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Review on Improvement the Turbine Oxidation and Hot Resistant against Corrosion by Nickel–Based Superalloy

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Abstract. High-temperature oxidation has been an important scientific and technological subject for many years since it is a life-limiting factor in most equipment operating at high temps. Turbine blades used in Iraqi electrical gas power stations frequently require expensive maintenance by traditional processes. These blades are made of nickel superalloys such as IN738LC, where this alloy was used as a substrate material in this research to repair its corroded surfaces. Currently, coatings used for high temps involve thermal barrier coatings (TBC), overlay, and diffusion. The protective properties of diffusion coatings are related to forming SiO₂, Cr_2O_3 , and Al_2O_3 scales on the silicide, chromite, or aluminide at high temperatures. Diffusion coatings were first created and are the most often utilized.

Keywords: turbine oxidation, hot resistant against corrosion, superalloy.

Introduction

Protective coatings are a surface layer of materials, either metallic or ceramic or combinations thereof, which can preclude or inhibit the direct interactions between a substrate and a possibly harmful environment [1–5]. Extreme environments may lead to a loss in the material due to the processes of oxidation/corrosion along with a reduction in mechanical characteristics of the substrate because of the deleterious elements that diffuse to the substrate at high-temp protective coatings interact with oxygen in the atmosphere to form dense, adherent oxide scales inhibiting diffusion of the damaging environmental species to the substrate [6]. Protective coatings are generally rich in elements, including Al and Cr, and act as reservoirs for these elements [7–11]. A new scale is formed from this reservoir when the scale is lost due to thermal or mechanical forces. The lifespan of a protective coating is regulated by the capability of the coating to form a protective scale and retain or replace this scale [12].

The efficiency of various alloys exposed to high temps depends on their mechanical resistance and the characteristics of the corrosion/oxidation [13]. The successful applications of those alloy kinds, which are usually referred to as superalloys, are a result of their high long-time creep strength and the stability at the increased temp degrees that are combined with their exceptional resistance against corrosion (which is usually with a protective coating) in an aggressive environment that is encountered throughout the service [14]. The turbine blades have been considered critical components in stationary and aeronautical gas turbines. The engine's efficiency has been tightly associated with the material's ability to withstand higher temperatures. Stimulated with civil air transportation and military aircraft demands after 1955, the cast super alloys substituted initial wrought superalloys. Nickel-base super alloys have matrix γ phase, with a face-centred cubic (FCC) structure, which contains a dispersion of the ordered inter-metallic precipitate particles of kind γ' -Ni₃Al [14].

This review comprehensively evaluates advancements in nickel-based superalloys and coating technologies designed to enhance oxidation resistance, hot corrosion resistance, and mechanical performance in high-temperature turbine applications. By addressing the degradation challenges faced by turbine components in aggressive environments, the review identifies effective protective coatings and strategies to mitigate these issues. The primary aim of this review is to critically analyze existing literature on the development and application of nickel-based superalloys and associated protective coatings. The review focuses on understanding the mechanisms that improve oxidation and hot corrosion resistance while highlighting gaps in the research. It seeks to propose potential avenues for future investigations and provides recommendations to improve turbine component performance and durability under extreme operating conditions.

1. Superalloys

Superalloys have advanced mechanical characteristics at higher temperature degrees that approach melting point and good resistance to high-temperature corrosion. They represent the main material class utilized for high-temperature components. In fact, they are the only materials that are commercially available and retain their corrosion/oxidation-resistant and mechanical characteristics at high temperatures [15].

Superalloys, particularly Nickel-base superalloys, are a metallic material class commonly utilized as technologically significant materials in a variety of industry sectors, such as electric power generation equipment, high-temp chemical vessels, gas turbines, nuclear reactors, and thermal capacitors for the automotive industries [16,17].

Nickel-based superalloys are utilized as materials for the hot components of aero-engines, marine, and landbased gas turbines. Those superalloys have good mechanical characteristics but low resistance to oxidation at high temperatures and aggressive gas environments. To improve their lifetime, the superalloys must be protected from oxidation, heat, and corrosion degradation. An aluminide coating deposited on the Ni-based superalloy provides good corrosion and oxidation resistance to the elements [18].

The term super alloys covers a set of Co-, Ni-, and Fe-based alloys mainly designed for operating in a 500°— 1100°C temp range in land-based gas turbines and jet engines. Those alloys are multi-component complex alloys, which, besides Fe, Co, or Ni, include a variety of the W, Nb, Al, Cr, Mo, Ta, Ti, Zr, B, Re, Hf, and C amounts for obtaining the required strength, besides corrosion and oxidation resistance [19].

The present study is fundamentally focused on corrosion and oxidation resistance topics. Serious results drive coating technology development through corrosion and oxidation and the way mechanisms by which they happen. Hot gas turbine components operating in aggressive environments have undergone attack modes collectively called high-temp corrosion, including sulphidising, oxidation, chlorination, carburizing, erosion, and hot corrosion induced by the molten salts. Protective coating was one remedy for the lack of high-temp surface stability for metals and alloys in harsh environments [20].

There are three basic superalloy classes: Ni-base, Co–base, and Fe-base. Superalloys are utilized in numerous high-temp fields, from the gas turbines used in aircraft to industrial and marine applications. Today, the largest consumer of superalloys is aircraft in the gas turbine engine industry [21,22].

