

## Attention on Hot Corrosion & High Temperature Oxidation of Alloys with Its Affecting Parameters: A Review

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### Abstract

*Hot corrosion, oxidation and wear degradation of metals and alloys have been identified as serious issue for certain components that are used under cyclic condition, aggressive and high-temperature environment. To avert these problems understanding and comprehensive knowledge of this problem is very important. This work gives a understanding of Hot Corrosion & high temperature oxidation in a metals and alloys, presenting how different environmental conditions and chemical composition of the alloys affect the material. The basic knowledge, mechanisms and understanding of the process are collected from the paper which is cited at the end of the paper. In this paper the knowledge of the evaluation methods like weight change kinetics. X-ray diffraction (XRD), scanning electron microscopy (SEM), and energy dispersive X-ray spectroscopy (EDS) were used to characterize the corrosion products for the functioning of the alloys is introduced.*

**Keywords:** Hot Corrosion, High temperature oxidation, Coating, SEM, EDX

### 1. Introduction

Many times total annual costs of floods, hurricanes, tornadoes, fires, lightning, and earthquakes are less than the cost of corrosion. Corrosion is a serious problem because it definitely acts to the depletion of our natural resources. The rapid industrialization of many countries shows that the competition for the price of metal resources will increase. Higher temperature and pressure usually involve more severe corrosion condition. Failure of a small component or control may be result in failure or destruction of the entire structure. [1].

Corrosion is defined as the destruction or deterioration of a material because of reaction with its environment. Corrosion can be fast or slow [1].

The corrosion process is endothermic and the spontaneity increased by increasing temperature [14]. One method divides corrosion into low-temperature and high-temperature corrosion. The most preferred classification here is wet corrosion and dry corrosion. Dry corrosion is most often linked with high temperatures. An example is attack on steel by furnace gases [1]. A large number of plants including coal conversion, power, refineries, synthetic fuel plants, oil and gas wells, pipelines, many other process plants and foundry can feel this problem very strongly [1].

#### 1.1. High temperature Oxidation Mechanism

There are, with the exception of gold, no pure metals or alloys stable in air at normal condition. All metals approach to form oxides although in many case the rate of reaction is very slow at low temperatures. Reaction rates increase quickly with any increase in temperature, and at very high temperatures most reactions are completed within a few

minutes [2]. Oxidation process depends on composition of alloys, environmental factors, free energy of oxide formation, oxygen affinity and concentration of alloying element

### 1.1.1. High temperature oxidation can be divided into two limited procedures:

1. Oxidation processes where oxygen atoms do not dissolve in the base metals:

In the first case reaction begins at the metal/gas interface and this reaction's products form an intermediate layer between the alloy and the gas. In order for the reaction to proceed further, one or both reactants must penetrate the scale, i.e. either metal must be transported through the oxide to the oxide/gas interface and react there, or oxygen must be transported to the oxide/metal interface and react there. Since all metal oxides are ionic in nature, it is clear that ions and electrons must migrate in order for the reaction to proceed. Cation migration leads to scale formation at the scale/gas interface, whereas anion migration leads to scale formation at the metal/scale interface [2].

2. Oxidation processes where the base metal exhibits solubility for oxygen:

A small quantity of a less noble alloying element is present in the base metal which exhibits solubility for oxygen, and the alloy is exposed to the atmosphere oxidizing for both alloying elements. Oxidation starts with dissolution of oxygen into the surface layer. When the concentration of oxygen in the surface layer reaches balance concentration for the oxidation of less-noble alloying element, the reaction occurs and solute oxide starts to grow on the surface. Therefore, a concentration gradient is created and oxygen atoms diffuse inward during the alloy. At an individual position, the concentration of oxygen increases over time and, again, when the equilibrium concentration for oxidizing the solute element is obtained the reaction occurs and oxide particles precipitate from the solid solution, this process has the name "internal oxidation" and the layer, composed of oxide particles precipitated in a matrix is called "subsurface" [2].

