in power generation may enable advanced turbines to operate more efficiently but at a significantly higher temperature condition compared to today's current power plant condition. Such advanced turbines with oxy fuel or hydrogen fuel operate approximately up to 1760 °C, while the current coal-fueled power plants operate at a temperature only up to 900 °C. Due to the high temperature operating condition, these technologies may require a change in its material design. One of the most important components in a power plant that will be affected is the turbine blades, since the availability of the power plant mainly depends on the lifespan of the blades.

The materials used to build turbine blades will likely require high temperature resistance in order to withstand such conditions. One of the potential means of protecting the blades is by applying a thermal barrier coating (TBC) on their surfaces. Such a coating may help to protect the nickel based super alloy blade from hot gas steam. Nevertheless, the TBC layer is also in contact with both the increasing operating metal temperature and the kinetics of the base material, each of which gradually degrades TBC durability, exposing itself to damage failures such as undulation, spallation, and cracking.

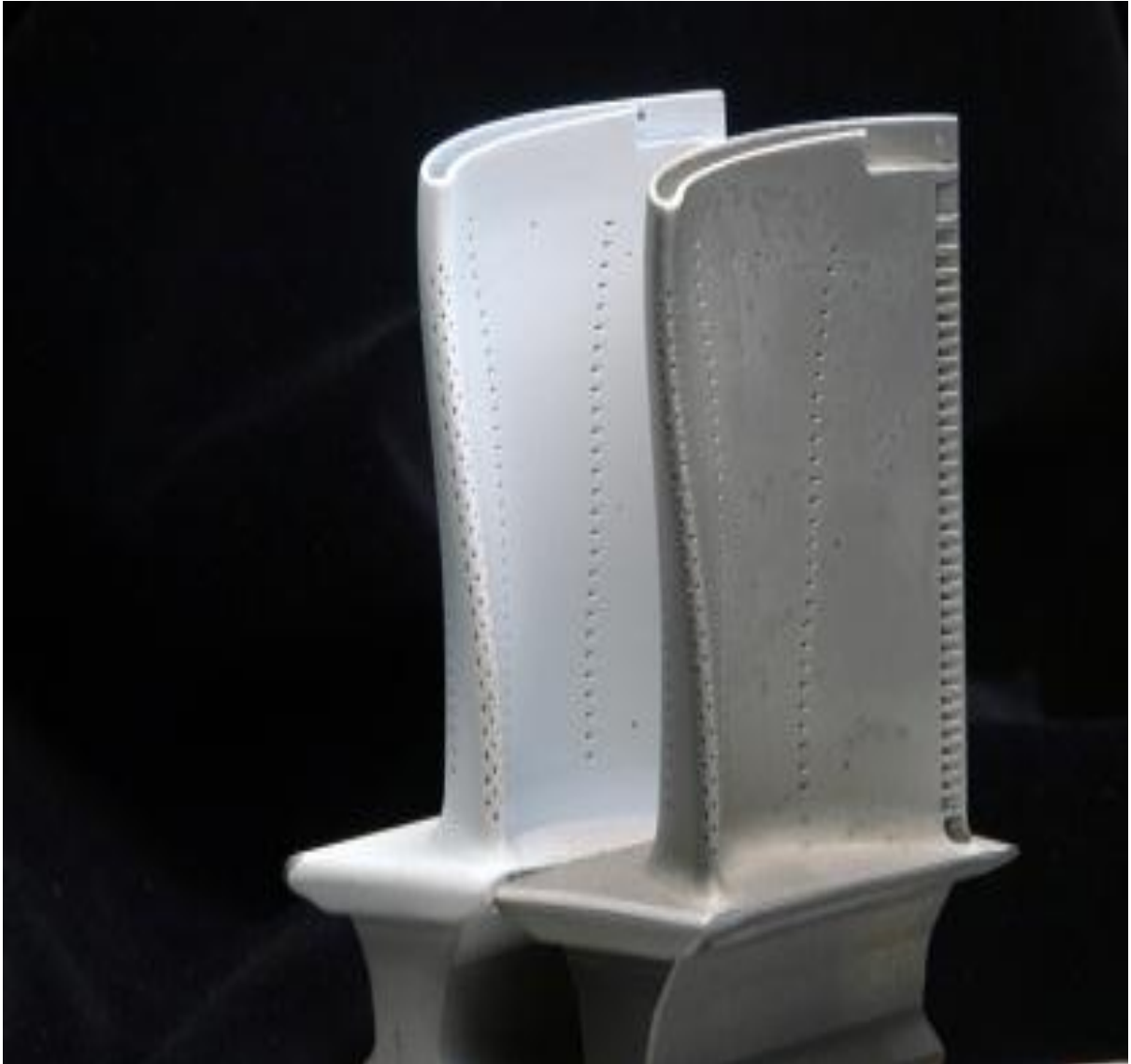


Figure 7.sample of coated and uncoated blade

3.2.2 BACKGROUND

Thermal Barrier Coating is widely used in aircraft and industrial gas turbine engines.

Commercial manufactured TBC system consists of two layers, a ceramic top coat and underlying metallic bond coat. The top coat is a composition of yttria-stabilized zirconia (YSZ) that can be composed by air plasma spraying (APS) or electron-beam physical vapor deposition (EB-PVD). The top coat has low thermal conductivity, high oxygen permeability, and relatively high coefficient of thermal expansion. Due to its low thermal

conductivity characteristic, its main function is to provide a thermal insulation on the turbine blades surface from the hot gas steam.