1.1. Nickel Base Super Alloy

Ni-base superalloys have excellent efficiency, typically combining ductility, high melting point, high strength (creep, fatigue, and tensile strength), toughness, and resistance against corrosion at greater temperatures. One of the significant applications of Nickel-base superalloys is producing blades and vanes in gas turbines [23]. Figure 1 illustrates a Ni-base superalloy chart that contains different Ni and Fe amounts. The contents of the Chromium are constant at about 18-20 % [24].



Fig.7. - Chart of Nickel-base super alloy [24].

Ni-base alloys range from simple two-component (i.e., binary) alloy systems to very complicated alloys containing up to 12 alloying elements. The main elements that are related to Ni in commercial alloys consist of Fe, Cr, Mo, and Co; however, as it has been inferred earlier, several other elements have been included in alloy kinds for imparting specific properties, such as required strength, resistant against corrosion, and ductility. For instance, Al added to the Ni alloys introduces the hardening of the precipitation through forming AlNi₃, or γ' phase (Figure 2). Additions of Ti and Nb also create the hardening precipitates and inter-metallic. Even non-metallic materials are sometimes added to the Ni alloys. For instance, some of the powder metallurgy alloys can be strengthened through dispersing inert particles like yttria, which are sometimes coupled with precipitation of γ' . The γ phase dissolves up to 4wt. % Al below 400°C. Solubility is increased by increasing temp. However, γ' phase has a narrower phase field, meaning that composition does not significantly depart from the AlNi₃. β field is quite broad, indicating that Aluminum concentration may widely depart from the stoichiometric composition AlNi in this phase. In addition, β phase's melting point is considerably higher than pure Nickel's. Those β phase properties are highly preferable in coatings at high temps. The high aluminium concentration helps provide a large aluminium reservoir for protection from oxidation by forming and replenishing the Al₂O₃ scale [15,25,26].



Fig. 8. - Nickel-Aluminum Phase Diagram [27].

1.2. Nickel-Cobalt Base Super Alloy

It can be defined as a unique complex alloy class based on Nickel and Cobalt, exhibiting exceptionally high strength and maintaining strength across a wide range of elevated temps called the 'super alloys.' Some alloy kinds are utilized at over 80% of the melting point in load-bearing applications. Both metals are attractive since their crystal structures and high melting points are amenable to extensive alloying. While Nickel shows an FCC crystal structure, Cobalt is a hexagonal close-packed (HCP) crystal at room temperature. The addition of an alloying element is generally utilized to stabilize the Cobalt in FCC form. Several strengthening mechanisms have produced practical alloys with Nickel and Cobalt [28].

1.3. Nickel–Iron Alloys

Which can be defined as an alloy class (Muzyka & Brown, 1987) that contains 25-60% Ni and 15-60% Fe with austenite FCC structure as a matrix and strengthened with the precipitates with extra advantages from the strengthening of the grain boundary and the solid solution. Those alloys cost less compared to the Nickel and Cobalt base superalloys. Nickel–Iron alloys may be classified into five groups:

• The first group is relatively Iron-rich, with 25-35% Nickel and < 2% Titanium. The strengthening phase is the coherent FCC (the gamma prime) precipitates. Using temp has been limited to 650° C (i.e. 1200° F).

• The second group is rich in Nickel, with more than 40% with an increased contribution from solid solution. The strengths of that alloy group exceed the ones of the affluent group. The commercial members of this alloy group are the Inco X750 and Inconel 901.

• Third group: abundant in Nickel and owes strength to the coherent BCT (i.e., the body-centered tetragonal) (referred to as the double prime gamma) precipitates. Inco706 and Inco718 are examples of this group, with Inco718 representing one of that class's most utilized alloys. Those alloys' temp capability ranges from cryogenic to 650°C (1200 F).

• Fourth group: an iron-rich Fe–Ni-Co alloy with low thermal expansion accomplished by removing Mo and Cr, stabilizing the ferrite in structure. The strength of this group of alloys is derived primarily from the coherent FCC precipitates. Commercial members of this class are Inco 903 and 909, with temp capability limited to 650 °C. Eliminating Cr makes the alloys more susceptible to oxidation and corrosion [24,26,29].

• Fifth group: The distinctive characteristic of this Nickel-rich group is the absence of coherent precipitates. Some group members derive strength from nitrides, carbides, and carbonitrides precipitates. Others (such as N-155 and Hastelloy X) have strengthened their solid-solution capabilities. The latter's application temp for the non-stressed application has been limited to $1093^{\circ}C$ [24].

1.4. (Ni-Cr) Phase Diagram

Ni–Cr alloys grew in importance in the 1930s because of the cost of gold. Nickel-chromium alloys have sufficient characteristics to be used with ceramics. The elastic modulus and hardness of Nickel-Chromium alloys provide the ability to utilize a thinner material's cross-section, which provides more space for the porcelain veneering while remaining to offer good resistance. An additional benefit is their linear thermal expansion coefficient, like veneering porcelain. Thermal expansion similarity reduces risks of fractures and cracks throughout the processing. The sensitivity of the Ni could be a concern with those alloys (Figure 3). When choosing those alloys, a patient's sensitivity to Ni must be evaluated thoroughly and carefully. Binary Ni–Cr alloys were recognized early as having high-temperature oxidation resistance. It should be mentioned that a higher Cr is required for a temperature increase. The commercial alloys mainly include 20–30% Cr for the stabilization of a protective Cr scale and always include several minor additions for improving their chemical and mechanical characteristics: typical

'Nichrome' (UNS N-06003, EN/DIN 2.4869) includes 1% Silicon and 0.01–0.04 reactive element. In comparison, the Nimonic 75 includes 0.50% Titanium [30].