## 1.2. Hot corrosion

Definition: Hot corrosion is an accelerated form of oxidation that occurs in metal and alloy at higher temperature in the presence of salt contaminants such as  $\text{Na}_2\text{SO}_4$ ,  $\text{NaCl}$ ,  $\text{V}_2\text{O}_5$  that combine to form molten deposits, which damage the protective oxide layer [10], [3], [6]. Hot corrosion starts where a porous non-protective oxide scale is developed at the surfaces and sulphides in the substrate [6], [10]. Hot corrosion is a serious problem in boilers, gas turbines, internal combustion engines, and industrial waste incinerators. As a consequence the load-carrying abilities of the components are reduced [5].

**Characteristics of hot corrosion:** High temperature degradation can be classified as High temperature hot corrosion also called type -1 and Low temperature hot corrosion also called type-2. Various parameters may affect the development of these two forms, including alloys composition and thermochemical condition, contaminants composition and flux rate, temperature and its cycles, gas composition, velocity and pressure, and erosion processes [3].

### 1.2.1 Type 1 hot corrosion (HTHC):

This kind of hot corrosion is noted mainly within the temperature range 850-950°C [7], [8], [12], [3]. It begins with the condensation of fused alkali metal salts on the surface of the component. A cycle of subsequent chemical reactions take place if firstly attacked the protective oxide film and progression to deplete the chromium element from

the substrate material. By chromium depletion, oxide of the base material accelerates and porous scale begins to form. The dominant salt in type 1 is  $\text{Na}_2\text{SO}_4$  due to high thermodynamic stability [7], [8], [12], [3]. When combustion takes place, sodium sulfate can form from sodium and sulfur, the latter being present in the fuel. [3].

For example, the melting point of  $\text{Na}_2\text{SO}_4$  (884°C) can be lowered by the addition of NaCl, as an eutectic is found with a melting point of about 620°C. Furthermore, in combustion gases, NaCl itself will react with sulfur oxide and oxygen, forming  $\text{Na}_2\text{SO}_4$ . The presence of sodium chloride removes the incubation period, which otherwise is typical of type 1. Potassium sulfate ( $\text{K}_2\text{SO}_4$ ) behaves similarly to sodium sulfate with regard to type 1. Therefore, the definition of alkalis in the fuel or in the air often sums up the content of sodium and the content of potassium. Vanadium is an unavoidable contaminant in certain liquid fuels. When vanadium-containing deposits cover components exposed to high temperature, accelerated hot corrosion occurs. Extremely aggressive liquid phases of vanadium may form at temperature as low as 535°C, depending on the ratio between Na and V. In addition to their own relatively low melting point, the vanadium compounds markedly increase the solubility of the oxide when mixed with  $\text{Na}_2\text{SO}_4$  [3].

HTHC can generally be divided into four progressive stages from initial onset to failure:

1. In this stage, slight roughening of the surface caused by some growth and localized breakdown of the oxide scale layer is evident. At this stage, neither chromium depletion in the substrate layer nor loss of mechanical integrity is observed.
2. In this stage, the roughness of the surface is more marked as oxide layer breakdown continues. While chromium depletion commences at this stage, mechanical integrity is still not affected.
3. In this stage, the oxidation of the base material has penetrated to significant depth, with obvious build-up of scale. Progression to stage 4 will accelerate with or without the continued presence of sodium.
4. In stage 4, catastrophic attack occurs. The attack penetrates deeply into the blade while forming a large "blister" of scale. Failure is likely at this stage due to loss of structural material.

The macroscopic appearance of type 1 is characterized in many cases by severe peeling of the metal and by significant color changes in the area of accelerated attack. Microscopically, the morphology of type I is characterized by a sulfidation and depletion region beneath the porous, nonprotective, scale. The reaction products frequently exhibit oxide precipitates dispersed in the salt film [3].

