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INSTITUTE OF ENERGY TECHNOLOGIES

**GAS TURBINE OXIDATION LIFE ASSESSMENT AND LIFE CALCULATION
METHODS**

ALATTİN ÇETİN

**A THESIS SUBMITTED FOR THE DEGREE OF
MASTER OF SCIENCE IN APPLIED PROPULSION SYSTEM DESIGN &
ENGINEERING FOR AEROSPACE TECHNOLOGIES**

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SUMMARY

Gas turbine engines operate at high temperatures and pressures, making them susceptible to oxidation of metal components. Oxidation occurs when metal reacts with oxygen to form an oxide, which can lead to brittleness and premature failure of the engine parts. To ensure safe and reliable operation, oxidation life assessment and calculation methods are used to estimate the service life of gas turbines.

The oxidation process is influenced by factors such as temperature, chemical composition, presence of other elements, and catalysts. Oxidation-resistant high-temperature alloys are in high demand to meet the increasing need for materials that can withstand elevated temperatures and have long service lives. Coatings are applied to engine parts to protect against wear, corrosion, and thermal fatigue, to improve performance and to extend the service life.

Software like COSP and COATLIFE are used to predict the oxidation behavior of coatings. These models consider factors such as coating and substrate materials, environment, and operating conditions. By comparing these models with material test data, the most accurate method is determined, leading to improved predictions and better coatings.

Once the most accurate method is identified, a life calculation software can be developed to predict the lifespan of parts exposed to oxidation in gas turbine engines. This software would be a valuable tool for engineers and designers, allowing them to anticipate part failures and schedule necessary maintenance or replacements in advance.

Key Words: Gas turbines, Oxidation, Coatings, High-temperature, Predictive modeling

ÖZET

Gaz türbinli motorlar yüksek sıcaklık ve basınçlarda çalışmaktadır, bu da onları metal bileşenlerin oksidasyonuna duyarlı hale getirmektedir. Oksidasyon, metal bir oksit oluşturmak için oksijenle reaksiyona girdiğinde meydana gelmektedir, bu durum parçaların daha kırılgan olmasına ve erken hasarlanmasına neden olabilmektedir. Güvenli ve güvenilir çalışmayı sağlamak, gaz türbinlerinin servis ömrünü tahmin etmek ve maliyetli arızaları önlemek amacıyla oksidasyon ömrü değerlendirmesi ve hesaplama yöntemleri önem arz etmektedir.

Oksidasyon; sıcaklık, kimyasal bileşim, diğer elementlerin varlığı ve katalizörler gibi faktörlerden etkilenmektedir. Oksidasyona dayanıklı yüksek sıcaklık alaşımlar ve uzun hizmet ömrüne sahip malzemelere olan artan ihtiyacı karşılamak yüksek talep görmektedir. Kaplamalar, aşınmaya, korozyona ve termal yorgunluğa karşı koruma sağlamak, performansı artırmak ve hizmet ömrünü uzatmak için motor parçalarına uygulanmaktadır.

COSP ve COATLIFE gibi modeller, kaplamaların oksidasyon davranışını tahmin etmek için kullanılmaktadır. Bu modeller, kaplama ve substrat malzemeleri, çevre ve çalışma koşulları gibi faktörleri dikkate almaktadır. Bu modelleri malzeme test verisi ile karşılaştırarak, en doğru yöntemi belirlenmiştir.

En doğru yöntem belirlendikten sonra, gaz türbini motorlarında oksidasyona maruz kalan parçaların ömrünü tahmin etmek için bir ömür hesaplama yazılımı geliştirilecektir. Bu yazılım, mühendisler ve tasarımcılar için parça hasarlarını tahmin etmelerine ve gerekli bakım veya değişimleri önceden planlamaya olanağı sağlayacaktır.

Anahtar Kelimeler: Gaz türbinleri, Oksidasyon, Kaplamalar, Yüksek sıcaklık, Tahminsel modelleme.

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LIST OF ABBREVIATIONS AND ACRONYMS

<u>Abbreviations and Acronyms</u>	<u>Explanations</u>
M	: Metal
K	: Temperature-dependent equilibrium constant
ΔG	: Gibbs free energy
ΔG_f°	: The standard free energy of formation of the oxide
ΔH	: The enthalpy of reaction
ΔS	: The entropy change
T	Temperature ($^\circ\text{C}$)
x	: The oxide scale thickness
t	: Cycle Time (h)
t_{eff}	Effective time
F	Fraction of oxide spalled
$W_{\text{ox}}(n)$	Weight of oxide formed during a thermal cycle (mg/cm^2)
$W_s(n)$	Weight of oxide spalled during thermal cycle (mg/cm^2)
$W_r(n)$	Weight of oxide remained on the coating surface after a thermal cycle (mg/cm^2)
$W_c(n)$	Cumulative weight change per unit area (mg/cm^2)
$W_m(n)$	Cumulative metal loss (mg/cm^2)
Q_0, q	Spallation constant
k, k_p	Oxidation kinetic constant ($\text{mg}^2/\text{cm}^4\text{h}$)
Z	The ratio of the molecular weight of the oxide to the atomic weight of oxygen in the oxide
RL	Remaining life
ρ	Density (kg/m^3)
X_{Al}	Aluminum content (at. %)

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1. INTRODUCTION

Gas turbine engines operate on the principle of internal combustion and utilize the Brayton cycle. Air from the atmosphere is compressed by a compressor and then passed through a combustion chamber where fuel is sprayed and ignited. This results in high pressure and high temperature air, which then enters a turbine to produce mechanical energy. This energy is used to power the compressor and any unused energy can be harnessed for external work, such as generating thrust in a turbojet engine or powering a fan or propeller via an independent turbine. Gas turbines are relatively simple in design and consist of three main components: the compressor, combustor, and turbine [1].

The temperature of the gas entering the turbine is a critical factor in the performance of gas turbine engines. It influences the engine's specific power, weight, and efficiency. Over the past few decades, there has been a significant increase in the average temperature of the gas at the turbine entry, from 1200-1300 K to 1700-1800 K [2].

To improve the efficiency of gas turbine engines, there is a focus on operating at higher temperatures by utilizing advanced turbine designs and optimizing the cooling systems in the hot sections. However, this increased operating temperature also exposes the components to various failure mechanisms. These can include creep, low-cycle fatigue (LCF), high-cycle fatigue (HCF), cracking, thermal-mechanical fatigue, oxidation, and hot corrosion. These failure mechanisms occur as a result of the harsh conditions experienced by the parts in the hot sections of the gas turbine.

In gas turbine engines, the materials used in the hot sections are subjected to harsh conditions including high temperatures, high pressures, and chemical environments. The working conditions in gas turbine engines often lead to failures in the components. These failures can be attributed to various factors, like ambient temperature, which can cause a different type of corrosion including uniform corrosion, pitting, galvanic corrosion, intergranular corrosion, stress corrosion cracking, and corrosion fatigue [2].

Oxidation is important mode of failure for evaluating the life of gas turbine engines. High operating temperatures are significant factors in the oxidation and degradation of engine components. As a result, the service life of hot section components is adversely affected. The parts in hot section in modern gas turbines operate under the most arduous conditions of temperature and stress than any component in the engine. They are most critical components in the engine [3].

Oxidation-resistant materials or coatings are utilized to prevent oxidation in the hot sections of gas turbines. However, it is important to note that these materials and coatings have a limited lifespan in terms of their resistance to oxidation. To prevent potential failures, it is necessary to calculate the expected oxidation life of the engine components in advance. This ensures that the parts are replaced or maintained before reaching their maximum oxidation life, minimizing the risk of failure due to oxidation.

2. LITERATURE SURVEY

The service life of parts used in gas turbine engines is influenced by various factors such as stress, temperature, and environmental conditions during operation. To prevent any potential failures, it is crucial to determine the expected life of these parts.

In general, the damage mechanisms that result in reduced parts life are listed below. More than one mechanism can be effective at the same time, especially in hot zone parts [4].

- Creep
- Low cycle fatigue
- High cycle fatigue
- Thermal mechanical fatigue
- Crack
- Corrosion
- Erosion
- Oxidation
- Foreign object damage

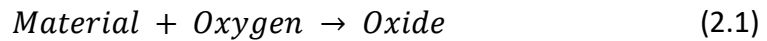
In this thesis, the kinetics of oxidation, materials and coatings used against oxidation, oxidation life calculation methods, experimental studies and the life calculation method will be determined as a result of the studies.

2.1 Oxidation

The formation of oxide occurs when a metal reacts with oxygen. The resulting oxide scale can consist of multiple layers. The process of oxidation is a chemical reaction influenced by various factors such as the material's chemical composition, temperature, presence of other elements, and catalytic agents. The oxidation reaction is controlled by two important factors: thermodynamics and kinetics. For

metallic elements to react with oxygen in the environment, if the energy balance favors it.

The general equation for the oxidation of a material can be written as:



For example, the oxidation of aluminum can be represented by the following equation:



In this chemical reaction, aluminum combines with oxygen to produce aluminum oxide (Al_2O_3). The rate at which this reaction occurs is affected by factors such as temperature, the presence of oxygen, and the presence of other elements, including impurities or alloying elements.

Thermodynamics determines whether the oxidation reaction is feasible or not, while kinetics determines the rate at which the reaction proceeds. Kinetics is more important in practical applications since it determines the quantity of metal consumption and, as a result, the lifespan of the material.

2.1.1 Thermodynamic of Metal Oxidation

At high temperatures, a chemical reaction can start between the oxidant gas, oxygen, and the metal. The reaction starts with the absorption of oxygen by the metal, and then oxide is formed. The part of this study is concerned with the oxide scale obtained for metal surface. With the exception of noble metals such as gold, platinum, and palladium, most metals react with oxygen when exposed to high temperatures. This is due to fundamental thermodynamics, as the overall oxidation reaction has a highly negative free energy. Oxide nucleation or scale growth can occur on the surfaces of metals undergoing reactions with oxygen. However, the ability of the scale to protect the underlying metal depends on the growth kinetics[5].



M is the reacting metal, M_xO_y is its oxide and “ x ” and “ y ” are the moles of the metal and oxygen, respectively, in 1 mol of the oxide.

The law of mass action offers at equilibrium conditions:

$$K = \frac{a_{M_xO_y}^{2/y}}{a_M^{2x/y} a_{O_2}} \quad (2.4)$$

The Equation 2.4 provided involves a constant, K , which is influenced by the temperature and the thermodynamic activity of a specific species, represented by a_i . In most cases, solid materials, such as metals and oxides, are assumed to be in their standard state, where their activities are considered to be equal to one. At elevated temperatures and moderate pressures, it is possible to consider the oxidant gas, such as oxygen, as an ideal gas. This approximation enables us to estimate its activity by considering its partial pressure in atmospheres. This simplifies the equation:

$$K = \frac{1}{P_{O_2}} \quad (2.5)$$

P_{O_2} is the partial pressure of oxygen.

Although equilibrium thermodynamics may not always provide precise predictions for reaction outcomes, it offers insights into potential reaction products, the likelihood of substance evaporation or condensation, and the conditions in which products may react with concentrated residues. This understanding helps to elucidate substance behavior under varying conditions [5].

From a thermodynamic standpoint, the reaction (2.3) of any metal occurs spontaneously in the forward direction when ΔG is negative. In the case of the reaction (2.3), ΔG can be expressed as follows:

$$\Delta G = \Delta G_f^\circ + RT \ln K \quad (2.6)$$

ΔG represents the change in Gibbs free energy, R is the gas constant, and T is the absolute temperature. This equation assumes that the metal and oxide are in their pure, standard states. If $\Delta G = 0$, the system is at equilibrium, indicating that the reaction has reached a balance between the forward and reverse reactions. On the other hand, if $\Delta G > 0$, the reaction is thermodynamically unfavorable, meaning that the reaction is not favored to occur spontaneously.

$$\Delta G_f^\circ = -RT \ln K = -RT \ln P_{O_2} \quad (2.7)$$

The pressure at which the oxide dissociates can be defined as the equilibrium condition where the forward and reverse reaction rates are equal, as stated in the equation:

$$P_{O_2} = \exp\left(\frac{\Delta G_f^\circ}{RT}\right) \quad (2.8)$$

The metal M will undergo oxidation to form the oxide M_xO_y only if the dissociation pressure is exceeded by the partial pressure of oxygen in the environment.

Another significant thermodynamic property that relates to the stability of metal oxides is the standard free energy of formation, or standard Gibbs free energy of formation. This can be calculated as:

$$\Delta G^\circ f(\text{oxide}) = \Delta H^\circ f(\text{oxide}) - T\Delta S^\circ f(\text{oxide}) \quad (2.9)$$

The equation provided calculates the standard free energy of formation for an oxide, using the standard enthalpy of formation ($\Delta H^\circ f(\text{oxide})$), temperature (T), and standard entropy of formation ($\Delta S^\circ f(\text{oxide})$). This value is useful in determining the stability of the oxide under various temperature and pressure conditions.

$$\Delta G = \Delta H - T\Delta S \quad (2.10)$$

Furthermore, Equation 2.10 illustrates that a graph of ΔG against temperature (T) can be approximated as a straight line, with a change in slope indicating the formation of a new phase.

The Ellingham diagram depicted in Figure 2.1 is a visual representation that illustrates the comparative stability of various oxide compounds based on temperature and oxygen pressure. It serves as a valuable tool to predict the thermodynamic stability of oxide compounds and to gain insights into the corrosion characteristics of materials in diverse environments [6].

The presented diagram focuses on the reaction of metals with oxygen to produce oxides (similar diagrams can be constructed for metals reacting with sulfur, chlorine, etc., but the oxide form is the most commonly used one). The oxygen partial pressure is standardized at 1 atmosphere, and all the reactions are normalized to consume one mole of O_2 .

The diagram is a representation of the relationship between Gibbs free energy (ΔG) and temperature. As the enthalpy (ΔH) and entropy (ΔS) remain relatively constant with temperature, the plot of free energy versus temperature appears as a series of straight lines. The slope of the line corresponds to the entropy change (ΔS), while the y-intercept represents the enthalpy change (ΔH). The slope of the line changes when any of the involved materials undergo phase changes, such as melting or vaporization.

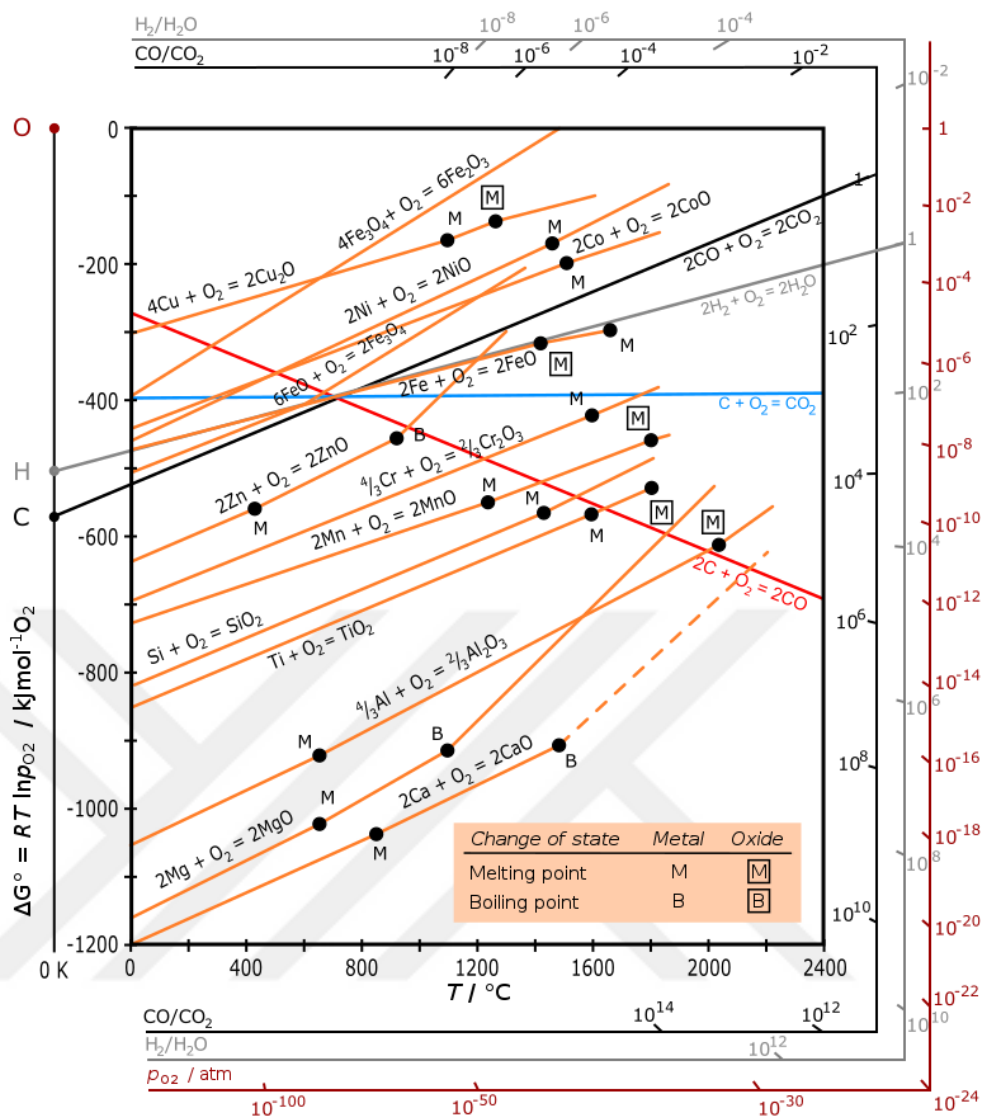


Figure 2.1 Ellingham Diagram [7]

The Ellingham equation provides a means to determine the direction of a reaction under varying conditions. When ΔG° is negative, the reaction is spontaneous and will proceed in the direction that minimizes ΔG° . Conversely, when ΔG° is positive, the reaction is nonspontaneous and will only occur with the input of external energy.