Fig. 9. Ni-Cr Phase Diagram [30].

2. Gas Turbines

Gas turbine blades must satisfy a lifetime of as high as 25000 h. Moreover, super or high-efficiency alloys are utilized to make them because they must withstand various degradation types (like thermo-mechanical fatigue, creep, corrosion, and oxidation) that occur throughout service exposure to aggressive environments. Gas turbine blades for land-based power plants are composed fundamentally of Nickel-base superalloys because Ni can retain the highest retainers at high temperatures compared to others [26,29].

The gas turbine comprises three main sections: the compressor, combustor, and turbine (even though, from the viewpoint of the material, the other main groups of components– i.e., casing, rotor, and auxiliaries – are essential as well). The combustor, turbine, and compressor sections have been represented in Figure 4. The ambient air enters the gas turbine at the inlet of the compressor. While air passes through sequential compression stages (alternating static airfoil rows referred to as the stators or the compressor vanes and rotating airfoils referred to as the compressor blades), temp and pressure increase. At the same time, the work is carried out to decrease the air volume. Then, compressed air passes to the combustion section, where air is heated further by introducing and burning the fuel. In a combustor, there is a volume increase. However, the pressure stays almost constant. Gas produced throughout the combustion expands through the turbine section (a turbine is like a compressor, which includes alternating rotating blades and static vane rows). The expanding gas performs the work because it results in the rotation of turbine blades. This rotation is driving an external generator and the compressor [31].



a)

Fig. 10. - a) Turbocharger; b) Path of Exhaust Gases in Turbocharge [29,31].

b)

Ultimately, combusted gas exits the turbine via the exhaust duct. The pressure-volume diagram in Figure 5 characterizes this cycle.



Fig.11. - Schematic pressure-volume diagram for industrial gas turbines utilized with Permission from Siemens Energy [26,29].

In general, the gas turbines use large excess air amounts for the combustion (a large air fraction is utilized as well for cooling combustor), with a typical ratio of air/fuel from approximately 40 to 1 (throughout the take-off) to 100 to 1 (at a speed of cruising) for the aircraft gas turbine engines. Those air-to-fuel ratios correspond to approximately (0.12 to 0.18) mole oxygen fractions in the combustion zone, which is why the gas atmosphere of the combustion is very oxidizing. Sulfur partial pressure in the atmosphere might be shallow, ranging between (10-40) atm and (10-26) atm over a range between (330 to 1230) °C (620 to 2240) °F. Those partial sulfur pressures are well below those required for forming the chromium sulfides, often noticed in the alloys that suffer hot corrosion attacks [32,33].

2.1. Gas Turbines Components

Demanding operating conditions for the gas turbine engines resulted in various coatings designed to protect the superalloy turbine's components from corrosion, resulting from fuel impurities, atmospheric contaminants, and increased temps. To achieve the high-temperature mechanical characteristics that are needed by the modern technology of the gas turbine, superalloys had to sacrifice hot resistance against corrosion and oxidation, which was inherent in the previously utilized heat resistance alloys with higher Chromium contents. As a result, the coatings are dependent upon for protecting the components of the superalloy, like the vanes and turbine blades, from environmental attacks. Developing and applying high-temp coatings enhanced efficiency and fuel economy in marine, aircraft, and land-based industrial turbines [34–36].

Throughout the 1st quarter of the 20th century, Chromium has been added to Co, Ni, and Fe in various amounts. The resultant products had remarkable resistance to the atmospheric (i.e., the moisture) environments and to oxidation at high degrees. By World War II, some of those alloys, which include other alloying elements, became used for applications like dental prostheses, resistance wires, cutlery, and steam turbine and furnace components. With the development of gas turbine engines throughout WWII, the need for materials resistant to corrosion to operate in the demanding conditions of the mechanical load at high temps has become apparent. At this point, the fledgling superalloy industry had begun expanding. Through the modification of stainless steels, higher levels of strength have been accomplished without a need for the particular strengthening phases at high temps. Phases like η (a Ni-Al compound) were presented to Ni–Cr alloy families right before the war for producing high strength at high degrees. Increased temp degrees have forced the alloy developers to include those phases ($\gamma \& \eta$) in Fe-base alloys to take properties of high-temp strength beyond the ones of modified stainless steels like the 19-9-DL. Alloys were first produced in Germany, and, following the modification, they reached the US as A286 or V57 and have remained used until now [37].

Nevertheless, the need for creep-rupture strength is continuously increasing. A part of this need has been met in the early years through the adaptation of Co-base corrosion-resistant alloy (i.e., the Vitallium) to be used in the superchargers of aircraft engines and, after that, in airfoils in hot sections of the gas turbines. Similar co-based superalloys remain used today. Nonetheless, the requirements of the creep-rupture for the applications of the aircraft gas turbines soon out-stripped the ones of Fe-Ni-base superalloys and Co-base superalloys, which is why Ni-base superalloys, which have been modified to provide more hardening phase γ , has become increasingly utilized [37].

2.2. Superalloys Used for Gas Turbine

The successful utilization of Ni-based superalloys in both the land-based and aero-gas turbine industries is a testament to the possible commercialization of new materials, mainly intermetallic. Power generation and air travel would not be possible as we know them if not for the superalloys developed during the last 60 years [38].