The metallic bond coat is normally made of MCrAlY overlay or a platinum modified diffusion aluminide (β -NiAl-Pt). The work on this study mainly focuses on APS TBC system with MCrAlY bond coat. Since the top coat has very high oxygen permeability while the bond coat is rich with aluminum properties, both layers inevitably form a protective, thermally grown oxide (TGO) scale of α -Al₂O₃ during thermal operation. This TGO scale provides strong attachment between the YSZ top layer and metallic bond coat layer.

All the layers existed in TBC system equip the TBC system with the capability of thermal insulation as well as oxidation resistant to protect nickel-based super alloy metal below it. TBC systems are able to create high temperature drop from about 140⁰C up to 250⁰C with cooling systems, which subsequently reduces the metal operating temperature. Nevertheless, the TGO is gradually thickening over the period of time during high temperature exposure.[8]

Hence, the crucial failures that associate with the TBC system are typically spallation and cracking of the thickening thermal growth oxidation (TGO) scale. Majority of the reviewed papers, then, agree that thermal growth oxidation (TGO) layer that is formed due to bond coat oxidation and interdiffusion with metallic bond coat strongly contributes to such failures. The following section will discuss the constitutes of the TBC systems in more details.

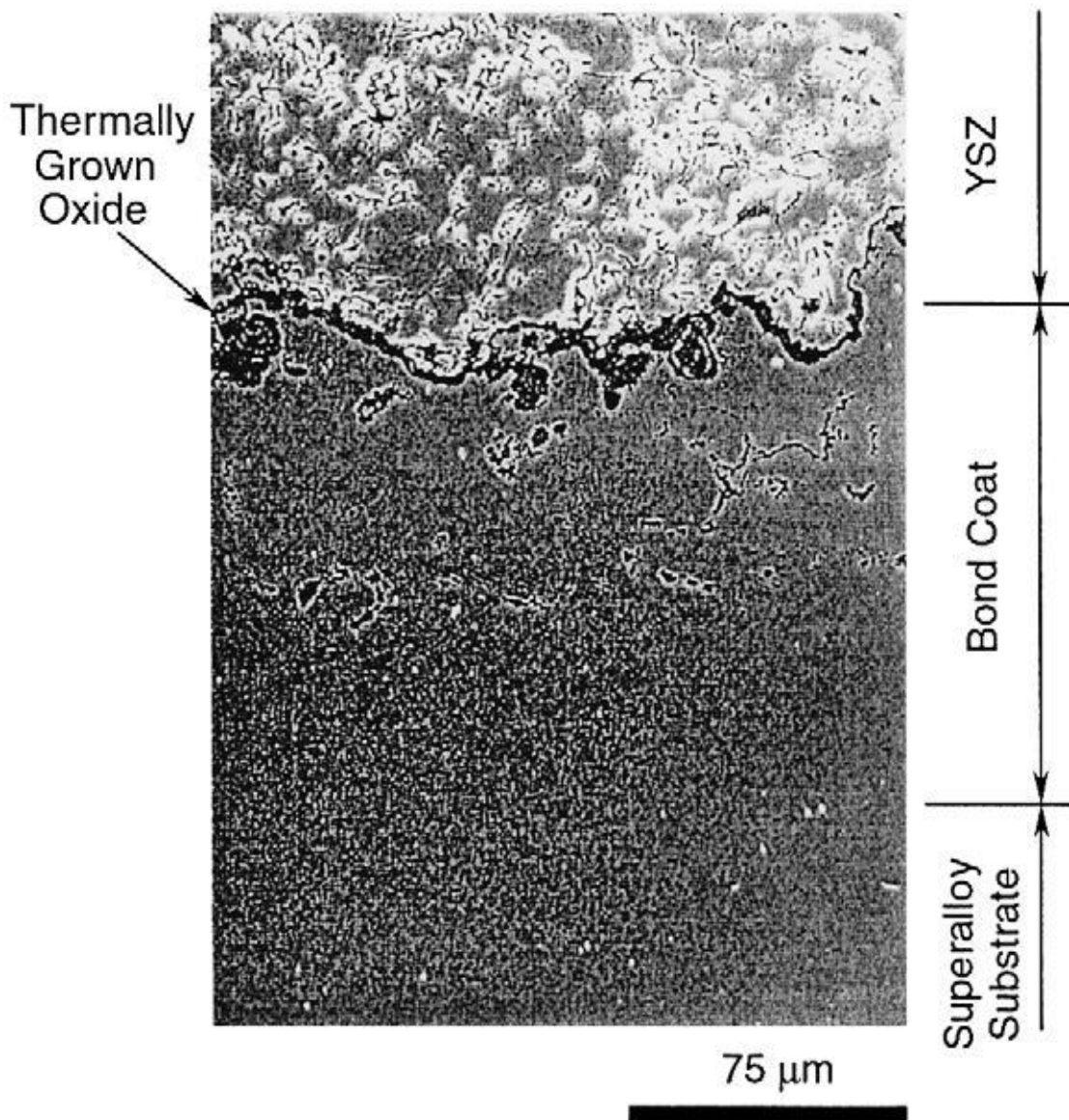


Figure 8. Microstructure of a typical plasma sprayed thermal barrier coating after 500 hours oxidation at 950°C (Busso). [9]