By analyzing the positions of different oxide compounds on the diagram, their relative stability can be determined. The curves in the diagram for the formation of metallic oxides are typically straight lines with a positive slope, which is proportional to ΔS . The lower the position of a metal's line on the diagram, the greater the stability of its oxide. For instance, the line for aluminum (Al) is located below that for iron

(*Fe*), indicating that the oxide of aluminum is more stable compared to oxide of iron. It is also observed that the stability of metallic oxides generally decreases with increasing temperature.

2.1.2 Kinetics of Oxidation

While thermodynamics can predict the stable oxidation products based on free energy changes, it does not offer details about the rate at which oxidation occurs. Additionally, thermodynamics does not adequately account for the various steps involved in the creation of the oxide. However, the following qualitative summary can be applied to these steps: [8]:

Adsorption: The adsorption of oxygen molecules.

Decomposition: The formation of atomic oxygen.

Migration: The migration of atomic oxygen atoms to low-energy regions

Ionization and Bond Formation: The ionization of atomic oxygen ions and the formation of bonds with metal atoms.

Layer Formation: The accumulation of adsorbed oxygen atoms on the metal surface, forming a layer.

Oxide Film Formation: The formation of a temporary oxide film on the metal surface by adsorbed oxygen atoms.

Diffusion: The continuous formation of a stable oxide layer. Oxygen or metal ions can diffuse through the oxide film.

It is important to note that the actual kinetics and mechanisms of oxidation can be complex and depend on factors such as temperature, pressure, alloy composition, and environmental conditions. Experimental observations and theoretical models are often used to gain a better understanding of the specific oxidation mechanisms for different materials.

The oxidation kinetics of metals and alloys exhibit various types of reaction rates. In many cases, the oxidation reaction follows a parabolic rate, where the rate of oxidation increases with time but at a decreasing rate. This parabolic rate indicates that the formation of an oxide layer on the metal surface provides a protective barrier that slows down the further oxidation process.

There are instances where the oxidation reaction follows a linear rate, meaning that the rate of oxidation remains constant over time. This linear rate may occur under specific conditions, such as at low temperatures or in the presence of certain reactive species.

In addition to parabolic and linear rates, other kinetics can be observed in oxidation processes. Some reactions may exhibit logarithmic rates, where the rate of oxidation decreases logarithmically with time. On the other hand, inverse logarithmic rates involve an initial rapid oxidation rate that gradually decreases over time.

The specific kinetics observed during the oxidation process are influenced by various factors, including the type of metal or alloy, temperature, the presence of impurities or alloying elements, and the surrounding environment. Experimental measurements and theoretical models are used to determine and characterize the oxidation kinetics for different materials under specific conditions.

2.1.2.1 Parabolic Kinetics

The formation of an oxide scale on the metal surface during oxidation leads to a diffusion-controlled process. Ions diffuse through the oxide scale driven by a chemical potential gradient. As the oxide scale thickness increases over time, the diffusion distance for ions also increases. Consequently, the rate of oxidation decreases since it becomes more difficult for ions to traverse the thicker oxide scale. In simple terms, the rate of oxidation is inversely proportional to the oxide scale thickness. A thicker oxide scale hinders ion diffusion, resulting in a slower oxidation rate, while a thinner oxide scale allows for easier ion diffusion, leading to a higher oxidation rate [8].

$$\text{Parabolic growth: } x^2 = kt \quad (2.11)$$

where x represent the thickness of the oxide scale after a certain exposure time t and k represent the rate constant, which is a function dependent on the temperature T .

2.1.2.2 Linear Kinetics

In cases where the oxide scale on the metal surface does not form a protective barrier, leading to oxide cracking, spalling, and the presence of volatile oxides or molten oxidation products, the oxidation rate tends to remain constant as time progresses. This constant oxidation rate is described by a linear kinetic model, where the rate of oxidation is directly proportional to time. In other words, the amount of oxide formed increases linearly with the duration of the oxidation process.

$$\text{Linear growth: } x = x_0 + kt \quad (2.12)$$

where x is the oxide scale thickness after exposure for time t ; k is the rate constant, a function of temperature T , and x_0 is constant.

In cases where the oxide scale is not protective, such as with alkali metals or in weak oxidation environments like dilute oxygen or mixtures of CO and CO_2 , linear rate laws have been observed. This means that the rate of oxidation is directly proportional to the thickness of the oxide scale [8].

2.1.2.3 Logarithmic Kinetics

At lower temperatures, specifically below 200°C (392°F), the oxidation of materials like nickel exhibits logarithmic rate laws. This type of growth mechanism involves the presence of localized electric fields in close proximity to the metal surface. When oxygen is adsorbed, electrons are transferred from the metal to oxygen, resulting in the formation of electric fields within the oxide layer. These electric fields act as driving forces that enable the movement of metal atoms through the oxide film. As a result, the growth rate of the oxide film changes inversely with time. In other words, as time progresses, the oxide growth rate decreases. This logarithmic behavior is characteristic of thin films formed at low temperatures and is attributed to the influence of electric fields on the oxidation process. [8].

$$\text{Logarithmic growth: } x = k_0 + \log(kt + 1) \quad (2.13)$$

where x represent the thickness of the oxide scale after a certain exposure time t ; k represent the rate constant, which is a function dependent on the temperature T , and k_0 represent a constant.

2.1.3 Mechanical Properties of Oxide Scale

Mechanical properties of oxide, which form on the surface of materials in oxidizing environments, play a significant role in materials performance. Generally, oxide scales are brittle and have lower tensile strength compared to the underlying material. They are also weaker in compression and shear. However, oxide scales can exhibit hardness and resistance to wear, which can be advantageous in certain applications. Key mechanical properties to consider include hardness, strength, elastic modulus, and fracture toughness. Harder oxide scales are less prone to cracking, while stronger scales provide better corrosion protection. A higher elastic modulus indicates greater stiffness and resistance to deformation. Fracture toughness measures the resistance to cracking or breaking under stress, with higher values indicating better load-bearing capability. The presence of impurities or alloying elements in the oxide layer can also influence the mechanical properties. For instance, oxide scales with higher levels of silicon or aluminum tend to be stronger and more resistant to wear compared to those without these elements [9].

Oxide layers can experience mechanical stress, which can lead to deformation or breakage of the layer. The mechanical condition of the oxide layer represents the alterations occurring in both the oxide and metal phases, and these alterations can be classified into two types: those that occur during the oxidation process and those that happen as the temperature changes. Stress generation in oxide layers on high-temperature alloys can lead to the loss of protective properties and accelerate material degradation [10] [11].

For an oxide layer to be effective in protecting the metal underneath, it must be a dense barrier that preventing the environment from reaching the metal. However, materials used at high temperatures often experience stresses that can cause them to fail, even if they have shown good corrosion resistance in laboratory

tests. This is because these stresses can cause the protective oxide layer to lose its effectiveness, resulting in unexpected behaviors and potential failure [9] [10]. The mechanical properties of the oxide scales play a vital part in protection, particularly under service conditions of the materials where the presence of stresses cannot be excluded [9].

2.1.3.1 Compressive Failure

There are two models that explain the occurrence of compressive failure in materials. In the first model (Figure 2.2 (a)), it is assumed that the oxide-metal interface remains strong and unaffected by void formation or segregation of trace elements. First-order failure occurs as a result of shear cracking, followed by the formation and a crack's growth at the oxide-metal interface. In the second model (Figure 2.2 (b)), spallation occurs due to decohesion at the scale-metal interface and buckling of the oxide layer. This causes cracks to form along the thickness or unstable growth of the interfacial segregation zone [9].

Metals that have been exposed to oxygen, an initial thin oxide layer forms, which acts as a protective barrier. However, over time, the growth of the oxide layer slows down, leading to the development of stress and wrinkles. If the stress becomes too high, the oxide layer can fail, either through crack formation or spallation, exposing the metal to the environment and accelerating oxidation. Once the oxide layer reforms and the growth rate stabilizes, its growth follows a linear pattern similar to an ideal, uninterrupted progression.

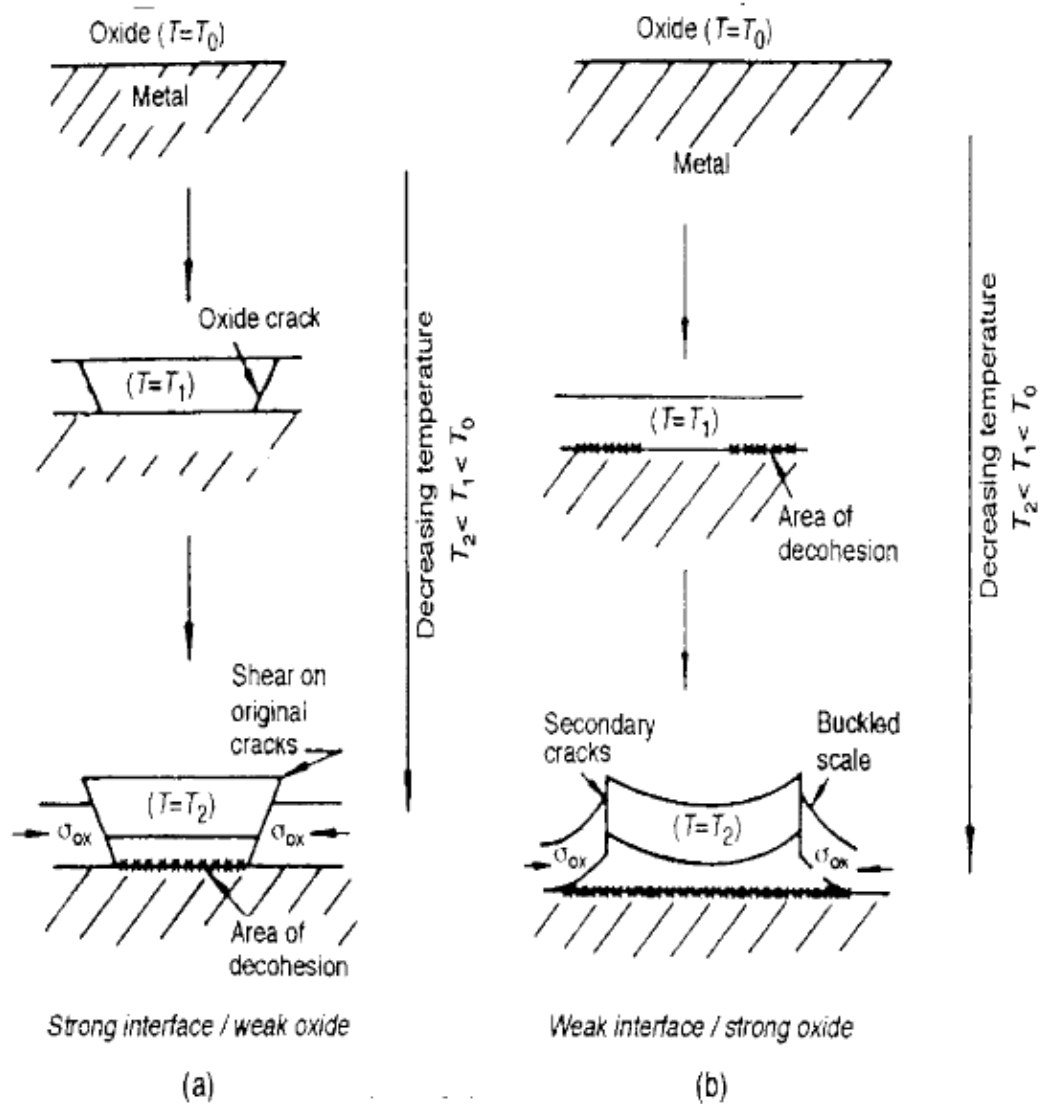


Figure 2.2 A diagram illustrating the different steps in the process of oxide spallation [9].

2.1.3.2 Stresses in Oxide Scales

Oxide scales become stressed as a result of internal forces within the layer that can lead to deformation or failure. These stresses can be caused by various factors, such as temperature changes, applied loads, or differences in properties between the oxide layer and the underlying material. Mechanical stresses are caused by external loads, whereas thermal stresses are caused by the oxide layer's expansion or contraction in response to temperature changes. Interfacial stresses occur at the

boundary between the oxide layer and the underlying material due to their differing mechanical properties [10] [12].

There are typically three types of stresses that need to be taken into account [13]:

- Growth stress,
- Thermal stress,
- External stresses

The presence of stresses in oxide scales can have a significant impact on the performance and longevity of materials in oxidizing environments. It is crucial to comprehend and manage these stresses in order to optimize the material's performance and durability.

2.2 Coating-Related Issues in High-Pressure Turbine Blades: Examining the Role in Aircraft Accidents

There have been a number of aircraft accidents in which the failure of a high-pressure turbine blade or other component has been identified as a contributing factor. In some cases, the failure of the blade or component has been attributed to coating-related issues, such as delamination or spallation of the coating.

One example of an aircraft accident in which the failure of a high-pressure turbine blade was identified as a contributing factor is the 2011 crash of an Airbus A330 in the Atlantic Ocean. In this accident, the failure of a high-pressure turbine blade was determined to be the result of a fatigue crack that had initiated at the blade tip. The blade was coated with a thermal barrier coating, and it was determined that the coating had delaminated from the blade, which likely contributed to the initiation of the fatigue crack.

Another example is the 2018 crash of a Southwest Airlines Boeing 737 MAX in Indonesia. In this accident, the failure of a high-pressure turbine blade was identified as a contributing factor. The blade was coated with a thermal barrier coating, and it was determined that the coating had spalled off the blade, exposing the substrate to high temperatures and leading to the failure of the blade.

In both of these cases, the failure of the high-pressure turbine blade had serious consequences for the safety of the aircraft. The failure of a blade or other component in a high-pressure turbine can lead to a loss of engine power and damage to other components, which can be dangerous for the passengers and crew of the aircraft. Coating-related issues can contribute to the failure of a blade or component, and it is important to ensure that coatings are applied and maintained properly to minimize the risk of such failures.

2.3 Common Metals Oxidation in Commercial Alloys

Most alloys commonly used in high-temperature applications have certain limitations when it comes to their strength, thermal stability, creep resistance, toughness, and machinability. To overcome these limitations, commercial alloys commonly incorporate elements such as *Fe*, *Co*, or *Ni*, along with appropriate additions of *Cr*, *Mo*, *Al*, *Mn*, *Si*, *Ti*, *W*, and/or reactive elements to enhance various properties. The inclusion of alloying elements can exert a significant influence on the oxidation behavior, especially in situations that involve thermal cycling.