• Inconel alloy 706 can be defined as a precipitation-hardenable alloy with properties like alloy 718, except that it has highly enhanced machinability. It has a sufficient level of resistance to corrosion and oxidation over a wide variety of temperature degrees and environments. Like alloy 718, 706 has excellent resistance to post-weld

strain-age cracking. Applications often include gas turbine components and other parts, which must have high strength, good weldability, and machinability.

• Inconel 718 is a high-strength, age-hardenable alloy that is proper for the service at temp degrees from 253° C (i.e., 423° F) to 704° C (i.e., 1300° F). Inconel 718 has high fatigue strength and shows a high stress-rupture strength up to a temp of 704° C (1300° F) and oxidation resistance of as high as 982° C (i.e., 1800° F). It also offers good resistance against corrosion in many different environments. The exceptional property of the Inconel 718 is that it has a slow response to age hardening, which allows the material to be annealed and welded without any spontaneous hardening unless it has slowly cooled. The Inconel 718 may as well be repair-welded in entirely aged conditions. The typical applications represent jet engine components, pump parts and bodies, thrust reversers and rocket motors, and spacecraft [39].

• Inconel X750 is an age-hardenable Ni–Cr–Fe alloy utilized because of its oxidation, resistance against corrosion, and high creep-rupture strength of 816°C (i.e., 1500°F). This alloy has been made age-hardenable by adding Al, Nb, and Ti, combined with the Ni, throughout the suitable heat treatment for forming the inter-metallic compound Ni3(Al, Ti). X750, developed for jet engines and gas turbines, was adopted for many other utilizations due to its favorable characteristics. The exceptional relaxation resistance has made Inconel X750 suitable for springs operating at temps that might reach as high as 649°C (i.e., 1200°F). In addition, this material shows good ductility and strength at temps as low as 253°C (423°F). Inconel X750 also shows high resistance to the chloride-ion stress-corrosion cracking even in age-hardened conditions. The usual applications include gas-turbine parts (i.e., industrial and aviation), nuclear reactors, springs (i.e., steam service), vacuum envelopes, bolts, extrusion dies, heat-treating fixtures, bellows, aircraft sheets, and forming tools.

• *Inconel 617* can be defined as a solid-solution-strengthened alloy containing Co. Its perfect combination of oxidation resistance and high-temperature strength makes it a beneficial material for gas turbine aircraft engines and other areas that involve exposure to extreme temperatures, like the pressure vessels and steam generator tubing for the advanced high-temperature gas-cooled nuclear reactor [40].

• Inconel 738: Alloy IN-738 is a highly significant nickel-based superalloy. It is made by melting and casting it in a vacuum, and it can be hardened by precipitation. This alloy has exceptional strength against creeprupture at high temps, and it also has better resistance to hot corrosion compared to many other superalloys with lower chromium levels. This design aims to provide the gas turbine industry with an alloy that has excellent resistance to deformation at temps up to 980oC while also being capable of enduring prolonged exposure to the high temps and corrosive conditions often seen in engines. Alloy IN-738 demonstrates improved tensile qualities compared to increased temp stress-rupture and similar capabilities to Alloy 713C, which is commonly used. Additionally, it has much greater resistance to sulfidation. There are two variations of Alloy IN-738: IN-738HC, which has a high carbon content, and IN-738LC, which has a low carbon content [39].

The hot corrosion attacks are decreased with the temp decrease to lower than 927 °C (i.e. 1700°F). At temps of less than 760°C (i.e., 1400°F), the mechanism of the hot corrosion is changed under specific conditions. The attack can start dramatically increasing with the decrease in the degree of temp; however, after that, it has decreased again with the decrease of temps to less than approximately 649°C (1200°F). In such a regime of a lower degree of temp, the province of the land-based power gas turbines, attacks are resisted optimally by producing chromium oxide on the surface. As a result, the alloys for that application and region include the IN738 designed particularly for having higher levels of the Cr in some of the faces back up higher than 20pct. (IN939 is one of the alloys in this latter category.) Other alloys have been devised to provide optimal resistance to hot corrosion in higher-temp services. Examples of those alloys are IN792 [41].

3. High-Temp Oxidation

In engineering applications, most metals and alloys have lower thermodynamic stability than their oxides, so they react with the environment to reduce their free energy. Usually, such a reaction forms a solid oxide layer on the surface, separating metal from the environment. The rate and reaction path of specific metal/gas reactions are, in turn, regulated by several parameters, like temp, gas pressure, surface morphology, and alloy composition. [42].

Generally, there are three stages of the oxidation:

(i) The transient stage is identified by the simultaneous and temporary formation of oxide of each one of the active elements;

(ii) Steady-state stage, which is identified by the development of a protective oxide scale;

(iii) The break-away stage is identified by the accelerated attacks [43].

Oxidation resistance depends upon forming a defect-free, adherent oxide scale on the alloy surface. Generally, changes to protect oxidizers and exclusively protective oxides occur at higher temps and longer times. These changes involve attaining a complete external protective oxide scale, which is a steady state. The steady-state period or the time to break-away duration has been considered the most critical factor in the practical oxidation behavior. At this step, the overall reaction is regulated by the reactants' solid-state diffusion through the oxide scale, which reduces the reaction rate with the increase of time, which is a parabolic rate [44].