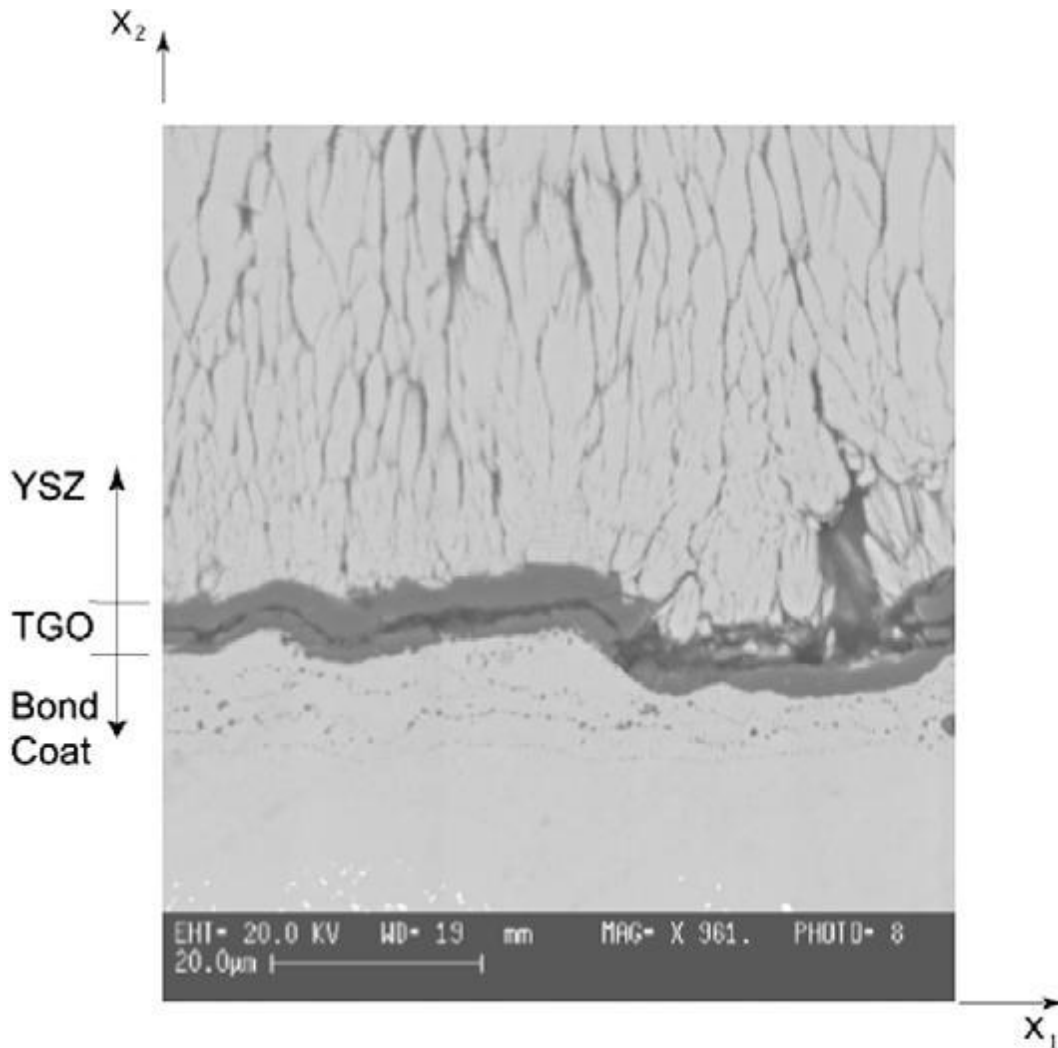


Figure 9A typical microstructure of an EB-PVD TBC system after 700 hours at 1000 °C (Busso). [10]

3.2.2.1 CERAMIC TOP COAT LAYER

The layer is made of Y_2O_3 (yttria) stabilized ZrO_2 (zirconia). Y_2O_3 is found to be empirically suitable to stabilize ZrO_2 compared to other different oxides (MgO , CeO_2 , Sc_2O_3 , In_2O_3 , CaO) because of its structure that can exist in three different polymorphs such as monoclinic, tetragonal, and cubic. The polymorphs structures of Y_2O_3 vary according to the composition and the temperature condition. For example, by adding 7 to 8 weight % which is around 4 to 4.5 mol% of Y_2O_3 into zirconia solid solution, Y_2O_3 can stabilize ZrO_2 tetragonal crystal structure especially metastable tetragonal-prime structure (t'-YSZ). This t' phase is considered as the most desirable and stable phase for TBC applications because it does not undergo martensitic transformation on cooling even

after multiple thermal cycles. As a result, Y_2O_3 has been found as a consistent stabilizer for zirconia solid solution, subsequently makes yttria-stabilized zirconia YSZ as the most applicable composition for thermal barrier coating applications. Nevertheless, the detailed reason is not yet being explained and remains one of the important aspects of ongoing research.

One of the most important material properties of the YSZ top coat is its low thermal conductivity, k at high temperature, which is around $2.3 \text{ Wm}^{-1}\text{K}^{-1}$ at 1000°C . The thermal conductivity is low because of the high distribution of point defects such as oxygen vacancies and substitutional solute atoms that can scatter heat-conducting phonons (lattice waves). Heat is transferred by lattice vibrations and radiation in electric insulators such as ZrO_2 .

Therefore, as more phonons and photons being scattered by the point defects in the lattice structure of the ZrO_2 ceramic, thermal conductivity can be efficiently reduced.