High-temperature oxidation-resistant alloys are always in demand, as there is a constant push for materials that can work at higher temperatures and have a longer service life [14].

2.3.1 Oxidation of Iron

Iron oxidation at high temperatures results in the formation of multilayered scales, including *FeO*, *Fe₃O₄*, and *Fe₂O₃* layers. The significance of iron oxidation has led to extensive research and a comprehensive understanding, reflected in a vast body of literature [15].

Below 570°C, the primary solid oxide phases that form during the oxidation of iron are magnetite (*Fe₃O₄*) as the inner layer and hematite (*Fe₂O₃*) as the outer layer of the oxide scale. However, when the temperature exceeds the eutectoid temperature 570°C, an additional inner scale composed of rapidly growing wüstite (*FeO*) is formed next to the metal.

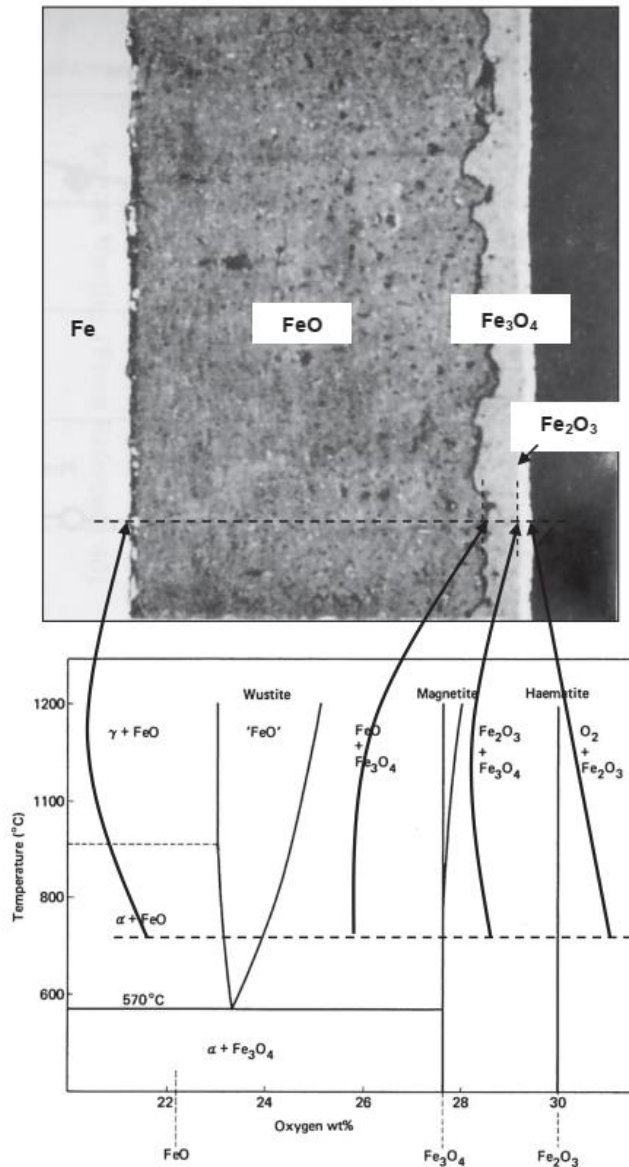


Figure 2.3 Cross-section of oxide scale grown on iron and iron–oxygen phase diagram [16]

Based on the Ellingham diagram illustrated in Figure 2.1, the oxide phase that remains stable at the lowest oxygen partial pressure (P_{O_2}) is located closest proximity to surface (FeO at temperatures above 570°C). Conversely, the oxide phase that is stable at the highest oxygen partial pressure (Fe_2O_3) is situated closer to the oxidizing environment. When the temperature is below 570°C , FeO becomes thermodynamically unstable and undergoes a transformation into a mixture of Fe and Fe_3O_4 .

The $Fe - O$ phase diagram, which illustrates the diffusion in different phases and the thickness distribution of the oxide layer on the metal, is depicted in Figure 2.3.

The phase diagram presented in Figure 2.3 indicates that the FeO phase is not present at temperatures below $570^{\circ}C$. Consequently, when iron oxidizes below this temperature, it is anticipated to form a bilayer scale consisting of Fe_3O_4 and Fe_2O_3 , with Fe_3O_4 adjacent to the metal. Conversely, at temperatures exceeding $570^{\circ}C$, the oxide layer sequence will be FeO , Fe_3O_4 , Fe_2O_3 , with FeO located closest to the metal [15].

2.3.2 Oxidation of Nickel

Nickel, which possesses favorable mechanical properties and resistance to various corrosive environments, is commonly utilized in applications that demand a combination of these qualities. Additionally, nickel has the capability to form a diverse range of alloys with desirable properties for engineering and corrosion resistance. In contrast to metals such as iron, cobalt, and copper, nickel exhibits comparatively higher resistance to oxidation at elevated temperatures [17].

Nickel is considered an ideal metal for oxidation studies because it forms only one oxide, NiO , forms under normal temperature and pressure conditions [15].

While NiO scales can develop over a broad range of temperatures, it is only at temperatures exceeding $900^{\circ}C$ that the grain size of the oxide becomes sufficiently large for lattice diffusion to become the dominant mechanism over grain boundary convection [16].

2.3.3 Oxidation of Chromium

The oxidation of pure chromium primarily results in the formation of a single oxide, Cr_2O_3 . Under specific exposure conditions, this oxide (chromium oxide) plays a vital role in both the oxidation of pure chromium and the protection of various essential engineering alloys. It forms a protective layer of Cr_2O_3 , which helps prevent further oxidation and corrosion [15].

The oxidation process of chromium is influenced by two significant factors: the thinning of scales due to the evaporation of CrO_3 and the buckling of scales caused by the development of compressive stress. Nevertheless, under normal atmospheric or oxygen conditions, Cr_2O_3 provides protective properties up to around 1000°C. At higher temperatures, the formation of volatile CrO_3 may occur [18].

2.3.4 Oxidation of Aluminum

Aluminum is a highly reactive metal that readily reacts with oxygen. However, when aluminum oxidizes, it forms a protective and inert aluminum oxide scale (Al_2O_3) on its surface. This oxide scale provides excellent resistance to various atmospheres and a wide range of chemical agents. The high stability of the Al_2O_3 scale also grants it the ability to inhibit the oxidation of other elements that are present in the alloy.

The stable oxide of aluminum at a thermodynamic level is $\alpha - Al_2O_3$. This oxide has a slow growth rate and forms a protective film on numerous high-temperature alloys and coatings [15].

At room temperature, aluminum is consistently coated with an "air-formed film" that is approximately 2-3 nanometers thick. This film is composed of amorphous alumina [19].

2.3.5 Oxidation of Silicon

On alloys that contain silicon or silicone, the formation of SiO_2 occurs through a slow oxidation process. However, the type of oxide vapor also has a significant impact on this system. The presence of silicone becomes particularly important at low oxygen pressures. When the oxygen pressure is close to the dissociation pressure of SiO_2 , a substantial amount of SiO is formed, which is in equilibrium with SiO_2 (solid) and Si (solid) [15]. This phenomenon can lead to the rapid flow of SiO_2 resulting the SiO_2 "smoke." The presence of SiO as a dispersed smoke facilitates a continuous and accelerated oxidation reaction.

2.3.6 Oxidation of Titanium

Titanium exhibits high reactivity and quickly develops a thin but robust oxide scale on its surface when exposed to environments containing oxygen. This oxide scale provides outstanding corrosion resistance, particularly at temperatures below around 500°C. The oxide that forms on titanium surfaces produced at normal or high temperatures is known as rutile (TiO_2). [17].

Oxygen and nitrogen penetration above about 600°C occurs. The titanium becomes brittle due to the presence of these substances. When deciding whether to employ titanium at high temperatures, you should examine this property.

2.3.7 Oxidation of Cobalt

There are three different cobalt oxides: Co_3O_4 , Co_2O_3 , and CoO . At temperatures above 900-950°C, only CoO is formed. However, below this temperature, a thin layer of Co_3O_4 can exist at the interface between the scale and the gas, above the CoO layer. The proportion of Co_3O_4 in the scale appears to increase as the temperature decreases from 800 to 600°C [20].

2.3.8 Oxidation of Alloys

The theory of oxidation of metals provides a basic understanding of how alloys behave when exposed to oxygen. However, the oxidation of alloys is much more complex and can be influenced by a number of factors [21]. These may include:

- Different metal components in the alloy reacting differently with oxygen
- The formation of excess oxide due to the presence of different metals
- Oxides having a certain degree of solid solubility
- Different metal ions exhibiting different mobility within oxide phases
- The metals in the alloy having different diffusivities
- The dissolution of oxygen in the alloy leading to the precipitation of oxides of one or more alloying elements in the sub-surface (internal oxidation)

The oxidation of alloys can be a complex process due to the interactions between the various metal components in the alloy and the oxygen in the environment. These interactions can lead to the formation of complex oxide structures with a variety of features, such as cracks, cavities, and irregular layers. The presence of these features can affect the protective properties of the oxide layer and may contribute to the corrosion of the alloy.

The integrity of the oxide layer can also be compromised by thermal stresses that arise during the operation of components under cyclic conditions. These stresses may cause the oxide layer to spall away from the alloy, exposing the metal underneath to the environment and increasing the risk of corrosion.

When an alloy composed of elements A and B comes into contact with oxygen, over time, a protective oxide layer is formed. The initial stages of the reaction between the alloy and oxygen are referred to as the temporary phase. This phase is followed by a steady-state scaling behavior, during which most of the thermodynamically stable oxide products are formed. As the reaction proceeds, there is a variation in the oxidant's activity, resulting in the dissociation or displacement of the least stable products. This leaves behind the most stable product(s) in close proximity to the alloy. In heat-resistant alloys, the oxide scales that form in a steady state generally consist of alumina (aluminum oxide) or chromium-based oxides such as chromia (chromium oxide). [22] [23].

Figure 2.4 illustrates the oxidation of a binary A-B alloy with different concentrations of A and B. In scenario a, where the concentration of A is sufficiently high, the oxide scale formed is predominantly composed of A oxide. In scenario b, where the concentration of B is sufficiently high, the oxide scale consists mainly of B oxide. In scenario c, where the concentrations of A and B are intermediate, the resulting oxide scale is a combination of A and B oxides. This schematic representation highlights the variation in oxidation behavior depending on the relative concentrations of A and B in the alloy [24].

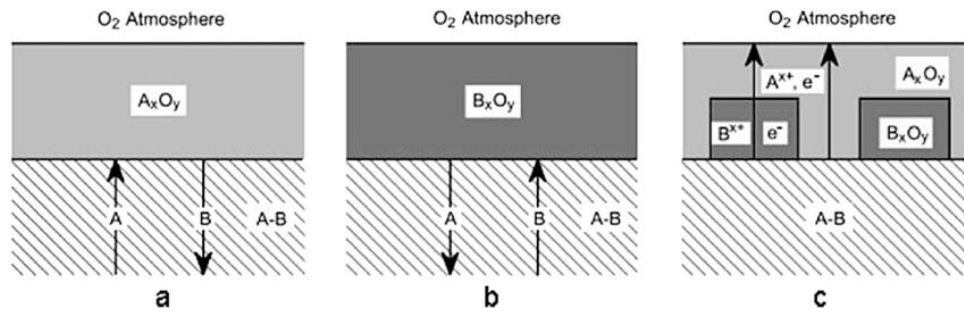


Figure 2.4 Oxidation processes of a binary A-B alloy [24]

When oxygen gas comes into contact with the A-B binary alloy, both elements react with the oxygen atoms. As a result, a thin oxide film is initially formed on the surface, composed of A_2O and B_2O . The early stages can be categorized into four steps:

- Oxygen adsorption at the surface,
- Formation of oxide nuclei,
- Lateral growth of the nuclei, and
- The formation of a compact oxide scale.

Once the lateral growth of the nuclei is complete, the metal surface is fully covered with a thin oxide film, effectively separating it from the surrounding gas environment. The properties of this thin oxide film are decisive in the oxidation resistance of the metal [24].

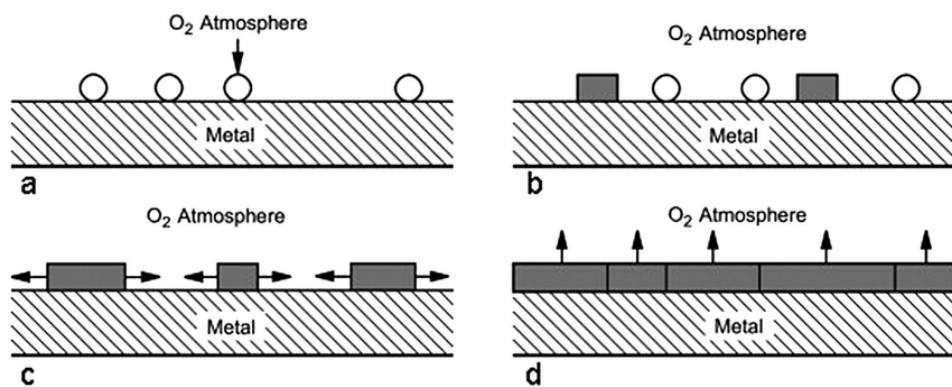


Figure 2.5 Oxide scale formation on pure metal surface [24]

Internal oxidation is considered undesirable due to its detrimental effects on the mechanical properties of an alloy. It can result in the development of internal stress and weakening of the grain boundaries, ultimately reducing the high-

temperature performance of the material. One example is observed in high-temperature alloys containing aluminum, where the internal formation of aluminum oxide (Al_2O_3) at the grain boundaries can promote crack initiation in the presence of tensile stresses [25]. The initiation of these cracks can lead to rapid component deterioration, with crack propagation occurring through mechanisms such as creep or fatigue.

The oxidation of commercial alloys can lead to the formation of subsurface voids, which can affect the mechanism of oxidation and the properties of the alloy. The vacancies in the subsurface region of the alloy significantly affect the mechanical integrity and properties of the alloy. The study conducted by Oleksak et al. [26] examined the role of metal vacancies in the high-temperature oxidation of alloys. The research demonstrated that the coalescence of metal vacancies at the interface between the oxide and alloy leads to the initial formation of low-density metal regions, which eventually develop into nanometer-sized voids.

2.3.9 Commercial High-Temperature Alloys

High-temperature alloys are widely utilized in various industrial applications that involve high temperatures, such as gas turbine engines, jet engines, and power generation systems. These alloys are specifically engineered to possess a unique combination of properties, strength, creep resistance, and corrosion resistance under high-temperature conditions.

There are several types of commercial high-temperature alloys, including:

Nickel-based superalloys: Nickel-based superalloys are widely preferred in turbine engines due to their exceptional strength, extended fatigue life, and excellent resistance to oxidation and corrosion at high temperatures. These alloys are particularly favored for the most critical engine components that operate above 800 °C. One of the remarkable characteristics of nickel-based superalloys, which makes them highly suitable for jet engines, is their remarkable resistance to creep and stress rupture at high temperatures. This property ensures the durability and reliability of the engine components under extreme operating conditions [27].

Iron-nickel based superalloys: Gas turbine engines utilize iron-nickel based superalloys for their exceptional structural properties and low thermal expansion at high temperatures. Compared to nickel or cobalt based superalloys, iron-nickel based alloys exhibit less expansion, making them ideal for engine components that require precise clearances between rotating parts. Another advantage of iron-nickel alloys is their relatively lower cost compared to nickel and cobalt-based superalloys. Blades, discs, and casings are the primary applications for iron-nickel based alloys in jet engines, where their unique combination of properties contributes to their effectiveness and cost-efficiency [27].

Cobalt-based superalloys: Cobalt superalloys offer a range of advantageous properties that make them suitable for use in gas turbine engines, despite being more expensive than nickel superalloys. One notable advantage is their superior resistance to hot corrosion in environments containing lead oxides, sulfur, and other compounds generated during the combustion of jet fuel. Cobalt alloys exhibit excellent resistance to attack from hot corrosive gases, leading to longer operating life and reduced maintenance requirements for engine components. However, it is important to exercise caution when comparing nickel and cobalt-based alloys, as there can be significant variations in hot corrosion resistance within each alloy group. It should be noted that certain nickel superalloys also demonstrate exceptional hot corrosion resistance. Additionally, cobalt alloys possess good stress rupture properties, although they may not match the performance of precipitation-hardened nickel-based alloys in this regard [27].