Thermodynamically, the oxide formation will only occur when the ambient oxygen pressure is larger than the oxide dissociation pressure in equilibrium with metal. In the case where the metals or the alloys are employed in

(1)

high-temp oxidizing environments, they are protected by oxide scale, forming and acting like a partial barrier to continuing environmental attacks, as:



Fig. 12. - The schematic diagram for oxide scale growth in high-temp oxidation process [44].

The oxide layer grows on metal by transporting ions, electrons, molecules, or atoms through the scale, as shown in Figure 6. The scale's capability for protecting underlying metal is acting as a mechanical barrier, and its mechanical integrity ceases inside it. Further growth behavior of the oxide scale depends upon transport mechanisms through the scale. The transport of metal ions outwards to the oxide/gas interface gives an outward-growing oxide, while the inward transport of oxygen ions gives inward growth of the oxide. In both cases, the transport rates will determine the growth rate of the oxide scale. The oxide's transport mechanisms may be divided into short-circuit and solid-state diffusion [45]. Typically, the alloys or the metals undergo oxidization at high degrees under an oxygen-containing atmosphere, which results in one oxide compound or more at the interface of gas/substrate. Such chemical species' growth can protect substrate material if this compound keeps providing a homogeneous, adherent, stable, and dense oxide layer to the surface. At the same time, it results in the reduction of oxidizing element transport to scale. Only a few oxide kinds show such properties at high temps, where all the diffusion processes are more activated.

Aluminum oxide (Al_2O_3) , chromium oxide (Cr_2O_3) , and silicon oxide (SiO_2) show these characteristics and possess specificities concerning the range of temp. Due to their complexity, the growth of such oxides has been of great interest. Essentially, several of the diffusion processes have been involved, in other words, diffusion in the volume and grain boundaries and anionic and cationic processes of diffusion, which may be revealed, for example, through the SIMS measurement.

The alloying elements' effect on the substrate may promote (Ti) or slow down (Zr, Y, Hf, and La) the formation of the oxide. Initial surface preparation also has an important impact on the formation of the oxide scale or, in other words, on developing the alumina layer. The chromium scale makes a good barrier that is hot-resistant against corrosion in temperatures between 950oC and 1000°C. Nevertheless, according to partial O_2 pressure at high temps, the vapor of the Chromium could be formed and volatilized. At the same time, CrO_3 was developed for high O_2 partial pressure (po₂), which resulted in the protective layer of the Cr_2O_3 being thinned down. Silica is relatively stable at high temps; however, it forms a glassy structure that is not sufficiently resistant to thermal shock. Numerous sequences of phase transformation that were impaired by starting the chemical composition of the raw material were reported in the literature. Such polymorphic transformation is also impaired by volume contraction in oxide de scale, which might be critical in establishing a protective layer of the oxide [46].

4. Hot Corrosion

Corrosion of the materials, including Nickel and Cobalt base super alloys induced by the molten salts in oxidizing gas at increased temperature, has been referred to as 'hot corrosion' to distinguish it from conventional low-temp corrosion. It results from accelerated oxidation at temperatures that are usually in the range of 700° C to 925OC, where the alloys and the metals get covered by contaminant salt films. Salts in the vapor phase are benign in general. The range of the temp within which the hot corrosion takes place is highly dependent upon gas constituents and salt chemistry, in addition to the composition of the alloy. Such corrosion was noticed in the petrochemical process equipment, coal gasifiers, boilers, internal combustion engine exhaust systems, gas turbine engines on aircraft, and industrial and marine applications. The partial pressures and temps of sulfur and oxygen in some industrial operations, even though gases separately, have no considerable corrosive effect, the overall environment in those operations results in forming molten and solid salts, which play a role in the corrosion [47,48].

Kind I hot corrosion, or high-temp corrosion, occurs at temps 800° and 950° C (i.e., 1470° and 1740° F). It has been believed that the deposit of the molten sodium sulfate is necessary to initiate the hot corrosion attacks. Usually, the morphology of Kind I hot corrosion is identified with a thick, porous oxide layer with an underlying alloy matrix depleted in Cr, which is succeeded by the internal Cr-rich sulfides. Kind II hot corrosion or low-temp generally happens in a temp range between 670° and 750° C (i.e., 1238° and 1382° F). Kind II hot corrosion has been identified through the pitting attack with little or no internal attacks underneath the pit. Co-base alloys are more susceptible to Kind II hot corrosion involving 100μ m [28]. The process of hot corrosion degradation of superalloys typically includes two stages :(a) a stage of initiation, throughout which alloys are behaving much like they would have behaved if there were no deposits, and (b) a stage of the propagation, in which deposit results in protective characteristics of oxide scales to be considerably different from the ones [49]. The low-temp hot corrosion mechanism includes forming base metal sulfates, which require a specific partial sulfur trioxide pressure to stabilize. Those sulfates react with the alkali metal sulfates to form compounds with low melting points, preventing the formation of a protective oxide [20].



Fig. 13. - Corrosion rate vs. temp [20].

5. Oxidation Law

As can be seen from Scheme 1, the product of the solid reaction MO will separate the two reactants if we consider reaction $M(s) + 1/2 O_2(g) = MO(s)$.