In addition, YSZ has a high thermal-expansion coefficient, α , which is around $(11.10^{-6} \text{ }^\circ\text{C}^{-1})$. It is comparable to the metallic bond coat thermal expansion coefficient $(14.10^{-6} \text{ }^\circ\text{C}^{-1})$. And thus it can lessen the thermal expansion mismatch stress between the metallic bond coat and ceramic top coat. YSZ ceramic top coat is also resistant to erosion and external impact because of its high hardness property, which is approximately 14 GPa. The density of YSZ layer is relatively low just about $6.4 \text{ Mg}\cdot\text{m}^{-3}$, yet it is useful for parasitic weight consideration in moving engine components. Another crucial aspect of the YSZ top coat is its high melting point.

This ceramic layer is resistant to elevated temperature up to approximately $\sim 2700^\circ\text{C}$ which makes YSZ as the most significant component in TBC system. There are two most important types of YSZ top layer coating depositions, air plasma spraying (APS) and electric-beam physical vapor deposition (EB-PVD). This paper, however, focuses on the APS TBC system life damage simulation since it is commonly used in power plant turbines.

3.2.2.1.1 ELECTRON-BEAM PHYSICAL-VAPOR DEPOSITED (EB-PVD) TBC

The ELECTRON-BEAM PHYSICAL-VAPOR DEPOSITED (EB-PVD) top coat is approximately $125 \mu\text{m}$ thick. The microstructural features of the top coat consist of a

thin region on polycrystalline YSZ with equiaxed grains near the ceramic/metal interface. The EB-PVD top coat is deposited into columns of YSZ grains with diameter of 2 to 10 μm . The columnar YSZ grains grow outwardly from the equiaxed-grain region to the top surface. Within the columnar YSZ grains, there is nanometer-scale porosity, and channels, normal to the ceramic/metal interface that separates the YSZ columns. This columnar grains separation can disconnect at elevated temperature, alleviating the effect from the stress that rises from thermal expansion mismatch. This behavior is known as "strain tolerance". The EB-PVD top coat is smoother than APS deposition. Plus, it is more durable and expensive compared to APS case. Thus, it is typically used in the most harsh temperature condition like in aircraft engines.

3.2.2.1.2 AIR-PLASMA-SPRAYED (APS) TBC

Unlike EB-PVD top coat, a typical APS top coat is slightly thicker than EB-PVD top coat with a thickness of 300 μm to 600 μm . The AIR-PLASMA-SPRAYED (APS) top coat structure consists of "splat" grain morphology which each "splat" has 1 to 5 μm thickness and about 200 to 400 μm diameter. Besides inter- "splat" boundaries, there are also cracks that exist parallel to the ceramic/metal, creating 15 to 25 vol% porosity within the APS TBC that contributes to low thermal conductivity and low elastic modulus of the system.

The weakness of the APS TBC is the undulating nature of the ceramic/metal interface that is actually needed in sticking together the top coat and the metal bond coat. This nature is found to be the cause of the undulation failures due to the stress it creates. The commercial production cost of APS system is relatively low. Hence, it becomes a preferable choice for applications that operate in slightly lower temperature condition and fewer thermal cycles such as in conventional power plant gas-turbine engines. However, the thermal-cycle life of APS top coat is usually shorter than EB-PVD TBC's life because of the growing microstructural defects parallel to the interface and also the roughness of the interface within the APS TBC. Table 1 below shows the material properties comparison of APS and EB-PVD TC systems at a room temperature.

3.2.2.2 BOND COAT LAYER

Metallic coatings for super alloys are typically NiCrAlY type which contains 15 to 25 weight % Chromium (Cr), 10-15% Aluminum (Al), and 0.2-0.5% Yttrium (Y) and β -NiAl phase. The bond coat has a typical thickness of 40 to 100 μ m, depending on the deposition method. Similar to YSZ top coat deposition, the metallic coatings are commonly deposited by using EB-PVD method or low pressure plasma spraying (LPPS) in today's gas turbines applications. The LPPS process is relatively cheaper than EB-PVD and becomes a favorable selection. Nonetheless, EBPVD has a quality advantage over LPPS.

The key physical property of the bond coat is its oxidation behavior. The metallic bond coat should be able to oxidize in order to form a nonporous and adherent oxide layer, which is called thermal growth oxidation layer. Therefore, the composition, microstructure, and surface condition of metallic bond coat are considered important to study in order to observe its influence on a TGO formation. The function of TGO layer is discussed in more detail in section 3.2.2.3 **Thermal Growth Oxidation layer**.

3.2.2.3 THERMAL GROWTH OXIDATION (TGO) LAYER

The thermal growth oxidation layer (TGO) α -Al₂O₃ is formed during the thermal operation and the oxidation of the metallic bond coat. The Al in bond coat slowly depletes and thickens the TGO layer. This TGO layer is considered the most crucial layer in the TBC system. Its growth during the thermal operation is responsible for the spallation failure of TBC system in many ways. One of the causes is from the stresses created inside the TGO. As the TGO thickens, the volume expands and at the same time the volume expansion is restrained by the top coat and bond coat layers. The restriction creates compressive "growth" stress (< 1 GPa) within the TGO.

Another source of stress is from thermal expansion mismatch between the TGO and the bond coat during cooling process. This thermal compressive residual stress is quite high as it can reach a maximum stress value that is about 2 to 6 GPa when the TGO is cooled down to ambient temperature. All these internal stresses can initiate and aggravate the development of micro cracks inside the TGO during thermal operation. As a result, total damage failure due to TBC spallation will occur from micro cracks

coalescence. Thus, one way that can be used to predict the damage failure of TBC is by investigating the stresses created inside the TGO layer.