Titanium-based alloys: Titanium and aluminum alloys are commonly used in aero engine systems due to their favorable weight characteristics. Titanium has the highest strength-to-weight ratio of all materials and exceptional corrosion resistance and fatigue properties, making it ideal for manufacturing various engine parts, including the aero fan, booster disk, compressor blades, and fan frame, in both cast and wrought forms. [28].

The oxidation resistance of commercial superalloys can vary significantly depending on factors such as the type of alloy, temperature, and specific environment. A comprehensive study was conducted by Barrett [29] to better understand this variability by examining the behavior of 34 commercial superalloys

subjected to cyclic oxidation in air at 1100 °C for 200 hours, with some alloys tested at different temperatures and durations. The study involved monitoring weight change and identifying the scale phases formed. This extensive dataset allows for direct alloy-to-alloy comparisons and provides insights into the overall compositional effects on oxidation behavior.

A comprehensive database was compiled by Barrett et al. [30] to encompass a wide range of high temperature alloys. This study involved the testing of 68 commercial alloys, which included iron-base ferritic and austenitic stainless steels. The alloys were subjected to a temperature of 982 °C (1800 °F) for a duration of 10,000 hours, with each cycle lasting 1000 hours and repeated 10 times.

This extensive test results provided valuable information on the long-term oxidation performance of the alloys under high temperature conditions. The results database is a valuable resource for researchers and engineers, providing important information about the behavior of materials in industries that require reliable performance at high temperatures.

2.4 Coatings

In the aerospace industry, the technique of aluminizing was first introduced in the late 1960s for gas turbine engines [31]. Since then, aluminide diffusion coatings have become standard practice in the hot sections of gas turbines. These coatings are applied to enhance the resistance of the turbine components to high-temperature oxidation and hot corrosion. In particular, platinum aluminides have proven to be a cost-effective and efficient solution for protecting the superalloy components in the high-pressure turbine of both air and industrial gas turbines.

Coatings have played a crucial role in advancing gas turbine technology, allowing for the utilization of high-strength superalloys by providing vital protection against hot corrosion and oxidation. This protection is crucial in meeting the durability and performance requirements of these alloys. Coatings also will remain pivotal in achieving the desired combination of properties in gas turbine components. Coatings are essential for safeguarding components against degradation mechanisms

like oxidation, wear, and high temperatures, while also improving their overall performance and lifespan. [28].

The coating specifications for gas turbine engines are determined by several factors, such as the operating temperature, fuel type, material composition, and desired coating durability. Key requirements for these coatings include exceptional resistance to high temperatures, resilience against wear, protection against corrosion, resistance to thermal fatigue, and a low coefficient of friction [32]. To fulfill these requirements, a broad array of coatings can be employed in gas turbine engines, including ceramics, metals, and composite materials [33]. In the turbine section of the engine, in particular, coatings are required to provide corrosion resistance, wear resistance, insulation, and abrasability [32].

2.4.1 Coating Requirements

The development of thin oxide scales on the surface of the coating is the key of environmental performance of metallic coatings. These oxide scales act as a barrier, preventing oxygen and corrosive salts from reaching the underlying base alloy. Consequently, the structural strength of the component is primarily derived from the base alloy, while the coatings play a vital role in enhancing environmental resistance by forming a protective scale. However, in order for these coatings to offer durable protection, specific criteria need to be met [34].

The requirements for coatings play a critical role in protecting the coated component [8]. The following requirements must be met:

Oxidation/corrosion resistance: The coating should form a stable and protective surface scale with a homogeneous thickness. The growth rate of the protective scale should be slow, and the scale should adhere well to the surface. Additionally, a high concentration of the scale generator is necessary.

Stability: To ensure long-lasting protection, the coating should avoid undergoing undesired phase changes, and the diffusion rate across the interface at the operating temperature should be minimized. To minimize the formation of brittle phases, it is crucial to maintain sufficient stability in the composition across the

interface. By meeting these requirements, the protective scale formed by the coating can effectively enhance the environmental resistance of the component.

Adhesion: The coating should adhere well to the substrate, and the properties of the coating and substrate should be matched to reduce thermal stress. Growth stresses should be minimized by optimizing the process parameters, and the surface condition should be optimized (either rough or smooth) to ensure good adhesion.

Structural properties: The coating should be able to withstand service-related creep, fatigue, and impact loading without failing its intended function.

Ensuring that these requirements are met is crucial for the effective protection of the coated component. In the case of gas turbine engines, coatings are particularly important in providing corrosion resistance, wear resistance, insulation, and abrasability, especially in the turbine section of the engine [35].

2.4.2 Choosing Optimum Coatings

Choosing the optimum coating requires careful consideration. Figure 2.6 gives a summary of the most popular coatings, arranged in accordance with the applications to which each is most commonly applied.

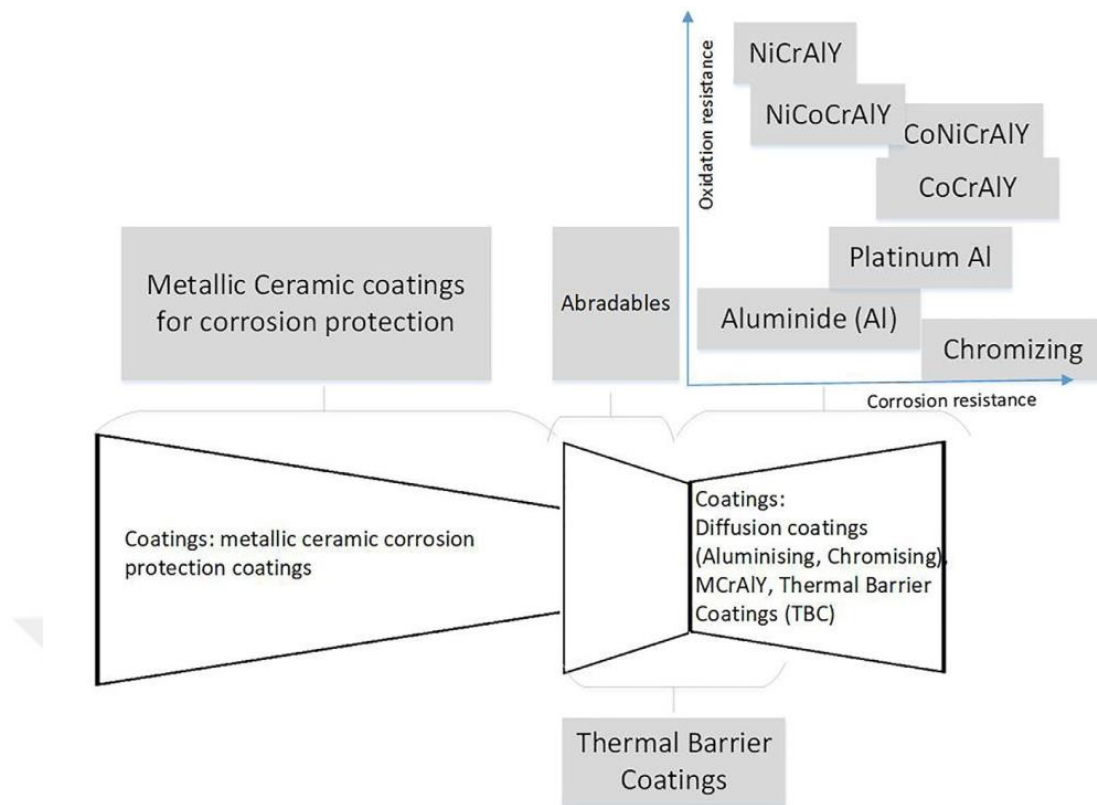


Figure 2.6 Most common gas turbine coatings [28]

2.4.2.1 Aluminide Coating

Aluminide coating, also known as aluminizing, is a high-temperature chemical process where aluminum diffuses into the surface of the base metal, forming a protective layer of Al_2O_3 . Aluminide coating is achieved through a diffusion process, where aluminum atoms penetrate the surface of the base metal. Aluminide significantly enhances the material's resistance to oxidation at high temperatures [36].

The coating is typically deposited using a powder composed of an activator (such as NH_4Cl), a metallic donor (Al), and an inert filler (Al_2O_3). When aluminide coatings are exposed to high temperatures, the β -NiAl phase selectively oxidizes, forming a protective Al_2O_3 scale. Different methods can be used to deposit aluminide coatings, including chemical vapor deposition (CVD), the pack cementation process, and the fluidized bed CVD process [37].

Overall, aluminide coatings are effective in increasing the resistance of materials to oxidation at high temperatures, making them widely used for protecting nickel-based superalloys in applications where corrosion and oxidation resistance are crucial.

2.4.2.2 Platinum-Al Coating

The addition of noble metals, specifically platinum, to aluminide coatings enhances their ability to resist oxidation and hot corrosion. This is because platinum has excellent high-temperature oxidation resistance and can form oxide layer on the surface to protect the coating.

Pt-Al coatings are thin layers composed of a mixture of platinum and aluminum that are applied to surfaces using physical vapor deposition (PVD). In the PVD process, a target material composed of platinum and aluminum is vaporized in a vacuum chamber, and the vapor is deposited onto the surface of the object being coated. The deposited material forms a thin, continuous layer of Pt-Al on the surface of the object.

These coatings improve corrosion resistance, wear resistance, and other properties of the object. Pt-Al coatings are particularly suitable for high-temperature and high-stress applications, such as gas turbine engines. However, they are more expensive to apply compared to some other coatings, like aluminide coatings. Pt-Al coatings can be brittle and may crack or spall under certain conditions. The PVD process used for Pt-Al coatings is complex and requires specialized equipment, which increases the cost and difficulty of application. Due to the high cost and complexity, Pt-Al coatings are typically applied in thin layers, which may limit their effectiveness in some applications. It is important to consider the specific requirements of the application and the material being coated when evaluating the advantages and disadvantages of Pt-Al coatings [38].

The process involves applying a thin layer of platinum (2 to 10 μm) onto the component through either electroplating or physical vapor deposition. This is followed by a diffusion heat treatment, carried out in a vacuum or inert atmosphere at temperatures ranging from 850 to 1050°C for a few hours. The purpose of this heat

treatment is to enhance the adhesion of the platinum layer to the substrate alloy. Subsequently, the component undergoes aluminiding through pack, above-the-pack, or CVD processes. Further heat treatments are frequently performed after the coating step to create the required microstructure and phase distribution in the coating. [8].

2.4.2.3 CoCrAlY Coating

CoCrAlY coating is widely used in high-temperature applications, such as gas turbine engines, because it provides exceptional resistance to high-temperature oxidation and hot corrosion. The name CoCrAlY refers to the main elements in the coating, which are Cobalt [Nickel], Chromium, Aluminum, and Yttrium.

CoCrAlY coatings are typically applied using thermal spray techniques like high-velocity oxy-fuel (HVOF) or plasma spray. The mechanical properties and performance of CoCrAlY coatings at high temperatures can be analyzed by examining their microstructure and composition [39].

2.4.2.4 CoNiCrAlY Coating

CoNiCrAlY coating, which stands for Cobalt Nickel Chromium Aluminum Yttrium, is composed of these main elements. This type of coating is commonly applied using thermal spray techniques like air plasma spraying (APS) or laser powder bed fusion [40].

2.4.2.5 Chromizing (Chromium-Modified Aluminide Coating)

Chromizing is a surface treatment method where a layer of chromium is deposited onto a metal surface to enhance its wear resistance, corrosion resistance, and resistance to high-temperature oxidation. This process can be combined with aluminiding to further improve the metal surface's resistance to high-temperature oxidation. Chromizing is frequently employed on high-temperature alloys like nickel-based alloys to enhance their performance in high-temperature environments [8].

2.4.2.6 Comparison of Coatings

Platinum-Al Coating, Aluminide, CoCrAlY, CoNiCrAlY, and Chromizing are all types of coatings that are commonly used in high-temperature applications to improve the corrosion resistance and thermal stability of materials. Each coating has its own set of advantages and disadvantages [8] [38] [41].

Table 2.1 Comparison of Coatings [8] [38] [41].

	Advantages	Disadvantages
Pt-Al	excellent high-temperature oxidation resistance good adhesion to the substrate	high cost difficulty in applying the coating
Aluminide	good high-temperature oxidation resistance low cost ease of application	limited corrosion resistance low wear resistance.
CoCrAlY CoNiCrAlY	excellent high-temperature oxidation resistance, good wear resistance good adhesion to the substrate	Limited corrosion resistance high cost.
Chromizing	excellent wear resistance and good high-temperature oxidation resistance	Limited corrosion resistance high cost.

2.4.3 Coating Technology

In general, there are two types of coating processes. The first requires diffusion to replace the composition of an alloy's surface, while the second involves the deposition of a metallic or ceramic coating with improved oxidation resistance. As a

result, these two processing methods are known as diffusion and overlay coating, respectively.

Metallic coatings are designed specifically as a corrosion and oxidation resistant alloy applied to a part surface and indicated by the M-Cr-Al-X series; M can be Fe, Ni or Co and X is an oxygen-active metal. Y can be Ce, Hf, Si or a combination of these elements. The interaction with the substrate during plating is often negligible for this coating class. Furthermore, thicker coatings with a longer service life can be produced. Greater design flexibility is enabled by reduced substrate interactions, a variety of corrosion-resistant alloys, and the ability to accumulate thicker coatings.

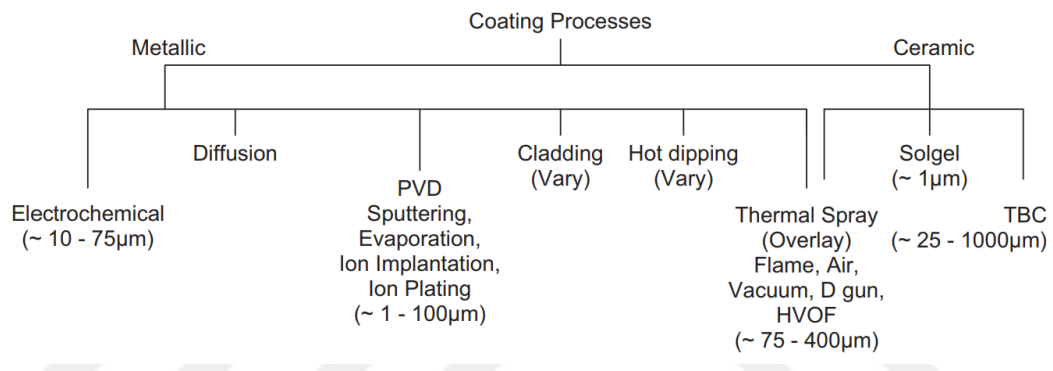


Figure 2.7 Some common coating processes [8]

Surface protection can be achieved through a variety of coating processes. The selection of these processes is determined by the component design and use. For instance, coatings needed for hot corrosion protection might not be the ideal coatings needed for oxidation protection. Figure 2.7 illustrates various operations involving typical coating thicknesses. Prior to the coating process, it is essential to prepare the component surfaces meticulously. This preparation involves thorough cleaning techniques such as sandblasting, ultrasonic cleaning, and baking. These methods help remove contaminants, impurities, and oxides from the surface, ensuring a clean and suitable substrate for the subsequent coating application [8].

2.4.3.1 Diffusion Coatings

Diffusion coatings are applied to gas turbine engine components to enhance their performance and durability. These coatings involve the introduction of a coating material into the component's surface, which then diffuses into the substrate material through the application of heat and pressure.