### 1.2.2. Type II hot corrosion (LTHC):

This form of hot corrosion is observed mainly within the temperature range 650-800°C [12], [3]. Type 1 forms typical pitting, resulting from the formation of a mixture of  $\text{Na}_2\text{SO}_4$  and  $\text{CoSO}_4$  with low melting temperature (The melting temperature of the  $\text{Na}_2\text{SO}_4$ - $\text{CoSO}_4$  eutectic is 540°C).  $\text{CoSO}_4$  itself is a corrosion product of a reaction between the surface of blades made of cobalt-based alloys and  $\text{SO}_3$  from the combustion gas. Similarly, the formation of  $\text{Na}_2\text{SO}_4$ - $\text{NiSO}_4$  eutectics has been suggested for nickel-based superalloys. Thus, a high partial pressure of  $\text{SO}_3$  in the gaseous phase is required for the LTHC reactions to occur, in contrast to HTHC [7], [8], [12], [3]. The localized nature of attack is related to localized failure of the scale as a result of local chloride attack, thermal cycling, or erosion. For example, salt may be trapped locally in crevices to occur. As opposed to type 1 hot corrosion, in type 2 chromium depletion neither incubation period nor microscopic and are generally observed [3].

## 2. Cyclic condition

The purpose of testing in cyclic conditions to create an accelerated environment as observed in real work culture for hot corrosion testing. Oxidation and Hot Corrosion testing has been done and for each cycle weight change has been measured. Boiler Steel SA-192 shows poor performance for oxidizing environment because there is higher weight gain up to 50 cycles and shows very poor operation for corrosive environment because there is spallation behavior appears in cycles up to 50 cycles [10]. Thermal cycles are also often reported to increase the propensity for cracking/spallation [12].

## 3. Major identified problem

Cracking and spalling may occur due to (1) high residual tensile stresses from processing, (2) a marked thermal expansion mismatch, (3) poor ductility or toughness and (4) poor adherence to the substrate material [15].

## 4. Prevention approaches

Several approaches have been employed to control hot corrosion. These approaches include proper selection of structural alloys, application of coatings, washing of hot parts, air filtering and control of both fuel cleanliness and composition.

### 4.1 Alloy selecting

For a product it is a big work, because in it we have to select the optimal one who can provide the best output. Alloy made by several elements and additive it is difficult to choose the best among nearly equal specification. But this is possible by previous works and standardization work. But still it is difficult to choose by means of our criteria. But Cr and Ni alloy is very good anti corrosive and for hot oxidation process both for type I and type II.

### 4.2 Coating

It is widely used method under this understanding of problem. Coating can be done by metallic and ceramic material under the requirement condition.

There are a number of important factors to be considered when work on a coating process for an industrial application. These include capital investment, ease of manufacturing coating performance and environmental issues [9].

Coating-base metal interaction can influence mechanical properties as a result of (1) mismatch of processing parameters (temperature, time, heating and/or cooling rates), (2) interdiffusion and structural changes because of insufficient chemical compatibility, (3) susceptibility to crack formation as given above which causes stable crack growth by creep or fatigue in the structural base metal [16], [17].

Coatings serve more than one functions For high temperature oxidation resistance, a coating should: (a) Resist oxygen and metal ion diffusion, (b) Have a low vapour pressure at the operating temperature, (c) Have a melting point above the operating temperature, (d) Have low reactivity with the substrate, and (e) Have low reactivity with the high temperature environment [8].

Conclusion of coating process: A rating of the properties of different coating systems is extremely difficult because they depend on coating system, deposition processes, and parameters. Tribological operation is also dependent on the counter body material, the load, type and complexity of wear environment. The wear and friction behavior of a coating is dependent on the lubrication conditions [11], [17]. So alloy and composite materials are required to provide the necessary mechanical properties and protective surface layer which immune the substrate surface from hot corrosion, wear and erosion also Alloy and composite coatings has high hardness and low value of porosity as compared to substrate steel that is desirable in hot corrosion resistance[8].

#### **4.3. Washing of hot components**

This minimize hot corrosion is delugemotoring washes using plain water. This allows for dissolving and carrying away salts and other contaminants, thus preventing the initiation of high temperature oxidation. Specific washing procedures are usually covered in details in the relevant maintenance manual for the engine model concerned. Washing may be required either before each flight or up to once a month, depending on the estimation of the severity of the corrosion environment. An alternative method of building wash frequency has been to monitor blade condition using a borescope inspection program, adjusting the wash schedule according to the inspection results [3].

#### **4.4. Air filtering**

A limiting level of 0.008 ppm (by weight) has been suggested for the content of Na in the air, below which hot corrosion will not exist. Therefore, secondary protection against hot corrosion may be attained by installation of high-efficiency air filters[3].