3.2.3 SUMMARY

Gas turbines constitute a wide and good option for power generation used for both, industrial and aeronautical applications. This technology is requesting for better and more reliable materials to use mostly in those areas in which temperatures are extremely high; like, first row of turbines and combustion chamber.

Blades materials for turbine area in gas turbines have advanced rapidly in the last 2 decades. Nowadays, those blades are constructed using special alloys and are covered by special coats. Those modifications are intended to increase the allowed temperature up to 1500oC without cooling. In this sense, the overall efficiency increases.

Ceramic coating is applied to the surface of the turbine blade using several methods. The most important ones are: ELECTRON BEAM PHYSICAL VAPOR DEPOSITION (EB-PVD) and ARC PLASMA SPRAYABLE (APS) powder method.

4 Chapter Four: Case Study

Arbitrary turbine blade drawn using CATIA software and the top ceramic layer and bond layer are added to the blade, TGO layer neglected because of its small effect on the temperature distribution.

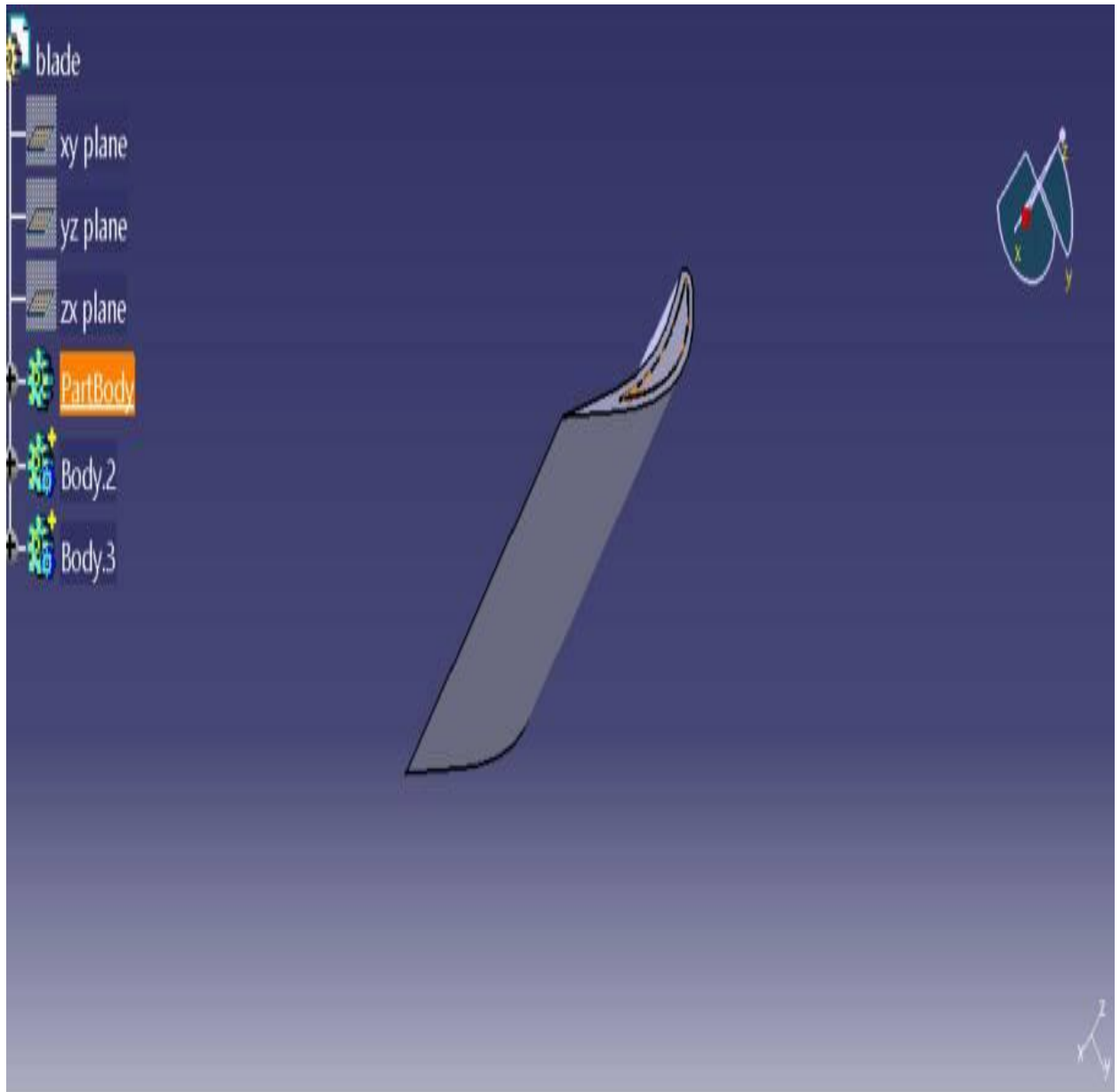


Figure 10. Turbine blade model by CATIA V5

Then the blade transmitted to ANSYS software and the materials of the blade, top coating ceramic layer and bond layer are choose to be nickel for the basic blade material, yttria stabilized zirconia (YSZ) for the top coating ceramic layer and NiCrAlY for the bond coat layer. Defined in ANSYS software as follows:

Blade material (nickel)

The nickel material properties are already defined on ANSYS 16.0 software.