For the reaction to proceed further, one reactant or both must penetrate the scale; in other words, either one of the metals has to be transported via oxide to the interface of oxide–gas. The oxygen must be transported to the oxide–metal interface and then reacted there due to mechanisms through which reactants could penetrate the oxide layer, which has been considered a significant part of the mechanism through which high-temp oxidation occurs. In particular, the same can be applied to the sulfide formation and growth and other similar products of the reaction. The p-B ratio is defined as:

$$R_{PBB} = \frac{Voxide}{n.V metal} = \frac{M \text{ oxide.}\rho \text{ metal}}{M \text{ metal.}\rho \text{ oxide}}$$
(2)

where R_{PB} – Pilling – Bedworth ratio

n- number of atoms of metal per molecule of the oxide

M- atomic or molecular mass

 ρ – density

V-Molar volume

According to the measurements, the connection below may be shown:

 \bullet $$R_{PB}$$ less than 1: the layer of oxide coating is too thin, possibly broken, and does not provide any protective effects (e.g., Mg)

• R_{PB} higher than 2: oxide coating chips off and does not provide any protective effects (for instance, Fe)

• $2 > R_{PB} > 1$: oxide coating is passivating and provides a protective impact towards additional surface oxidations, such as Al, Ti, and Cr-containing steel) [50].

6. Coatings for High-Temp Applications

Most coating kinds depend upon isolation with a "barrier" of a part to be protected from environmental conditions. This barrier's role is to minimize the liquid or gaseous species' diffusion toward a component and, on the other hand, prevent the elemental diffusion from alloy toward the external surface where they would be reacting.

Most generally, a barrier is dynamic in that it is formed through coating interaction with an oxidizing environment, which is usually the coating case, whether ceramic or metallic, which results in the formation of oxides like Chromium, alumina, and silica. There is a wide range of available coating methods, and selecting the optimal process depends on functional requirements (such as substrate metallurgy, shape, and size), coating material's adaptability to the intended method, needed adhesion level, and equipment availability and cost. In general, all of the processes of the diffusion coating operations are formed due to five distinctly similar processing steps:

- 1. Generating vapor that contains Cr, Si, and Al.
- 2. Transporting that vapor to the component.
- 3. Vapor reaction with the substrate alloy element for the formation of various inter-metallic.
- 4. Diffusion in the alloy.

5. Post-processing heat treatment is used to obtain the desired composition and microstructure. Several different manufacturing methods have been developed for diffusion coatings. Figure 8 gives an overview of the most important procedures [51].



Fig. 14. - Diffusion coating manufacturing principle [51].

6.1. Pack Cementation

Pack cementation is an in situ CVD (for example, chemical vapor deposition) batch process that was utilized for producing oxidation—and corrosion-resistant coatings on inexpensive or otherwise inadequate substrates for more than 75 years [52,53].

During this procedure, the component that must be coated is submerged in a solution that contains the necessary coating material and a halide compound acting as a catalyst. The mixture and the substrate are enclosed in a sealed or partially sealed vessel and heated in a vacuum or pure argon gas at a designated temp. The halides of the material are conveyed to the surface of the material to be covered by evaporation with consistent heating. During this process, a contact occurs between the coated portion and the coating material. Novel phases or solid solutions are created inside the coating region. The significant parameters that affect the pack cementation process are [54]:

- 1. Chemical composition of the substrate;
- 2. Powder purity was utilized;
- 3. Time and Temp utilized in the cementation process;
- 4. The substrate surface state.

Figure 9 depicts the key stages of the pack cementation process. Metal halides are generated and conveyed via the gaseous phase to the component's surface for coating. At the surface, the halide reacts with the specimen and dissociates into the metal and the halogen anion.



Fig. 15. - Major processes throughout back cementation operation [51].

Pack cementation can be defined as a modified vapor deposition operation performed in a closed container at increased temp degrees (typically, 1000° C). Usually, a pack includes substrates that are to be coated and inert filler powders. The master alloy is rich in elements that require deposition and activator salts (NH₄Cl, NaCl, NaF, or a combination). Activator salt reacts with master all to generate the volatile metallic halides, diffusing through materials of the porous filler (typically, α -alumina) to the surface of the subs trade. At the surface of the substrate, metallic halide vapors participate in many potential reactions [55]. The metal atom undergoes diffusion into the surface zone of the substrate. The coating development is similar to diffusion couples, and the interdiffusion is driven by the activity or concentration gradient between the environment (containing diffusing materials like Al) and the component's surface [56]. Upon being released at the surface, the halogen reacts with fresh metal atoms derived from the powder, sustaining the process in a continual manner. Halogens, such as chlorine and fluorine (although bromine or iodine may also be utilized), act as activators.



Fig. 16. - The main chemical reactions involved in the pack cementation process [57].

The pack cementation process is usually utilized to form diffusion coating coatings, which improve the oxidation resistance of various heat-resistant samples.

6.2. Physical Vapor Deposition (PVD)

Three main kinds of **PVD** processes involve atom-by-atom transfer mode. PVD is a group of processes where the material is converted into the vapor phase in a vacuum chamber and condensed on the surface of the substrate as a very thin film. PVD may be utilized to apply many different coating materials. Those processes include evaporation of the electron beam (EB) and sputtering, which can be combined with ion plating [58].

EB PVD: Commercial electrons beam physical vapor deposition (EB PVD) coatings are created in a vacuum environment, 10^{-2} - 10^{-4} pa, with a deposition rate usually higher than 25μ m min⁻¹. Generally, the components are preheated in a vacuum at 800° - 1100° C and rotated inside the vacuum chamber during deposition. The overlay coating thickness can be much thicker, 150- 300μ m, or other diffusion coatings [59].