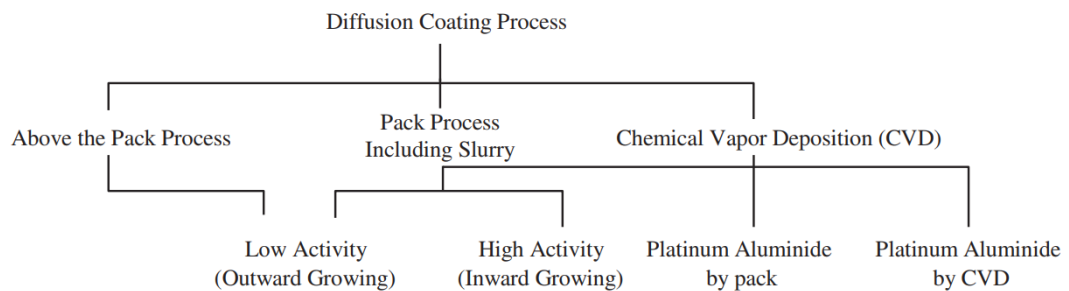


Figure 2.8 Various diffusion coating processes [8]

Aluminides are commonly used for oxidation protection, forming a protective alumina scale when exposed to high temperatures in air. Platinum incorporation in aluminides, as well as chromizing and siliconizing, provides better protection against hot corrosion. Diffusion aluminides have a wide range of Al contents., typically up to 30 wt%.

Components with complex forms can be coated with diffusion coatings, although the process requires high temperatures. To achieve the desired diffusion of coating elements into the substrate, heat treatment at temperatures up to 1100°C may be necessary. For the substrate's creep and fatigue strength to be restored, this heat treatment is necessary. The advantage of this process is that it can be performed using traditional furnaces, without the need for specialized equipment or facilities. By subjecting the components to controlled heat treatment, the diffusion coatings can effectively enhance their mechanical properties and performance.

There are several methods for producing diffusion coatings, involving the generation and transport of vapors containing Al, Cr, or Si to the component surface [8]. Diffusion occurs within the alloy as a result of the vapors' reaction with the substrate alloy.

2.4.3.1.1 Pack Process

Pack cementation is a process used to apply aluminide coatings to metal surfaces. It involves placing the metal component in a sealed container with a mixture of powdered aluminum and a fluxing agent. The container, or "pack," is then heated to a high temperature, typically between 850-1100°C, to enable the aluminum to react with the metal surface and form an aluminide coating.

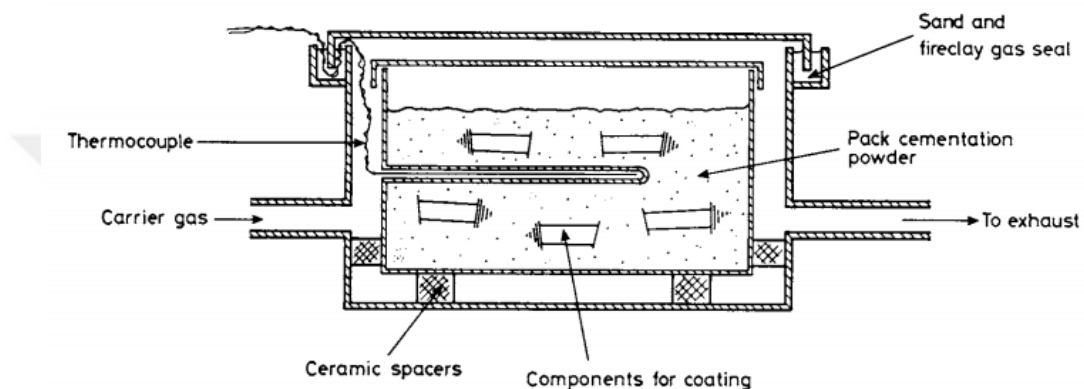


Figure 2.9 Schematic diagram of a pack cementation retort [42].

During the process, the aluminum and fluxing agent produce a vapor that reacts with the metal surface, leading to the formation of the aluminide coating. The fluxing agent aids in the removal of oxide and other contaminants from the metal surface, facilitating the coating formation. The coated component is then gradually cooled to promote complete coating formation and minimize potential thermal stresses.

The pack contains three elements: a donor alloy that releases solute material at a controlled rate, a halide activator that breaks down during the process and helps transport the solute material from the pack to the component being coated, and an inert oxide diluent to prevent the pack from sintering [42].

One advantage of pack cementation is its ability to coat complex-shaped components, as the pack can be designed to match the component's shape. Furthermore, the process is relatively cost-effective compared to other coating methods, as it does not necessitate specialized equipment or facilities. However, the

process may be time-consuming and may not yield coatings with the same level of purity as techniques like chemical vapor deposition.

2.4.3.1.2 Above the Pack Process

The above-the-pack process is an alternative method for applying aluminide coatings to metal surfaces. Unlike the pack cementation process, the metal component is not placed inside a pack. Instead, it is placed in a sealed chamber and aluminum vapor is introduced from an external source. The aluminum vapor reacts with the metal surface to form an aluminide coating. The process is carried out at high temperatures and the coated component is slowly cooled to minimize thermal stresses.

Through a special plumbing system, the coating vapor is applied to the component's internal and external surfaces while being carried to the component by an inert carrier gas. The retort containing the component is then placed in a furnace and heated to the desired temperature for the desired amount of time.

Compared to the pack cementation process, the above-the-pack process can produce purer coatings since the aluminum vapor is not contaminated by fluxing agents or impurities from the pack. However, this process is more expensive and may not be suitable for coating complex-shaped components.

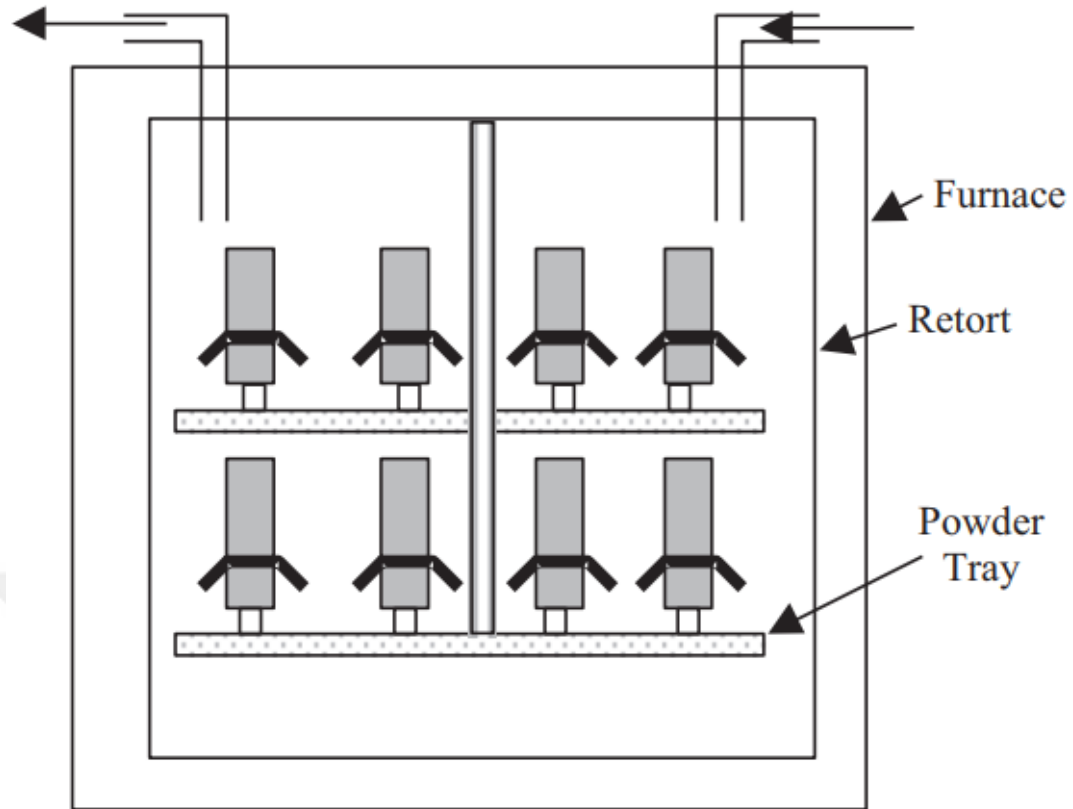


Figure 2.10 Schematic of the above-the-pack process [8]

The above-the-pack allows for the uniform coating of internal passages and holes, which is particularly beneficial for components like turbine blades in gas turbine engines [8]. These blades have internal passages and drilled holes for cooling air flow. A layer free of pack particle entrapment is another guarantee of the above-the-pack technique.

2.4.3.1.3 Slurry Aluminizing Process

The widely used method for applying aluminide protective coatings on turbine blades and vanes is through the application of aluminizing slurries by painting, followed by a process called diffusion annealing [2].

The slurry aluminizing process is a modified version of the pack cementation process used for applying aluminide coatings to metal surfaces. In this process, a slurry containing aluminum powder, a fluxing agent, and a carrier fluid is either injected into cavities or applied to the surface of the metal component using a brush

or spray. The slurry aluminizing process is advantageous for coating components with complex shapes or internal cavities that cannot be easily accessed using other methods. It is also cost-effective as it does not require specialized equipment or facilities. However, the purity of the coatings produced through this process may not be as high as those obtained through chemical vapor deposition or other methods.

2.4.3.1.4 Chemical Vapor Deposition (CVD) Processes

In chemical vapor deposition (CVD) processes, aluminum chloride ($AlCl_3$) is generated outside of the reactor before being introduced into the reaction vessel. This allows for accurate control of the flow rate and activity of $AlCl_3$, which results in consistent and uniform aluminide coatings.

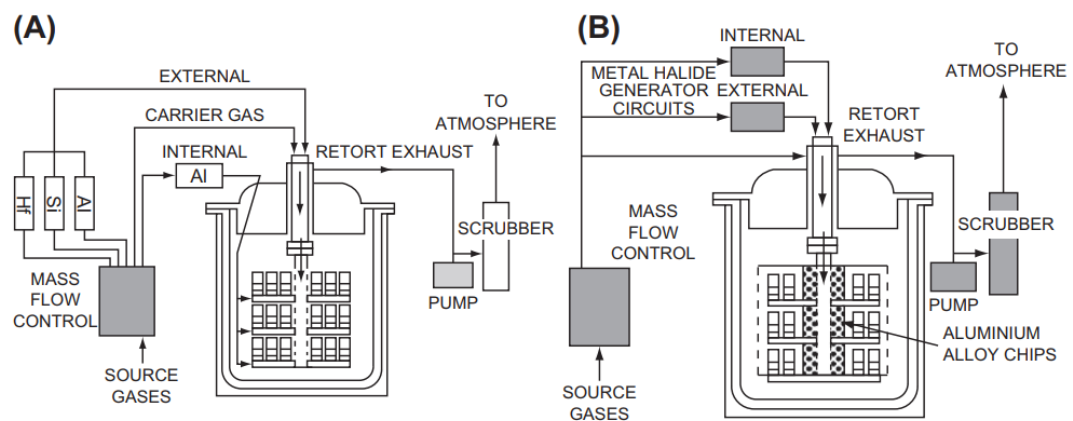


Figure 2.11 Chemical vapor deposition process for diffusion coatings. (A) Low-activity codeposition of Si, Hf, and Al; (B) high-activity plain aluminide [8].

One of the benefits of CVD is that the coatings are very clean, which improves their oxidation resistance. Additionally, the gas can pass through components, such as vane or blade with cooling channels. This means that both the internal and external surfaces of the components can be coated. In contrast, pack aluminizing might result in diluent particles blocking cooling pores, which must be removed after processing.

The ability to precisely manipulate the chemistry is another advantage of CVD. This allows for the incorporation of additional elements such as yttrium (Y), aluminum (Al), silicon (Si), and hafnium (Hf) into the coating at precise levels. These

elements can improve the coating's properties, such as its strength, toughness, and corrosion resistance.

Overall, CVD is a versatile and effective process for producing aluminide coatings. It offers a number of advantages over other methods, such as pack aluminizing. These advantages include [8]:

- Consistent and uniform coatings
- Clean coatings with improved oxidation resistance
- Ability to coat internal and external surfaces of hollow components
- Ability to incorporate additional elements into the coating to improve its properties

2.4.3.1.5 Comparison of Processes

In general, the pack process and slurry aluminiding processes are relatively inexpensive compared to the above-the-pack and gas phase CVD processes, but they may not produce coatings with high a level of purity. The above-the-pack process and gas phase CVD processes can produce coatings with high purity, but they are more expensive. All four processes involve high temperatures and may require additional heat treatment to achieve the desired properties of the coating and the substrate. The advantages and disadvantages of all processes are summarized in Table 2.2.

Table 2.2 Comparison of Process

Coating Application Method	Advantages	Disadvantages
Pack Process	Inexpensive	May not produce coatings with high purity
Above-the-Pack Process	Can produce coatings with high purity	More expensive
Slurry Aluminiding Process	Simple and inexpensive	May not produce coatings with high purity

Gas Phase CVD Process	Can produce coatings with high purity	More expensive
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2.4.3.2 Overlay Coatings

Overlay coating is a technique used to apply a protective layer of material onto a substrate surface to enhance its resistance against corrosion, wear, or other types of damage. Various methods can be employed for overlay coating, such as thermal spray, plasma spray, and high velocity oxy-fuel (HVOF) spray.

In thermal spray, molten or semi-molten particles are propelled onto the substrate surface using high-pressure gases or an electric arc, which solidify upon impact to form the coating.

Plasma spray involves using a high-temperature plasma torch to melt and atomize a stream of material, which is then sprayed onto the substrate surface to create a coating.

HVOF spray employs a high-pressure gas stream to propel heated feedstock material, either in powder or wire form, onto the substrate surface at high velocities.

Overlay coatings can be applied to different types of substrates, including metals, ceramics, and polymers, with the aim of improving their wear resistance, corrosion resistance, or other mechanical properties.

In this thesis, coatings applied to parts such as blades located in the flow path are examined. Since overlay coating is not applied to these parts, it is not detailed in this thesis.

2.4.3.3 Manufacturing Features of the Coating Process (Pack Process)

Figure 2.12 illustrates the common manufacturing steps involved in a pack process. When coatings are applied, they can lead to a reduction in certain mechanical properties of the coated item due to its brittleness. It is necessary to identify areas on the part where coating is not required due to being unaffected by excessive temperatures and corrosion. Coating should not be applied to these areas.

To prevent coating application on undesired regions, proper masking should be implemented during the coating process.

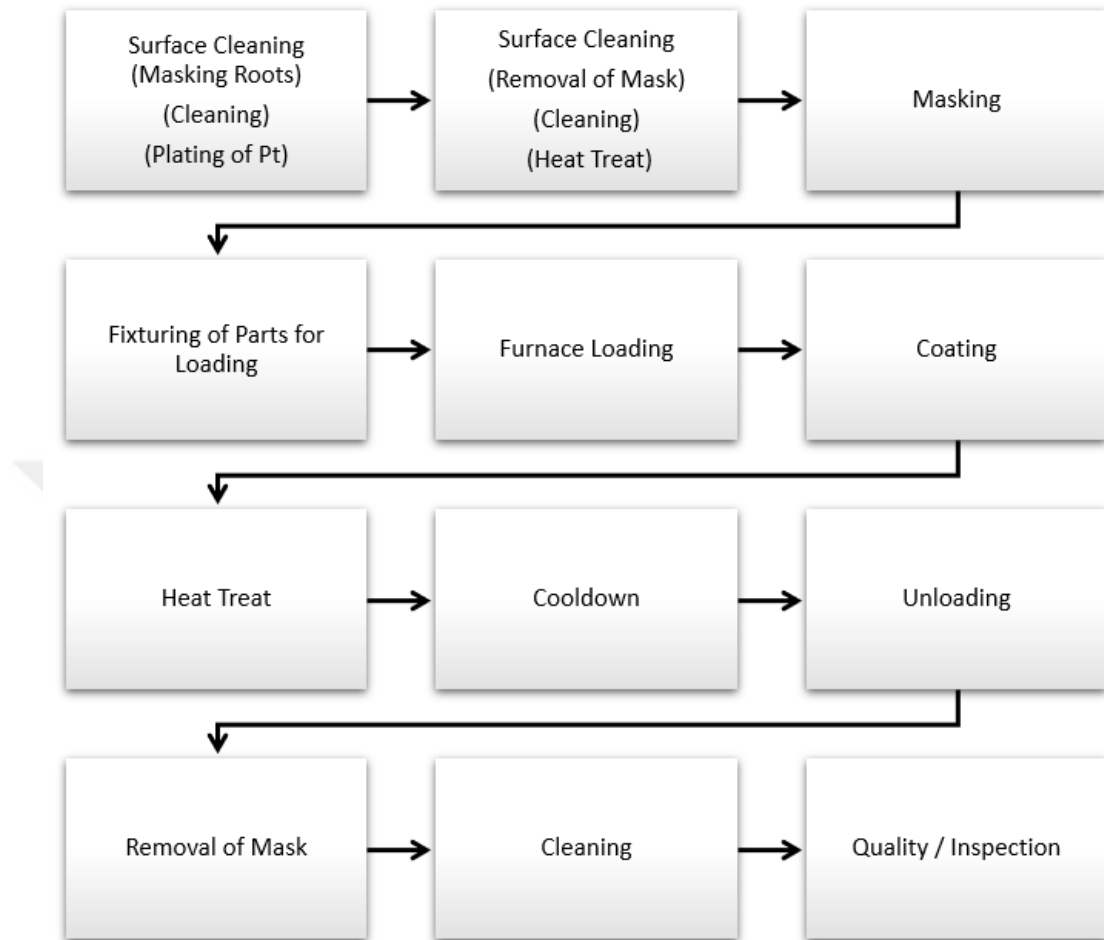


Figure 2.12 Manufacturing process steps for coating articles [8]

2.4.3.4 Coatings Repair

The overall service life of a component is divided into several segments between planned equipment revisions. During each set of revisions, the repaired component must provide an acceptable level of integrity to meet performance targets. During the coating removal process, approximately half of the diffusion zone, which is about half of the coating thickness, is also removed. This results in a decrease in the wall thickness of the part. Therefore, the number of repair cycles for coatings is limited. The thickness of the interdiffusion zone varies depending on the coating

application process, and the limit of coating cycles varies according to the thickness value.