Top coating ceramic layer (YSZ)

Material	Density(Kg/m ³)	Thermal Conductivity(W/m.K)	Specific Heat(J/Kg.K)
YSZ	5100	1.1	479

Table 2. Thermal properties of YSZ

The YSZ material defined on ANSYS 16.0 software as a new material based on following properties:

Bond layer (NiCrAlY)

Material	Density(Kg/m ³)	Thermal Conductivity(W/m.K)	Specific Heat(J/Kg.K)
NiCrAlY	7320	24	674

Table 3. Thermal properties of NiCrAlY

The NiCrAlY material defined on ANSYS 16.0 software as a new material based on following properties:

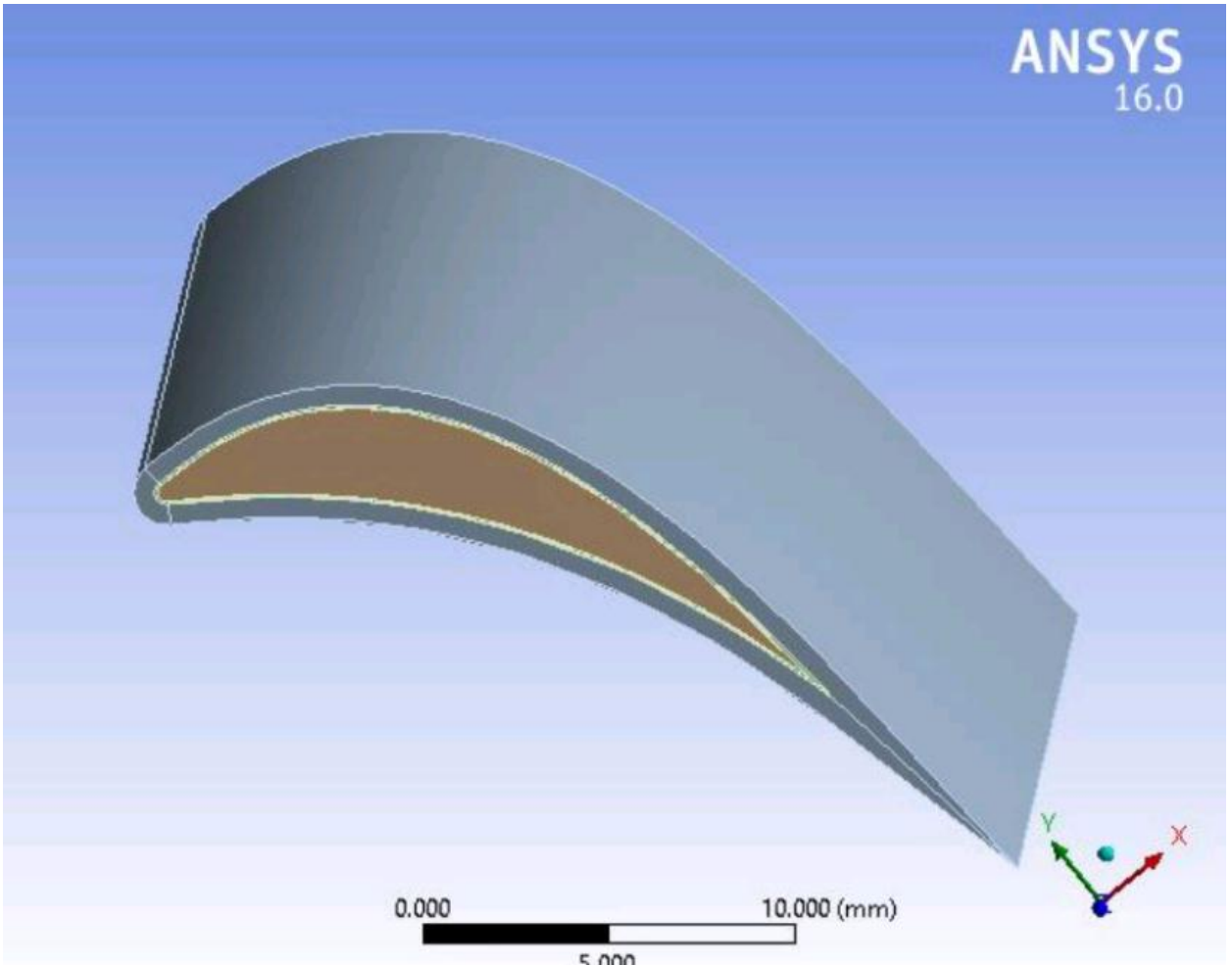


Figure 11. Coated blade in ANSYS 16.0 software

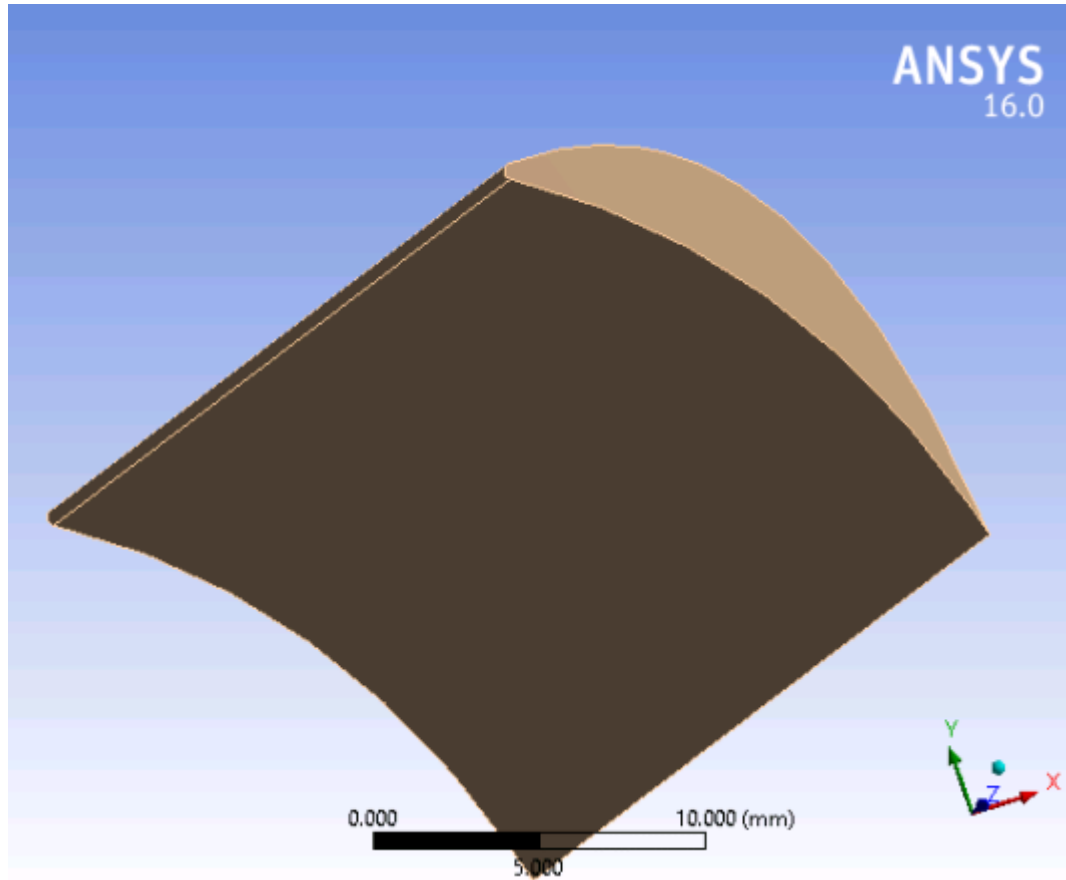


Figure 12. Uncoated blade in ANSYS 16.0 software

Thermal analysis was processed for each turbine blade. During the thermal analysis, 1643 K was applied to the top coating surface for a while. For comparing the blades, in