6.3. Chemical Vapor Deposition CVD

In the CVD processes (Figure 11), the $AlCl_3$ is produced outside the reactor before being sent to the reaction vessel, allowing accurate activity and flow rate control due to uniform and consistent layers of aluminide being created. A particular advantage of this system is coating cleanness, which yields enhanced resistance to oxidation and the fact that it can pass through, besides hollow components, like the turbine blades that have cooling channels so that the external and internal surfaces may be diffusion coated. On the other hand, pack aluminizing may result in causing the blockage of the cooling holes to be blocked with the particles of the diluent, requiring removal following the processing.



Fig. 17. - Diagram of low-activity co-deposition of Hf, Al, and Si in the CVD coatings [60].

Additional CVD advantage is that the chemistry may be regulated carefully, which enables the incorporation of additional elements like AI, Y, Hf, and Si into coating at an accurate level [60].

6.4. Plasma Thermal Spraying

Thermal plasma spraying can be defined as a procedure in which powder feedstock is injected in a hightemp plasma jet where finely divided non-metallic and metallic materials undergo deposition in semi-molten or molten states on the prepared substrate. It was utilized as one of the economical and sufficient methods for producing ceramic coatings on metallic substrates. Bulk powder production from spheroidization was fundamentally motivated by a strong drive for high-efficiency materials and the growing need for new materials processing technologies. The particles that are injected into the zone of the plasma will experience extreme rates of heating and temp degrees of up to 10000 K. Because the plasma spraying has been defined as a pretty high-temp process, injected particles with varying size distributions will melt, yielding aerosol of the molten droplets. Particles higher than the critical size range could only experience partial melting.

In contrast, small particles could have a vaporized material layer surrounding liquid droplet, so the plasma processing of the material with stringent requirements must be regulated carefully to produce the needed results because plasma technology's full potential depends on our capability to achieve an optimum match between process requirements and properties of the used plasma source and reactor designs. The plasma process has evolved into a highly flexible coating system that can be applied to many materials. One of the primary plasmas spraying applications is protecting components of aircraft engines by depositing the aerospace coating like the alumina or zirconium/ magnesium thermal barriers on the metal substrates. Lately, it has also been utilized as one of the tools for processing bio-ceramic materials like hydroxyl-apatite (HA) as both powders and coatings [14]. In the spray process, a plasma jet melts, coating feedstock in a powder form. Plasma is produced in a plasma gun. The typical gun's internal details have been illustrated in Figure 12. The process details can be summarized as follows:

A direct current between the stick-kind copper cathode (i.e., negative polarity) with the thoriated tungsten tip located along the axis of the gun and the water-cooled copper anode (i.e., positive polarity) generates electrical arcs (Figure 13). Being rigid, the thoriated tungsten tip decreases cathode wear [61].



Fig. 18. - Internal Metco Plasma gun characteristics [14].



Fig. 19. - Diagram of the Plasma Spray nozzle and internal processes [14].

6.5. Slurry Coating

The slurry-based diffusion coating can be found commercially; they offer similar chemistries to those in the traditional pack cementation aluminide coating. In the slurry cementation, halide activator and coating materials are blended as a particle-loaded paint system or slurry, using a water-base emulsion or an organic binder. The system slurry/paint may be applied as part to be coated by spraying, dipping, or almost at the room's temp. After that, the slurry spray is cured onto part via low-temp thermal treatment, usually about 200°C. cured prediffusion coatings could contain only Al+Cr, Al+Al₂O₃, Si+Cr and Al+Si depending upon final service conditions. Then, the precoated parts are heated in the furnace to allow the Aluminum diffusion (Silicon and other additions). This step's hold temp ranges between 650° and 1100° C, according to the substrate that will be coated and its final applications. Temp is selected such that the coating material contained in the slurry reacts and inter-diffuses with a substrate to form the final inter-metallic coating [48,62]. The chemical composition evolution of slurries follows industrial normalization as well. Paints and slurries can be applied easily; nevertheless, they have not been widespread in aero domains except for repairs. In the present day, due to process flexibility, the tailoring of elements must be performed to provide a sufficient response concerning several application domains, such as aeronautics [63].

7. Summary of Literature Reviewed

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Ref.	Coating	Powder	Condition of	Temp °C	The most important conclusions
	methods		hot corrosion		
[64]	Thermal	Ni-Cr-Al-Y	NaCl+V ₂ O ₅	1000	had studied hot corrosion in the components of
	barrier				gas turbines and concluded that hot corrosion
	coating				represents a mechanism of failure that causes
					high concerns in the engines of gas turbines.
[65]	Pack	Al-Cr	-	1100	Those coating kinds have very good resistance
	cementation				to high-temp oxidation, and their adequate
					temp of antioxidation may be increased to
					1100° C. The phases of NiAl and Ni ₃ Al have
					been considered the main constituents of the
					aluminized coating
[66]	arc ion	NiCoCrAlY	75 wt. %	900	Adding B and Si might enhance the coatings'
	plating (AIP)		$Na_2SO_4 + 25$		resistance to hot corrosion by promoting the
			wt. % K_2SO_4		growth of the continuous and dense layer of a-
					Al_2O_3 in the initial stage and enhancing the
					oxide scale adherence to coatings in successive
					processes of hot corrosion.
[67]	HVOF	NiCrBSi	Na_2SO_4 -	900	Formations of oxides in addition to Ni, Cr, or
	sprayed		$60\%V_2O_5$		Co could result in all coatings' resistance to hot
					corrosion.
[68]	Diffusion	Ni-30Cr-	75wt.%	900	The coating of the aluminized NiCrAlY had
	coating	8A1-0.5Y	$Na_2SO_4+25wt.$		shown considerably superior resistance to hot
			%		corrosion in the presence of 75wt. % $Na_2SO_4 +$
			K ₂ SO ₄ /NaCl		K ₂ SO ₄ /NaCl films due to forming a protective
					and continuous scale of Al_2O_3 .