#### **4.5. Fuel cleanliness and composition**

Fuel cleanliness affects the initiation and propagation of hot corrosion attack. Hence, the content of the alkali metal, vanadium, and sulfur in the fuel should be carefully controlled. Sometimes, the maximal content of impurities allowed in the fuel is defined as 0.2-0.6 ppm(Na+K), 0.5ppm V, and 1% S. However, these limits may change if a coating is applied on the blade and/or inhibitors are added to the fuel.

Often, additives are added to fuel; additives Mg, Cr, Ca and Ba decrease the corrosion rate. If high level of vanadium is to be used in the fuel, its effect can be combated by MgO addition. The effect of magnesia is to react preferentially with vanadium pentoxide( $V_2O_5$ ) to form  $Mg_3V_2O_8$  vandates with higher melting temperature. Zinc, added by means of protective coatings or anodes in the fuel tank, is effective in reducing LTHC attack. In the absence of excess NaCl, zinc decrease the decreases the solubility of the protective metal oxide in the salt and the electrochemical potential of the corrosion reaction. In the presence of excess NaCl, zinc (rather than other metals from the protective oxide layers) reacts easily with the chloride ion; simultaneously, it serves as a mean of transferring the chloride to the salt-gas interface, where it is transformed gas via silfitation reaction [3].

### **5. Temperature**

When we increase the temperature then corrosion rate also increase. At higher temperature is shows more weight gain per surface area [10], [17]. As temperature increased from 900°C to 950°C, the diffusion rate of ions increased as temperature increased. Hot corrosion behavior of all the alloys at 950°C was worse than that at 900°C. The oxidative

vaporization of  $\text{Cr}_2\text{O}_3$  increased at  $950^\circ\text{C}$  as compare to  $900^\circ\text{C}$  it means for the testing the range of temperature should be more from its actual utility work to make safe consideration. It was shown that, increasing corrosion temperature shortened the incubation period [13].

## 6. Effect of material and alloy

The uncoated steel showed substantial spallation of its oxide scale during hot corrosion. Degradation of metals is a severe problem in the industrial applications. It is not possible for single material to have different properties to meet the demand of today's industries. Stable  $\text{Al}_2\text{O}_3$  phase on the surface of the studied coatings ensure high oxidation resistance. Vanadium as an impurity in fuel oil causes serious corrosion problems because of the formation of  $\text{V}_2\text{O}_5$ . Cr and Al are added in Fe and Ni-based superalloys to enhance the oxidation resistance [8].

To improve the strength of nickel-based super alloys, there has been a trend to reduce the Cr levels within the alloys. With some of these alloys also having an increase in Al content, the high-temperature oxidation resistance has also improved. However, there has been a corresponding drop in hot corrosion resistance [12]. Loss of hot corrosion resistance causing by Cr reduction cannot be compensated by increasing Ta content. As is widely accepted, Cr is the most important alloying element in resisting hot corrosion attack. Under hot corrosion environment, sufficient Cr promotes the formation of a continuous and adherent chromium oxide ( $\text{Cr}_2\text{O}_3$ ) scale on the surface of the alloy. In alloys with high Cr content (12 wt.% Cr), Ta promoted the formation of  $\text{NaTaO}_3$  and  $(\text{Cr},\text{Ti})\text{TaO}_4$ , with the latter spinel phase acted as a diffusion barrier of ions. The corrosion kinetics was lowered by Ta addition. Ta substituted Cr for sulphur catcher and more Cr was saved for  $\text{Cr}_2\text{O}_3$  formation. The results imply that Ta may be an outstanding candidate to substitute Cr for effective hot corrosion resistant element.  $\text{Cr}_2\text{O}_3$  reacts preferentially with oxide ions ( $\text{O}^{2-}$ ) in molten  $\text{Na}_2\text{SO}_4$  to form chromate. The dissolution of  $\text{Cr}_2\text{O}_3$  stabilizes the melt chemistry so that the basicity of the salt is not sufficient to cause basic fluxing but is still not low enough to cause acidic fluxing. Thus, dissolution/re-precipitation of the protective oxide scale is avoided. Besides, Cr can effectively capture sulphur and thereby suppress the formation of other deleterious liquid sulphides. Therefore, typical hot corrosion resistant superalloys always have more than 12 wt.% Cr. Cr and Y are known to improve oxidation and corrosion resistance. Cr content determined the oxidation resistance of the coating and 30% Cr was found to be optimal. The oxidation rate was insignificant below  $900^\circ\text{C}$ , and severe oxidation took place above that. An increase in Cr content from 17 to 30% reduced the rate of oxidation and delayed the onset of severe oxidation at higher temperatures [11], [17]. The coating hardness is greatly influenced by the relative amount of Ti and Al present in the coating [11].