the uncoated model, temperature was applied on to the turbine blade surfaces. The simulations were solved under these circumstances.

A turbine blade was borrowed from one of our Sudan airforces department to do X-Ray florescent test to show its constructed materials percentage using X-Ray florescent gun (X-MET 5000).



Figure 13. A5 turbine blade



Figure 14. X-Ray florescent gun (X-MET 5000).

5 Chapter five: Result and Discussion

The thermal simulation results for the models can be determined from the figure. Evaluation of the figure is showed that coating material was decreased the turbine blade temperature from 1773k to 1596k. Using YSZ as a top coating material, 10% thermal protection was received for the turbine blade.

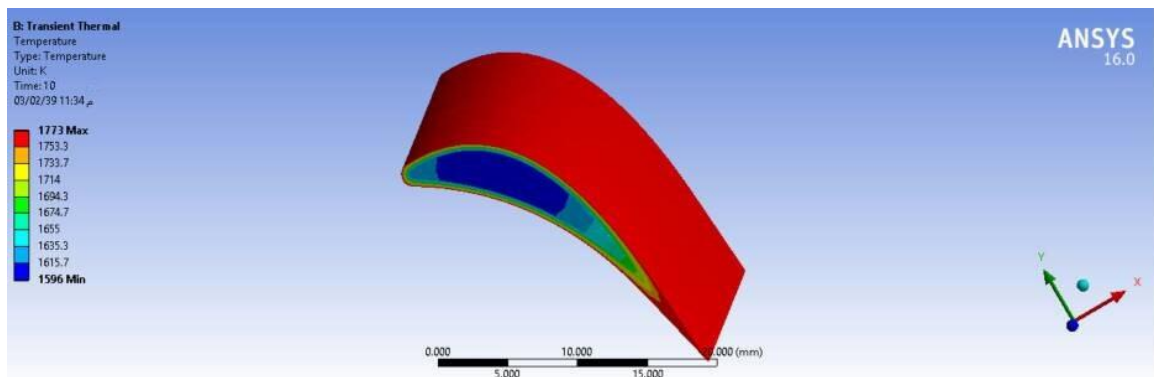


Figure 15. The thermal simulation results in temperatures (k) for the coated blade