The repair of coatings is typically one step in the broader process of component repair. The overall repair sequence can be summarized as follows [8]:

- Inspection of external surface and internal passages
- Determining repairability
- Cleaning the component
- Cleaning of cooling channels (alkaline autoclave/ultrasonic)
- Removal of old TBC (Thermal Barrier Coating) and metallic coating on the component:
 - TBC coating: Abrasive blasting or high-pressure water jet
 - Metallic coating: Chemical stripping
- Removal of oxides in cracks on the component
- Cleaning and drying of the component
- Inspection and dimensional measurement
- HIPing (Hot Isostatic Pressing) to eliminate porosity and restore dimensions
- Masking application
- Build-up of bond coat, depending on the type of bond coat, with specific steps
- Diffusion heat treatment
- Build-up of ceramic coating after associated coating with heat treatment
- Laser drilling of film cooling holes if required
- Application of heat treatment
- Surface finishing for improved aerodynamic performance

In Figure 2.13, a coupon repair example is given on a turbine vane leading edge.

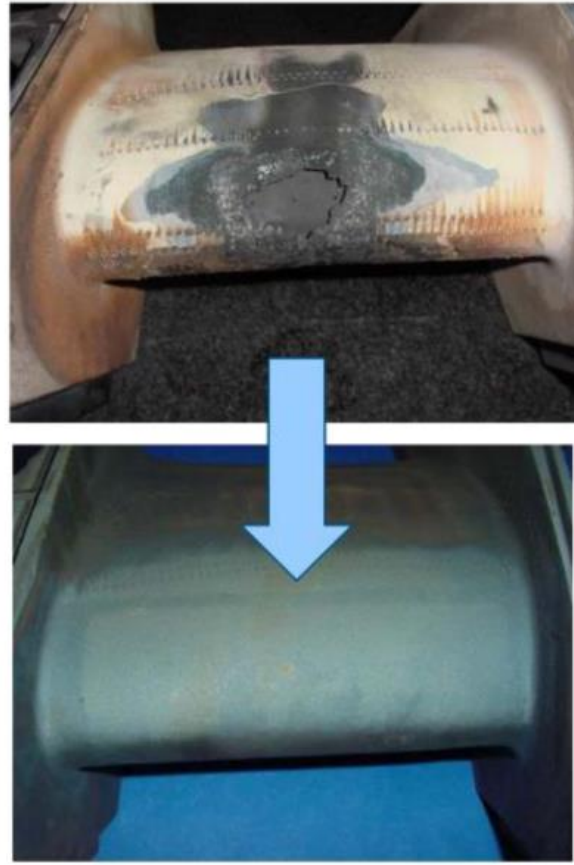


Figure 2.13 Turbine Vane Leading Edge Coupon Repair. Top: Leading edge coating loss and severely oxidized; Bottom: Coupon Attached, ready for coating [8]

2.5 Oxidation Life Calculation

The oxidation life of a material is the time it takes for the material to fail due to oxidation. The oxidation life of a material is important for the design and operation of many components and systems, including gas turbine engines, heat exchangers, and rocket engines. These components and systems operate at high temperatures and pressures, which can cause materials to oxidize.

Several studies have been conducted to evaluate the lifespan of metallic coatings in terms of cyclic oxidation, spallation, and diffusion of oxide-forming elements. Coating degradation occurs due to simultaneous oxidation and interdiffusion between the coating and substrate. Nesbitt and Heckel developed a numerical model to simulate this degradation. The accuracy of the model was tested

by comparing the predicted and measured aluminum and chromium concentration profiles. The obtained data from the tests were used for verification purposes. [43].

During high-temperature oxidation, microstructural changes occur in MCrAlY (CoCrAlY, CoNiCrAlY) coatings. Lee et al. investigated changes and developed a finite difference computer program to model these changes in the coating. [44].

Probst and Lowell have studied the behavior of materials during cyclic oxidation. As a result of these studies, a program has been developed. The lifetime simulation of the program is based on the assumption that the weight fraction of fragmented oxide scales in each thermal cycle is proportional to the initial amount of oxide scales present at the beginning of the cycle[45].

On the other hand, A computer model called COSP (Cyclic Oxidation Simulation Program) was created by Lowell. During the study, two different spallation models were compared. These are a simple uniform spalling model and a more complex random spall model. The study found that the simpler model provided accurate predictions in most cases. [46].

The COSP model has been updated by Smialek et al. This update included the incorporation of different growth laws and spallation modes. As a result, it enabled the evaluation of various input parameters and their effects on the oxidation process. [47] [48]. They also developed a deterministic model called DICOSM (Deterministic Interfacial Cyclic Oxidation Spalling Model) that incorporates iterative scale growth and spalling. This model considers interfacial spallation occurring at a constant area fraction only at specific thickness portions [49].

Chan conducted studies to evaluate oxidation life. As a result of the study, he developed a model that takes into account the spallation of an oxide scale on a coated metallic substrate during a cooling cycle. Based on micromechanics principles, this model seeks to more correctly estimate the oxidation life, incorporates a fracture mechanics approach to explicitly relate the weight of spalled oxide to the relevant physical and mechanical properties of the oxide. Unlike previous models, this approach allows for the consideration of possible temperature dependence observed in material parameters. Blades and vanes in the hot section of an engine operate within a temperature range. This model enables the safe estimation of model constants for accurately evaluating the oxidation life within this range. [50]. Chan's

studies is used by the Electric Power Research Institute (EPRI) for oxidation life calculations in COATLIFE.

2.5.1 COSP

The COSP method is a numerical simulation technique that uses mathematical models to calculate the oxidation life of a component. It takes into account factors such as temperature and time to determine the oxidation rate and predict the oxidation life. The COSP method can provide a more accurate prediction of the oxidation life compared to empirical models [46] [45].

The COSP has been used to predict the oxidation life of a variety of materials, including titanium, nickel, and steel. The COSP has been shown to be accurate in predicting the oxidation life of these materials. The COSP can be used for the design and optimization of components used in gas turbine engines.

COSP accounts for oxygen absorption during the heating phase as well as oxide loss during the cooling phase due to spalling. It forecasts the kinetics of weight change and metal loss by taking the balance of scale formation and scale loss into account. The method is predicated on two assumptions:

- (1) the amount of oxide spalled is directly proportional to the amount of oxide present
- (2) the growth kinetics remain constant from cycle to cycle, with the amount of oxide grown determined solely by the amount of oxide present at the beginning of each cycle [46].

This equation defines the fraction of oxide spalled:

$$F = \frac{W_s(n)}{W_{ox}(n)} \quad (2.14)$$

Specific weight is the ratio of weight to area. It is assumed that the fraction of material spalled, F , is directly proportional to the specific weight before spalling occurs According to the first assumption mentioned above:

$$F = Q_0 W_{ox}(n) \quad (2.15)$$

where Q_0 is a constant of proportionality that is measured in units of specific weight.

Equation 2.14 and Equation 2.15 can be combined to form Equation 2.16:

$$W_s(n) = Q_0 (W_{ox}(n))^2 \quad (2.16)$$

The oxide grows during the first heating cycle. (See Figure 2.14, point A):

$$W_{ox} = Z \sqrt{k_p t} \quad (2.17)$$

$$Z_{Al_2O_3} = \frac{M_{Al_2O_3}}{M_{O_3}} \quad (2.18)$$

The given Equation 2.17 represents the relationship between oxidation time (t), the proportion of oxide's molecular weight to oxygen's molecular weight in aluminum (III) oxide (Z), the molecular weight (M), and the oxidation kinetic constant (k_p).

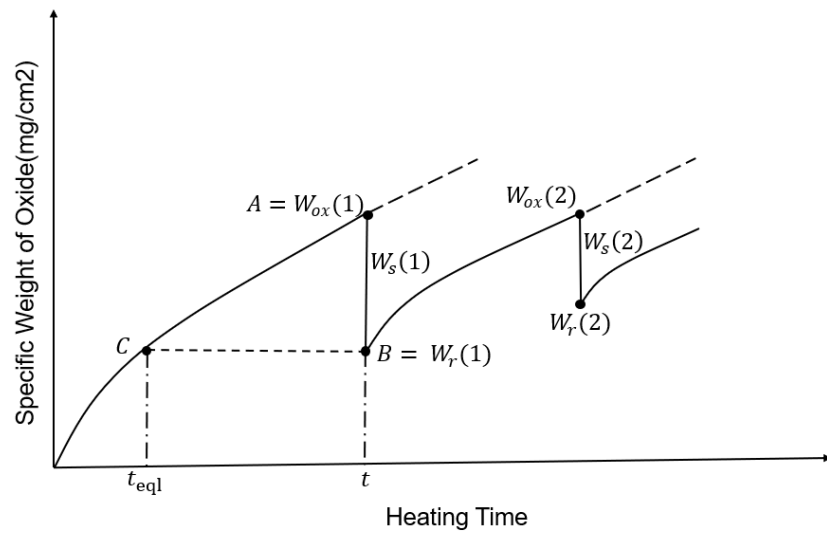


Figure 2.14 Definition of effective time

To calculate the spall specific weight:

$$W_s(1) = Q_0 Z^2 k_p t \quad (2.19)$$

The retained oxide's specific weight after cooling, $W_r(1)$, is obtained by subtracting $W_s(1)$ from:

$$W_r(1) = W_{ox}(1) - W_s(1) = Z \sqrt{k_p t} \left(1 - Z Q_0 \sqrt{k_p t} \right) \quad (2.20)$$

Point B in Figure 2.14 represents $W_r(1)$. Before estimating the oxide growth for the subsequent cycle, it is necessary to determine the effective time, t_{eff1} . The rate of oxidation increases as a result of the reduction in oxide layer thickness after spallation, which occurs at the end of a heat cycle. This augmented oxidation rate subsequent to spallation is addressed by incorporating the notion of an effective time. The effective time, denoted as t_{eff} , in cyclic oxidation denotes the duration needed to generate an oxide layer with an equivalent thickness under isothermal conditions. The elevation in oxidation rate that follows spallation is simulated by employing the concept of an effective time. [45].

The effective time refers to the duration necessary to generate an oxide layer with a specific weight, denoted as $W_r(n)$, under isothermal testing conditions. Graphically, this is accomplished by horizontally projecting point B to point C on Figure 2.14 and determining the corresponding value on the t_{eff1} abscissa. Alternatively, analytically calculating the effective time involves the following equation:

$$W_r(1) = Z \sqrt{k_p t_{eff1}} \quad (2.21)$$

Substituting and resolving for t_{eff1} :

$$t_{eff1} = t \left(1 - Z Q_0 \sqrt{k_p t} \right)^2 \quad (2.5.1)$$

Equation 2.17 can now be used to calculate the specific weight of oxide on the surface before cooling during the second cycle, $W_{ox}(2)$:

$$W_{ox}(2) = Z \sqrt{k_p(t_{eff1} + t)} \quad (2.22)$$

Following the second cycle's cooling phase, the specific weight oxide's spall:

$$W_s(2) = Q_0 Z^2 k_p(t_{eff1} + t) \quad (2.23)$$

At the end of the second cycle, the specific weight of the oxide remained is determined:

$$\begin{aligned} W_r(2) &= W_{ox}(2) - W_s(2) \\ &= Z \sqrt{k_p(t_{eff1} + t)} \left\{ 1 - Z Q_0 \sqrt{k_p(t_{eff1} + t)} \right\} \\ &= Z \sqrt{k_p(t_{eff2})} \end{aligned} \quad (2.24)$$

$$t_{eff2} = (t_{eff1} + t) \left[1 - Z Q_0 \sqrt{k_p(t_{eff1} + t)} \right]^2 \quad (2.25)$$

The remaining calculations for any cycle can be performed using the same procedure as described above. Equation 2.26 to Equation 2.29 can be generalized for any cycle, denoted as n , by:

$$t_{effn} = (t_{eff(n-1)} + t) \left[1 - Z Q_0 \sqrt{k_p(t_{eff(n-1)} + t)} \right]^2 \quad (2.26)$$

$$W_{ox}(n) = Z \sqrt{k_p(t_{eff(n-1)} + t)} \quad (2.27)$$

$$W_s(n) = Q_0 Z^2 k_p(t_{eff(n-1)} + t) \quad (2.28)$$

$$W_r(n) = W_{ox}(n) - W_s(n) \quad (2.29)$$

$$= Z \sqrt{k_p(t_{\text{eff}(n-1)} + t)} \left\{ 1 - ZQ_0 \sqrt{k_p(t_{\text{eff}(n-1)} + t)} \right\}$$

During cyclic oxidation, the cumulative weight change of the sample, $(W_c)_n$, can be determined by subtracting the weight lost due to spallation of the oxide layer from the weight gained due to the formation of the oxide layer. Therefore, the actual weight change of the sample after the i_{th} cycle, $(W_c)_n$, can be expressed as [45]:

$$W_c(n) = (1/Z)W_r(n) - (1 - 1/Z) \left(\sum_1^n W_s \right) \quad (2.30)$$

The loss of the oxide-forming element from the substrate or coating due to oxidation and spallation is represented by the cumulative weight of metal loss, W_m . This can be expressed as follows [45]:

$$W_m(n) = (1 - 1/Z) \left[W_r + \sum_1^n W_s \right] \quad (2.31)$$

2.5.2 COATLIFE

The COATLIFE method is similar to the COSP method but is designed to provide a more practical and user-friendly tool for calculating the oxidation life.

$$W_{ox} = Z \sqrt{k_p t} \quad (2.32)$$

The given Equation 2.32 represents the relationship between oxidation time (t), the proportion of oxide's molecular weight to oxygen's molecular weight in aluminum (III) oxide (Z), the molecular weight (M), and the oxidation kinetic constant (k_p).

The given Equation 2.33 represents the the effective time is defined as the time required to grow an oxide of a specific weight equivalent to $W_r(n)$ in an isothermal test. Similarly, the effective time should be calculated for the COATLIFE method.

$$t_{effn} = [t_{eff(n-1)} + t] \left[1 - q\Delta T^2 \frac{(W_{ox}(i))^m}{W_0^{m+1}} \right]^2 \quad (2.33)$$

During the cooling cycle of a substrate with a metallic coating, the spallation of an oxide scale occurs. According to Figure 2.15, σ_∞ represent the compressive stress acting on the oxide scale, which is a combination of stress and a thermal stress. The oxide scale contains pre-existing cracks. The geometric dimensions of the first shear crack, which are its depth (l_0) and its angle (ψ) with relative to the surface, are indicated. Under compressive stress, merge of shear cracks can be seen and form wing cracks with a length of l that propagate parallel to the oxide surface.