## 7. Testing and analysis

### 7.1. Thermogravimetric analysis

The parabolic rate constant (kp) is calculated on the basis of the first 10 h exposure time as the slope of the curve fitting. High temperature parabolic oxidation shows that a thermal diffusion process is the rate determining factor. As the exposure time increased, the scales are damaged by thermally induced stresses and the weight decreased dramatically. High temperature hot corrosion occurs in the temperature range of  $750^\circ\text{C}$ – $950^\circ\text{C}$ . In this corrosion mode both incubation and propagation steps are included. Cr in the substrate materials is being depleted, therefore the oxidation of the base material accelerates and a porous scale starts to form. The presence of chloride in the corrosion environment add

appreciably to metal loss at high temperature, either by formation of volatile chlorides or synergistically in combination with sulfates. It can say that chlorides migration inward the materials and cause accelerated corrosion.

### **7.2. Scanning electron microscope investigations (SEM)**

Samples were then characterized using optical microscopy and in a scanning electron microscope (SEM). Measurements of the chemical composition of the oxides were made using energy-dispersive spectroscopy (EDS). The morphology of the specimen and scale were examined by scanning electron microscopy. SEM was used to examine the cross section [14]. Observed a dense columnar morphology in cathodic arc deposited (Ti,Al)N coatings and the presence of macro particles at the coating surface by SEM [11]. The oxide, porosity and the amount of melted material in the coatings were characterized using SEM and X-ray diffraction (XRD), whilst the corrosion resistance of the coatings was evaluated by use of a salt spray chamber and potentiodynamic tests [8].

### **7.3. XRD analysis**

The XRD was used to identify the corrosion products formed at the surface of the corroded samples after exposure to the corrosive environment at different temperatures and time intervals [14]. SEM equipped with an energy dispersive spectroscopy (EDS) and X-ray diffraction (XRD) was used to characterize the original microstructure of the alloy and the corrosion morphology and to identify the corrosion products [13]. X-ray diffraction technique (XRD) was used to analyze the formed scale [14].

### **7.4. Thermodynamics study**

To confirm the corrosion rate for the material activation energy was determined by changing the temperature. The corrosion rate is a function of time at different hot corrosion temperatures. The corrosion increased with temperature as the chemical reaction rate increased. Although the corrosion process is endothermic and the spontaneity increased by increasing temperature [14].

#### **7.4.1. Phase analysis:**

A variety of oxides and spinels containing Cr, Ti, Ni, Al and Ta were produced, with  $\text{Cr}_2\text{O}_3$  and  $\text{TiO}_2$  being the common phases on all the four alloys. SEM observes of the cross-section morphologies. SEM equipped with EDS instead of XRD was chosen to analyze those samples that were severely corroded.

#### **7.4.2. Morphologies and structures:**

Cracks were produced because of cooling and surface tension. The outer layer were composed of gray Cr-, Ti-, Ni- and Al-containing phases and white Ta-containing oxides and spinels. The dominant constituents were Cr- and Ti-containing oxides. The amount of the Ta-containing phases increased as Ta content increased.

## **7. Conclusion**

1. Hot Corrosion is a very big problem and this failure mechanism of great concern in Furnace parts, Furnace tray, furnace fixture, Boiler, Gas turbine engines and gas turbine blades. The hot corrosion process must be either totally prevented or detected at an early stage to avoid catastrophic failure.

2. It associates with other failure and propagates other failure in component.
3. For any component it can be determined that which type of failure occurred by the study of every aspects.
4. It can be necessarily understand to avoid the accident, for the efficient use of the component and save the natural resources.
5. Material element has great importance to overcome this problem.
6. Coating is best way to control these problems.

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