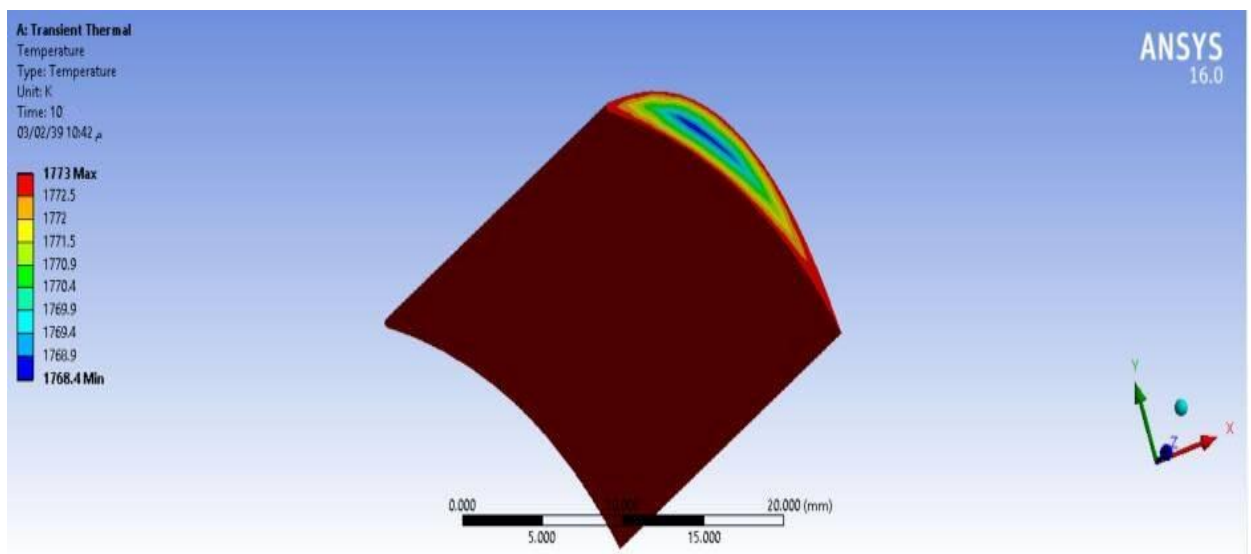


Figure 16. The thermal simulation results in temperatures (k) for the uncoated blade

To understand the general thermal behavior of the blades, maximum and minimum temperature values for the uncoated and coated turbine blades are given in table.

	MAX.TEMPERATURE(K)	MIN. TEMPERATURE(K)
Uncoated	1773	1768.4
Coated	1773	1596

Table 4. Rate of temperature drop

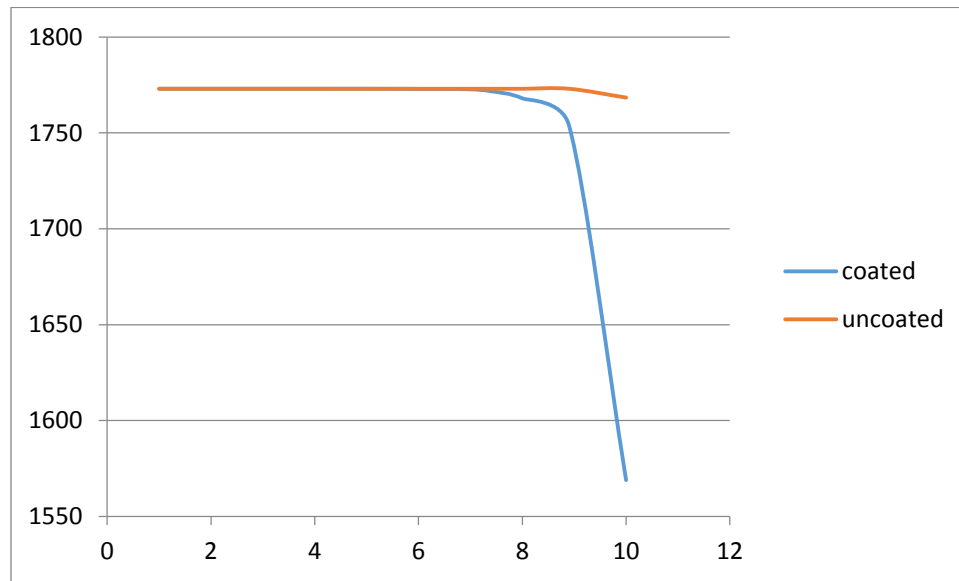


Figure 17. Coated and Uncoated blade temperature distribution curve

The coated blade curve is starting from its maximum value (1773 K) and remains constant for a while then decreasing rapidly to its minimum value (1596). The uncoated blade curve close to constant has the maximum value of (1773 K) that remains constant for a while and then changed to its minimum value (1768.4 K).

From X-Ray florescent test the results was represented as follows:

Screening Method:		Nickel
Analyte	Conc.	STD
Cr	9.46%	0.319
Ni	58.72%	0.157
Mo	2.31%	0.059
Cu	0.44%	0.064
W	3.88%	0.263
Ti	1.26%	0.167
Mn	0.12%	0.127
Fe	1.01%	0.089
Co	0.08%	0.035
Nb	0.02%	0.009
Ta	0.07%	0.091

Grade:
Reference: Nickel ID/Haynes 230

Figure 18. X-Ray florescent test results.

From these results the Nickel (Ni) has dominated percentage among other materials that constructed the blade as used in simulation assuming that blade is made from pure Nickel

6 Chapter Six: Conclusion and Recommendations

6.1 Conclusion

The usage of refractory material in rocket engine represented as a nozzle throat area developed using refractory material and in aircraft as thermal barrier coating TBC.

A simulation has done to coated and uncoated arbitrary turbine blade using ANSYS16. software to represent the thermal distribution and the benefits of using the TBC and the temperature reduction on the coated blade was 177 °C and this result was acceptable comparing with previous studies.[8] the X-Ray florescent test applied to the blade showed that the Nickel is the main constructed material in the alloy as used in the blade studied by ANSYS 16. Software

6.2 Recommendations and future work

1. It's recommended other projects can study the load affected on the blade.
2. Study the creep effect and the elasticity analysis
3. Calculate the thickness of Thermal growth oxide
4. Get blade and study its materials experimentally

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