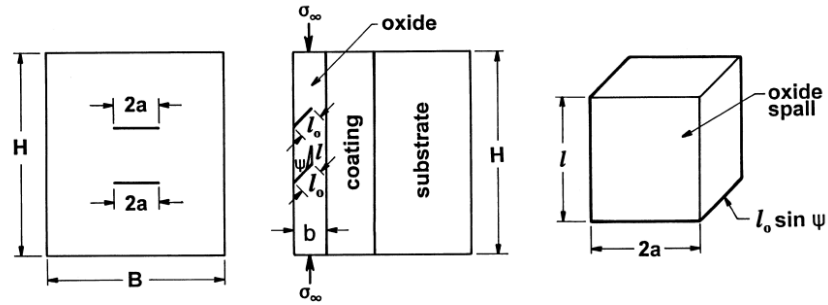


Figure 2.15 A diagram illustrating the mechanism of oxide spallation through the propagation of a wing crack between two shear cracks [50]

The wing crack with a nearby shear crack, leading to the spallation of the oxide layer. To simulate this phenomenon Chan expressed the weight of the cracked oxide on a micromechanical scale with Equation 2.34 [50]:

$$W_s = q\Delta T^2 \left[\frac{W_{ox}}{W_0} \right]^{1+m} \quad (2.34)$$

$$q = \frac{\zeta_0 W_0 \sin^2 2\psi \sin^3 \psi}{\pi} \left[\frac{E_{ox} \Delta \alpha \sqrt{l_0}}{K_{ox}} \right]^2 \quad (2.35)$$

The parameter q in Equation 2.35 has the advantage of incorporating various material parameters such as the length, angle and density of microcracks, Young's modulus of oxide (E_{ox}), fracture toughness of oxide (K_{ox}), and the difference in the coefficient of expansion between the oxide and the substrate or coating ($\Delta\alpha$). This allows for a comprehensive representation of these factors within the equation. The weight reference value, W_0 , can be chosen arbitrarily, such as 1 mg/cm^2 . Therefore, when using a phenomenological approach, only the constants q and m need to be determined from experimental data. To evaluate the values of q and m , the model can be fitted to experimental data, such as weight change measurements [50].

The overall kinetics of cyclic oxidation has been represented as a process that encompasses the formation and spallation of oxides during thermal cycling. The weight of the remaining oxide, W_r , on the surface of the coating after a thermal cycle can be described as follows:

$$W_r = W_{ox} - W_s \quad (2.36)$$

The model incorporates expressions for the cumulative weight change, total weight of spalled oxide, and weight of aluminum loss as functions of the number of thermal cycles. The expression for the cumulative weight change per unit area, W_c , after n thermal cycles is derived as follows [45]:

$$W_c(n) = (1/Z)W_r(n) - (1 - 1/Z) \left(\sum_1^n W_s \right) \quad (2.37)$$

As well as the weight of metal loss after the n_{th} cooling cycle:

$$W_m(n) = (1 - 1/Z) \left[W_r + \sum_1^n W_s \right] \quad (2.38)$$

3. LIFE PREDICTION METHODOLOGY

The metal loss in the coating can be attributed to two main factors: outward diffusion of aluminum to form the oxide scale during thermal cycles and interdiffusion of aluminum into the substrate. However, in the life prediction methodology calculations, the focus has been primarily on the contribution of outward diffusion, while the effects of interdiffusion have been neglected. This approach allows for the determination of thickness contraction and aluminum content in the coating during thermal cycles, taking into account the mass balance of aluminum loss resulting from oxidation and spallation.

The thickness parameters, h_0 , h_1 , and h_2 , as shown in Figure 3.1.

h_0 : initial thickness of the coating

$h_1(n)$: thickness of the oxide layer after the n_{th} thermal cycle,

$h_2(n)$: thickness of the depleted layer after the n_{th} thermal cycle.

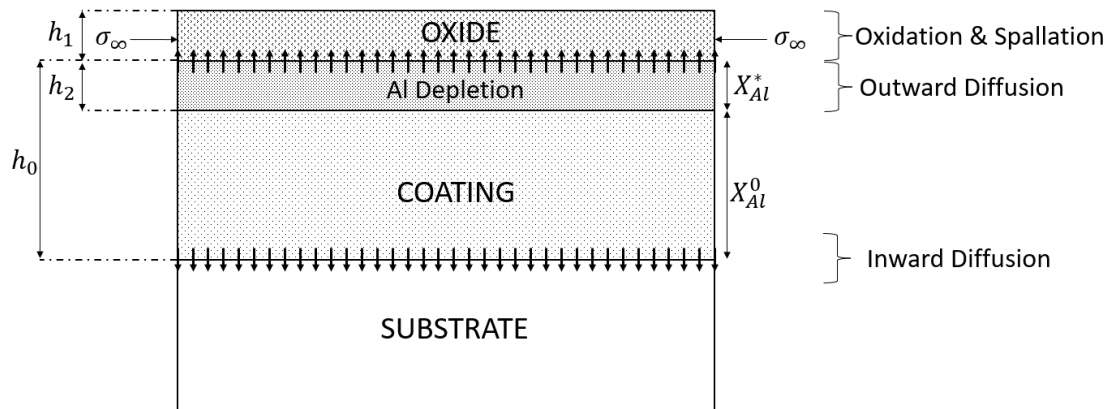


Figure 3.1 Potential causes for coating deterioration in a typical metallic coating

Therefore, the Al loss in the coating can be determined using the following equation:

$$(m_{Al}^0) - (m_{Al}^*) = W_m \quad (3.1)$$

$$(h_2(n)\rho_0 A \cdot X_{Al}^0) - (h_2(n)\rho_* A X_{Al}^*) = W_m(n) \quad (3.2)$$

$$h_2(n) = \frac{W_m(n)}{(\rho_0 A X_{Al}^0 - \rho_* A X_{Al}^*)} \quad (3.3)$$

where ρ_0 is coating density is, ρ_* is the depleted coating's density in the β phase, X_{Al}^0 is the initial aluminum content of the coating, X_{Al}^* is the critical aluminum content, and A is arbitrary unit area and can be taken as 1 cm^2 .

The thickness of the oxide layer can also be calculated with Equation 3.4.

$$h_1(n)\rho_{\text{oxide}} A = W_r(n) \quad (3.4)$$

The focus has been solely on the reduction of aluminum in the composition of the coating alloy. A mass balance has been established between the coating and the metal within the oxide. Based on certain assumptions, the density of the coating in the undamaged region is given as follows [51]:

$$\rho_0 = \frac{X_{Al}^0 M_{Al} + (1 - X_{Al}^0) M_m}{\frac{X_{Al}^0 M_{Al}}{\rho_{Al}} + \frac{(1 - X_{Al}^0) M_m}{\rho_m}} \quad (3.5)$$

where M_{Al} is the molar weight of aluminum, M_m is the mean molar weight of the other element compositions, ρ_{Al} is the density of aluminum, and ρ_m is the mean density of the other element compositions. The density of the coating in the depleted area is given by [51]:

$$\rho_* = \frac{X_{Al}^0 \left(\frac{X_{Al}^*}{1 - X_{Al}^*} \right) M_{Al} + (1 - X_{Al}^0) M_m}{\frac{X_{Al}^0 \left(\frac{X_{Al}^*}{1 - X_{Al}^*} \right) M_{Al}}{\rho_{Al}} + \frac{(1 - X_{Al}^0) M_m}{\rho_m}} \quad (3.6)$$

After the completion of the n_{th} thermal cycle, the mean aluminum content of the coating, denoted as $\bar{X}_{Al}(n)$, can be calculated using the following equation, assuming a uniform distribution throughout the coating:

$$\bar{X}_{Al}(n) = \frac{X_{Al}^* h_2(n) + X_{Al}^0 (h_0 - h_2(n))}{h_0} \quad (3.7)$$

The coating's useful life is deemed to be zero when the mean aluminum content reaches a critical amount, which results in degradation or failure of the coating, therefore the remaining life (RL) of the coating can be calculated [50]:

$$RL = \frac{\bar{X}_{Al}(n) - X_{Al}^*}{X_{Al}^0 - X_{Al}^*} \text{ for } X_{Al}^0 \geq \bar{X}_{Al}(n) \geq X_{Al}^* \quad (3.8)$$

The lifespan of an aluminide coating depends on having an adequate amount of aluminum present to form a protective alumina film, which slows down oxidation. If the aluminum content in the coating becomes too low to form a continuous oxide film, accelerated oxidation may occur on the exposed substrate.

3.1 Experimental Data

Coating and material data were selected from the literature. The first stage turbine blade with an aluminide coating (diffusion type) was utilized to compare the oxidation life methods. The blade material is GTD-111 alloy [52].

Table 3.1 provides information about the superalloy's composition. Additionally, the coating properties required for the coating life model are summarized in

Table 3.2. These properties include various parameters and characteristics relevant to the coating, which are necessary for estimating the expected lifespan of the coating under specific operating conditions.

Table 3.1 Nominal Composition of GTD-111 in Weight Percent

Material	C	Cr	Co	Mo	W	Pt	Ta	Ti	Al	Zr	Ni
GTD-111	0.1	14	9.5	1.5	3.8	-	2.8	4.9	3.0	0.01	Bal.

Table 3.2 Specifications of Aluminide Coating

	Thickness	$X_{Al}^0(at. \%)$	$X_{Al}^*(at. \%)$
Aluminide	33.8	38	19

According to the test data from the literature, the GTD-111 turbine blade with Aluminide coating was tested in temperature ranges between 25°C and 1066°C peak temperature with 1-hour cycle [52].

The oxidation life model includes three material constants (See Table 3.3): k_p , m , q and Q_0 . These constants are determined through experimental data analysis, where the goal is to accurately reproduce the weight change curves observed during oxidation. By fitting the model to the experimental data, the values of k_p , m , q and Q_0 can be determined, enabling the prediction of the oxidation life of the material under specific conditions. The evaluation of these material constants is crucial in ensuring the accuracy and reliability of the oxidation life model.

Table 3.3 Coating Life Material Constants

	$T_{max}: 1066^\circ C$		$T_{min}: 25^\circ C$	
Constans	m	Q_0 (mg/cm^2)	q ($mg/cm^2/^\circ C^2$)	k_p ($mg^2/cm^4/h$)
Aluminide	0.6	0.001539	1,42E-09	0.0036

4. RESULTS

Weight change curves obtained through experimental measurements, as well as the calculated results using two different methods, for GTD-111 alloy coated with an aluminide coating (See Figure 4.1). This comparison allows for an assessment of the accuracy and reliability of the calculation methods in predicting the weight changes observed during the thermal cycling of the coated GTD-111 alloy.

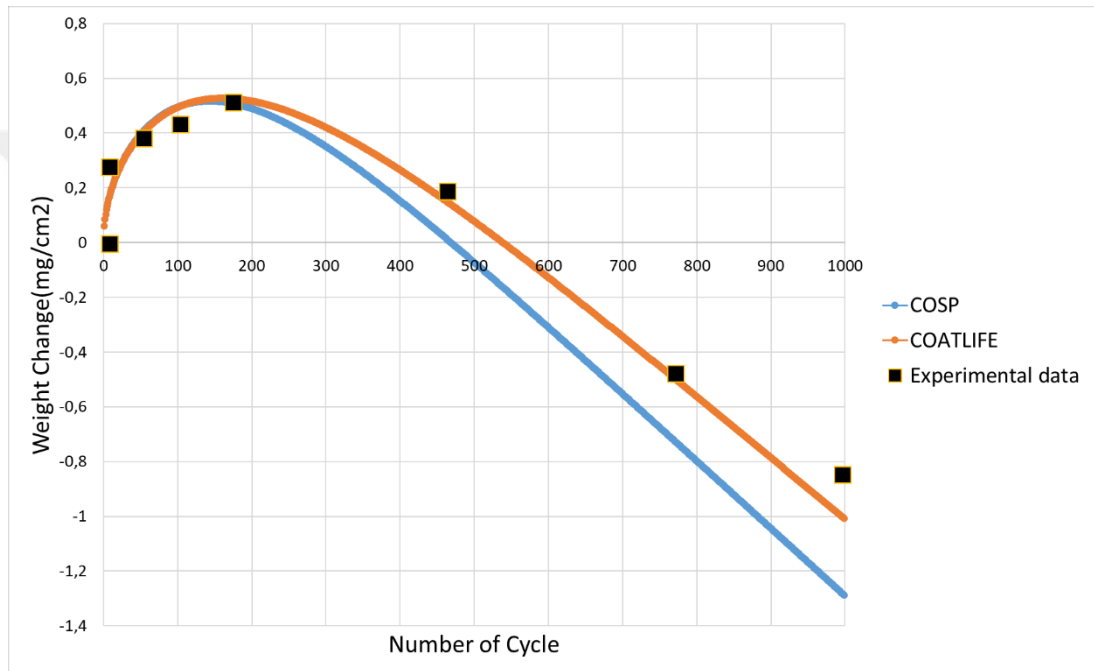


Figure 4.1 Comparison of Calculated and Experimental Weight Change

The comparison of different methods for weight change (W_c) revealed that the COATLIFE method exhibited greater compatibility with the experimental data. This finding indicates that the COATLIFE method more accurately predicts and aligns with the actual outcomes observed in practical experiments.

Weight of metal loss (W_m), weight of oxide (W_{ox}), weight of oxide spalled (W_s), remaining life (RL), mean aluminum content ($\bar{X}_{Al}(n)$) and coating thickness ($h_0(n)$) calculated using two different methods were further compared to identify any discrepancies between the two approaches. By analyzing these parameters, a comprehensive assessment of the differences between the two methods was made. This comparison allowed for a thorough understanding of the variations in the

calculated values obtained from each method. By identifying and evaluating the disparities between the parameters, valuable insights were gained into the strengths and limitations of each method, aiding in the selection of the most accurate and reliable approach for future calculations and analyses.

As previously mentioned, the key differences between the two methods based on the calculation of spallation mass. While COSP relies on assumptions to estimate the spallation mass, COATLIFE uses the mechanical properties of oxidation layer. By comparing Equation 4.1 and Equation 4.2, the differences can observe between the methods.

$$COSP: W_s(n) = Q_0 Z^2 k_p (t_{\text{eff}(n-1)} + t) \quad (4.1)$$

$$COATLIFE: W_s = q \Delta T^2 \left[\frac{W_{ox}}{W_0} \right]^{1+m} \quad (4.2)$$

This disparity in spallation mass calculation is illustrated in Figure 4.2, highlighting the difference between the two methods.

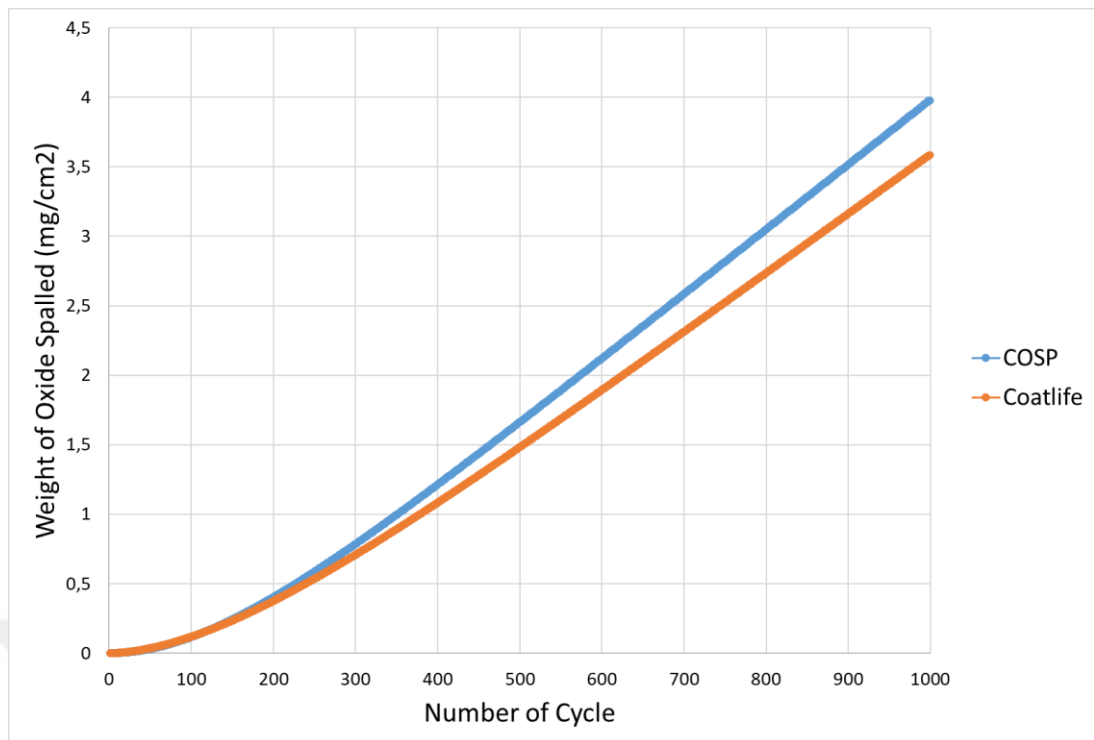


Figure 4.2 Comparison of Calculated Weigh of Oxide Spalled

In Figure 4.3, the graph illustrates the weight of metal loss observed. While the oxidation formation calculation is similar in both methods, there is a notable difference in weight of metal loss due to variations in the spallation calculation methods employed.