Table 2.1. Summary of Literature Reviewed about increasing hot corrosion resistance and oxidation of Inconel alloys by coating

Ref.	Coating methods	Powder	Condition of hot corrosion	Temp °C	The most important conclusions
[69]	pack cementation process	Al-Cr-Y	Na ₂ SO ₄ , NaCl	900	The oxidation kinetics for the uncoated IN600 alloy in the air, CO_2 , and water vapor are almost parabolic. The values of the constant of the parabolic rate (k _p) that have been obtained at 900°C in the air, CO_2 , and water vapor were 2.68x10 ⁻⁷ and 4.16x10 ⁻⁷ mg ² /cm ⁴ , respectively
[70]	pack cementation process	CoCrAlY	Na ₂ SO ₄	1150	the Pt+Hf-modified $\gamma'+\gamma$ and $\gamma+\beta$ -CoCrAlY coating showed the improved performance of the KindI hot corrosion compared to Platinum-modified β .
[71]	Slurry	A spray gun was applied to the Al slurry	-		Preliminary testing studies indicate that Al slurry coatings can replace Cd in aircraft components.
[72]	Slurry	Al-Al ₂ O ₃	-		Results have shown that a coated layer is created by dissolving Ni in the liquid Al at Al temperature, forming a layer of the intermetallic compound. The coated layer's main phase is Ni_2Al_3 , which includes small amounts of AlCr ₂ and NiAl ₃ . AlCr ₂ mainly exists in the layer neighboring the top surface.
Ref.	Coating methods	Powder	Condition of hot corrosion	Temp _o C	The most important conclusions
[73]	plasma spray	YSZ	V_2O_5 and Na_2SO_4	1050	Based on experimental results, the nano- structured coating showed more sufficient hot resistance against corrosion and oxidation resistance than the conventional coating.
[74]	arc ion plating	NiCrAlYSi	Na ₂ SO ₄ and NaCl	1173 k	After the NiCrAlYSi has coated K40S, a protective scale of a-Al ₂ O ₃ has been created on that coating
[75]	pack cementation process	NiAl	Na ₂ SO ₄ + NaCl	1173 K	The presence of Cobalt in a coating might promote the establishment of a protective scale of Al_2O_3 on the coating and restrain internal sulfur diffusion in coatings.
[76]	Air plasma spray (APS), Low-pressure plasma spray (LPPS), and (EBPVD),		Chloride and vanadium	900 and 850	Because of the low chromium content and high tungsten content, CM 247LC is easily corroded. In comparison to IN738LC
[77]	-	-	NaCl + Na ₂ SO ₄	950	It has been discovered that the rate of sulfide corrosion is regulated with the process of high- temp Ni alloy dilution within liquid Ni sulfide eutectic
[78]	-	-	$\begin{array}{c} NaCl \\ V_2O_5 + Na_2SO_4 \end{array}$	550, 650	Salt mix coatings of NaCl, V_2O_5 , and Na_2SO_4 led to relatively slow oxidations at both temperatures. Increased salt coating thickness has been found to enhance hot corrosion rates.
[79]	Plasma	YSZ	Na_2SO_4 and V_2O_5	1040°C	Microstructural studies conducted with the SEM have shown that plasma coatings are sound and have no large pores or interfacial cracks.
[80]	Slurry	MoSi ₂	-	-	Max coating thickness of 60 μ m was achieved for MoSi ₂ and 5 μ m for Mo ₅ Si ₃ coating.

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Ref.	Coating methods	Powder	Condition of hot corrosion	Temp °C	The most important conclusions
[81]	thermal spray	Ni-Cr	(Na ₂ SO ₄ +K ₂ S O ₄)	900	This study summarized the characteristics of the Chrome carbide nickel chrome coating types deposited by various approaches and the hot corrosion behavior of the Nano-structured as well as conventional coating types in molten salt environments.
[82]	pack cementation process	Al-Si-Y	-	-	The optimal resistance to the oxidations after 50hr at 5hrs for every one of the cycles for the addition of the Y_2O_3 and yttria-doped silicon- modified aluminide hardness is approximately three times higher compared to the hardness of the uncoated alloys following the cyclic oxidation in the air at 900 °C for 50 hrs.
[83]			600 °C	40 KNO ₃ - 60 NaNO ₃ (wt%).	The mass gain and oxidation rate have been increased, and the correlation between mass gain and time has been near the parabolic oxidation law.
[84]	Slurry	Al	-	-	Coating the aluminide could considerably improve the resistance to oxidation by forming a very thin scale of Al_2O_3 .

Conclusion

It is apparent from the literature review summary that numerous studies have been conducted on nickel-base superalloy following thermal spray and plasma spray processes. Several works have focused on applying thermal barrier coatings with alumina and zirconia on the substrate made from IN738LC alloy. However, there is a notable research gap in the area of slurry coating at room temp for IN738LC, providing an opportunity for further investigation and serving as a key motivation for this study. The study will explore slurry coating using a mixture of (Al+Cr, Al+Si, Al+Al₂O₃, and Cr+Si) with varying percentages, which has yet to be extensively examined by other researchers.

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