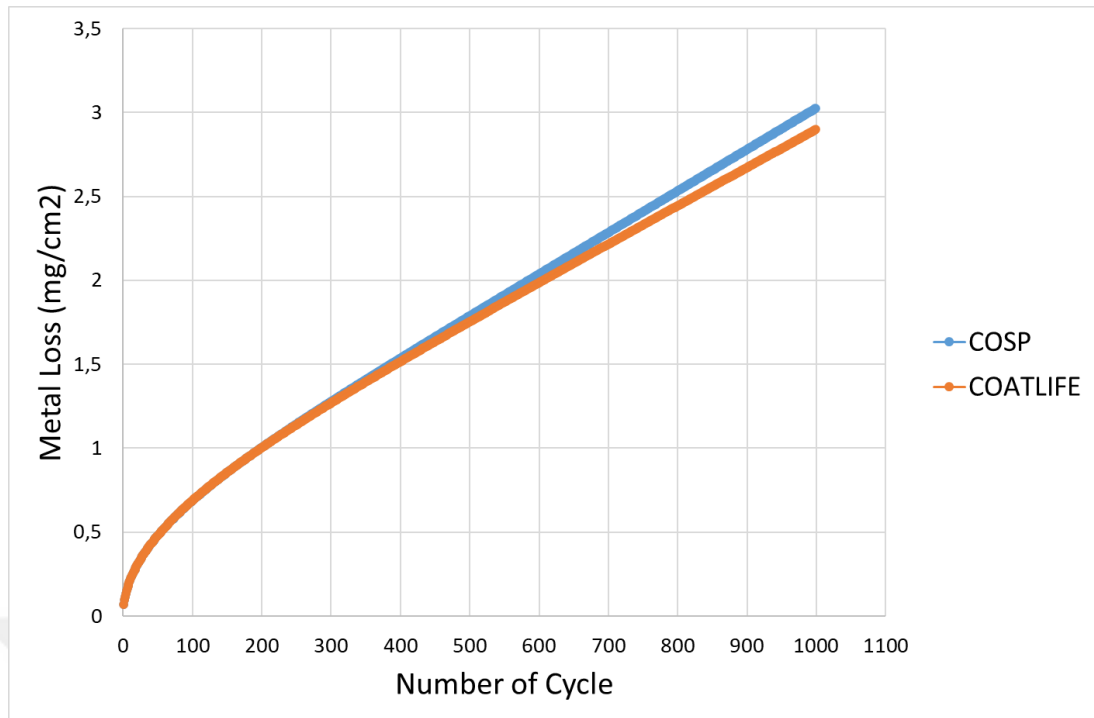


Figure 4.3 Comparison of Calculated Weight of Metal Loss

Figure 4.4 represents the time-dependent weight of the oxide mass formed. The discrepancy observed is primarily attributed to the variation in the calculation approach, particularly in the effective time (t_{eff}) calculation. This discrepancy directly impacts the weight of the oxide layer developed over time.

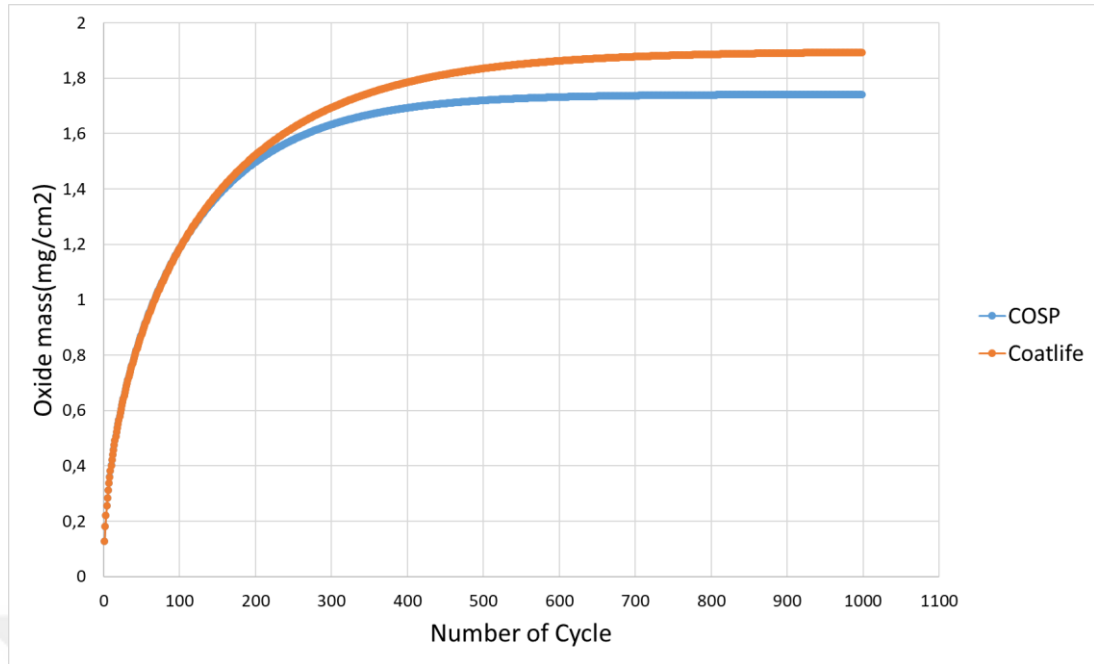


Figure 4.4 Comparison of Calculated Oxide Mass

The end of the coating's lifespan, as previously stated, occurs when the mean aluminum content ($\bar{X}_{Al}(n)$) value exceeds the critical aluminum content (X_{Al}^*). In order to comprehensively analyze the coating life, three key figures are presented: Figure 4.5 illustrates the remaining life coating, Figure 4.6 depicts the concentration of aluminum over time, and Figure 4.7 illustrates the changes in coating thickness during each cycle. These three graphs are useful for monitoring the lifespan of the coating. If the coating thickness reaches “0” or if the the mean aluminum content ($\bar{X}_{Al}(n)$) value on the graph reaches the critical aluminum content (X_{Al}^*) value, it indicates that the coating has completed its life.

The graphs also provide information about the specific cycle in which the coating reaches the end of its lifespan. By examining these graphs, one can determine the progress of the coating's degradation and accurately identify when its useful life has come to an end.

The life prediction methodology employed in this study relies on evaluating the extent of metal loss (See Equation 4.3). Due to the variation in metal loss results between the COSP and COATLIFE methods, the calculated coating life is correspondingly influenced.

$$h_2(n) = \frac{W_m(n)}{(\rho_0 AX_{Al}^0 - \rho_* AX_{Al}^*)} \quad (4.3)$$

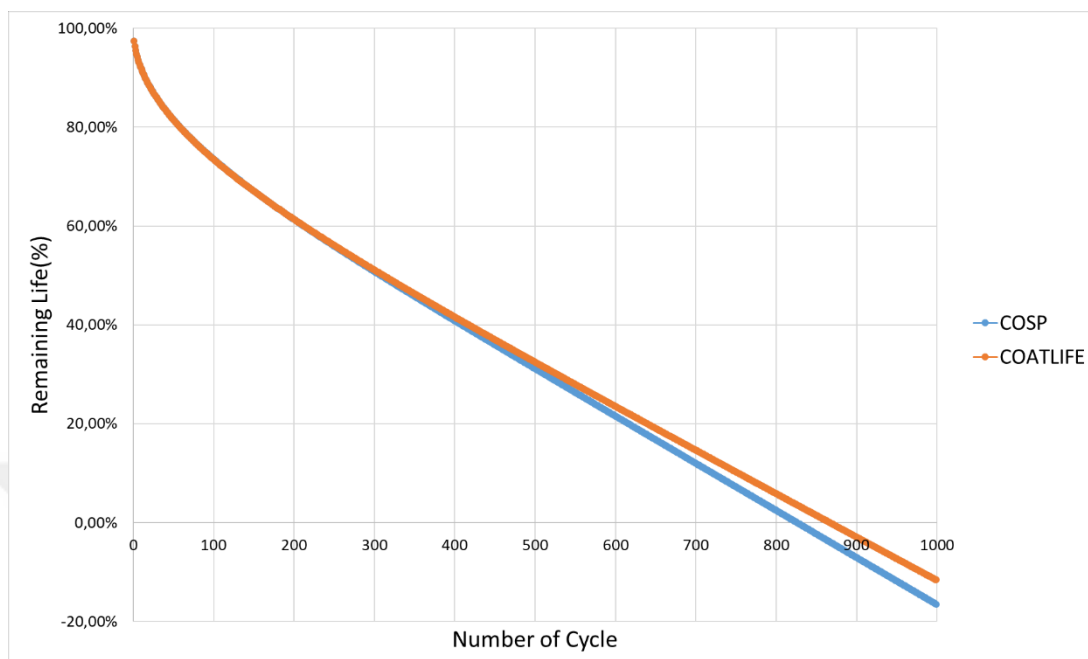


Figure 4.5 Comparison of Calculated Remaining Life

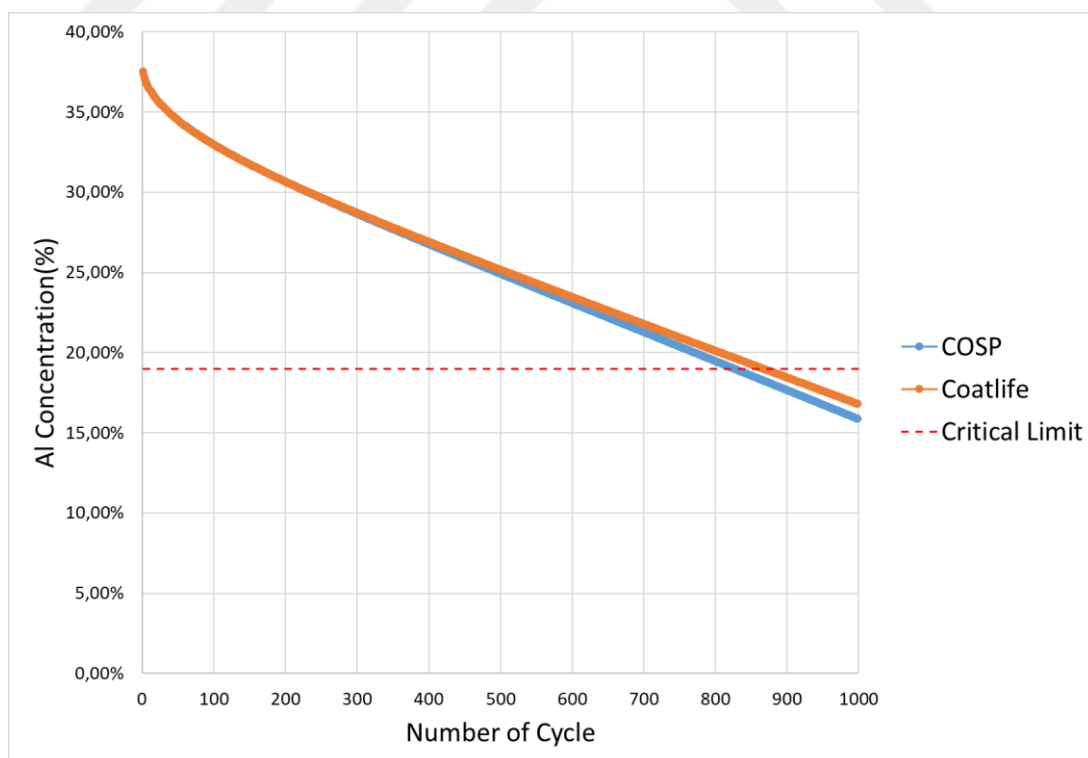


Figure 4.6 Comparison of Calculated Al Concentration

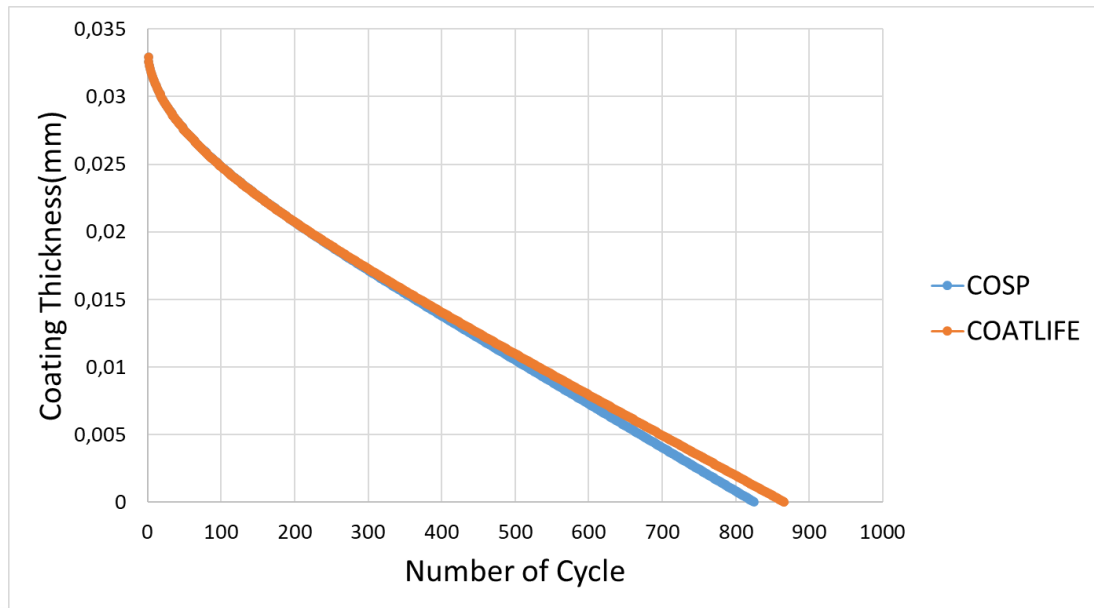


Figure 4.7 Comparison of Calculated Coating Thickness

The coating reaches the end of its life after 827 cycles according to the COSP method, while the COATLIFE method predicts a life cycle completion time of 867 cycles. This 4.84% difference between the two methods is indicative of the disparity in the coating life estimates.

Based on the evaluation, COATLIFE weight change (W_c) result demonstrates compatibility with the material data, suggesting that it provides reliable results. On the other hand, when conducting life cycle assessments, COSP yields more conservative results. This indicates that COSP takes a cautious approach, potentially leading to more conservative estimates or predictions in terms of the coating's lifespan and performance. It's important to consider these factors when interpreting the results and making decisions based on them.

5. CONCLUSION

This study focused on investigating the thermodynamics, mechanics, and kinetics of oxidation, particularly in relation to the materials used in gas turbine engines. The research delved into the intricate relationship between oxidation and the various materials employed in these engines. Additionally, a comprehensive overview of coatings and coating technologies was provided, highlighting their significance in mitigating oxidation-related issues. Various oxidation life calculation methods were thoroughly examined and compared, and the disparities between the two methods were documented. Notably, it was observed that these differences impacted the estimation of the remaining life of the coating. Through the comparative analysis, it became evident that the COATLIFE method exhibited better compatibility with the experimental data. On the other hand, when conducting life cycle assessments, COSP yields more conservative results for coating life span. The findings underscored the importance of accurately predicting the remaining life of the coating, emphasizing the significance of selecting an appropriate calculation method to ensure optimal performance and durability of the coatings.

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BIOGRAPHY

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