



## Hot Corrosion and its Mechanism: A Review

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**ABSTRACT:** A big challenge for engineers/ researchers is to protect the components of boiler, waste incinerator, gas turbine etc from the hot corrosion. The problem of hot corrosion is more precarious as the degradation of materials takes at rapid rate. The hot corrosion is of two types, high temperature hot corrosion and low temperature hot corrosion. The aim of the present study is to discuss the basic fundamentals of hot corrosion, types of hot corrosion and mechanism of hot corrosion under the light of present literature so that effective protective measures can be developed to protect the components of equipments working at high temperature.

### I. INTRODUCTION

Hot corrosion is an accelerated form of oxidation at high temperature in the presence of molten salts. A number of engineering systems operating at high temperature such as power plants, gas turbines and incinerators fail due to hot corrosion. Every metal or alloy oxidizes to form oxides at high temperature in the presence of oxygen. The oxides formed on the surface act as a protective layer. This protective layer of oxides does not allow oxygen to penetrate and prevent further oxidation. But, if contaminants such as sulfates, chlorides, or vanadates are present in the environment, they form a low melting point eutectic mixture and cover the surface with thin film of fused salt. It results in formation of porous non-protective oxide scale which allows the aggressive species to penetrate into the base metal and causes accelerated degradation of materials. This type of attack is known as hot corrosion. The phenomenon of hot corrosion was recognized in 1940s in connection with the failure of fireside boiler tubes in coal-fired steam generating plants [1]. Hancock (1987) and Eliaz et al. (2002) [2-3] defined the hot corrosion as an accelerated form of oxidation that occurs when metals are heated in the temperature range 700–900°C in the presence of sulphate deposits formed as a result of the reaction between sodium chloride and sulphur compounds in the gas phase surrounding the metal.

#### **Oxidation of Metal and Alloys**

Metals and alloys are very important constituents for all types of engineering components. With the advancement of technology a big challenge for researchers and

engineers is to develop the materials with higher strength and special properties. The properties of materials changes with the environmental conditions and material behave differently under different environment conditions.

The oxidation in simple words is chemical combination of a substance with oxygen. A chemical reaction in which an atom or ion loses electrons, thus undergoing an increase in valence. Every metal and alloy oxidized when it comes in contact with oxygen. Kalsi *et al* (2014) and Sidhu (2003) [4-5] define the oxidation as interaction of oxygen with metal to form oxides.



The rate of oxidation depends on the nature of the oxide layer formed on the surface of metal/alloy and surrounding environmental conditions. The layer of oxide formed on the surface of metal separate the oxygen from metal. For further oxidation oxygen must come in contact with metal by penetrating through oxide layer or metal diffuse out through oxide layer [6].

The degradation of materials via oxidation is a big problem. Metallic corrosion costs in the United States are about \$300 billion per year, which is approximately 3.1% of the nation's Gross Domestic Product (GDP).

#### **Hot Corrosion Mechanism**

Hot Corrosion can arise at high-temperatures in two cases i) when the deposit is in the liquid state right from the beginning ii) when the solid deposit turns into liquid during the exposure as a result of reaction with the environment.

These two types of hot corrosion processes are termed as Type I and Type II hot corrosions, and also called High Temperature Hot Corrosion (HTHC) and Low Temperature Hot Corrosion (LTHC), respectively [7-8].

#### **High Temperature Hot Corrosion**

HTHC also known as Type 1 hot corrosion is generally observed in the temperature range 825 to 950°C when the deposits are evidently in liquid passé [9-10]. The HTHC morphology is typically characterized by a thick, porous layer of oxides with the underlying alloy matrix depleted in chromium, followed by internal-rich sulfides. Eliaz et al (2002) [11] proposed that in the presence of fused alkali metal salts on the surface of the metal, a cycle of chemical reactions takes place, first attacking the protective oxide film and then depleting the chromium element from the substrate materials. Oxidation of the base material accelerates with depletion of chromium, which form porous scale. The  $\text{Na}_2\text{SO}_4$  is most thermodynamic stable salt in HTHC. Therefore  $\text{Na}_2\text{SO}_4$  can combine with other impurities present in the environment, such as chlorides, lead, phosphorous and vanadium to form compounds with lower melting points. The presence of eutectic mixture of NaCl (m.p. 801°C) and  $\text{Na}_2\text{SO}_4$  (m.p. 884°C) in the deposits lower down the m.p to 628 °C, which further accelerates the corrosion [12].

The external corrosion products consist of oxide precipitates dispersed in the salt film. The sulphidation of the alloy substrate can take place through the pore, gap or crack in the protective layer which results in a significant shift in the basicity of the salt film. Once the fused salt comes in contact with substrate, the rate and duration of the rapid corrosion kinetics is decided by the magnitude and gradient of salt basicity relative to the local solubilities for the oxide scale phases [13-15].

#### **Low Temperature Hot Corrosion**

Low temperature hot corrosion (LTHC) also known as type II hot corrosion is generally occur well below the melting of  $\text{Na}_2\text{SO}_4$  in the temperature range 650 to 800°C (Jaffee and Stringer, 1979; Driver et al., 1981; Wright, 1987). Type II hot corrosion occurs as result of the formation of base metal sulphates which react with alkali metal sulphates to form low melting point eutectics (the melting temperature of the  $\text{Na}_2\text{SO}_4$ - $\text{CoSO}_4$  eutectic is 540 °C) which prevent the formation of protective oxides [16]. Cobalt base alloy are more susceptible to Type II hot corrosion, which generally involves  $\text{Na}_2\text{SO}_4$  and  $\text{CoSO}_4$ . Type II hot corrosion is characterized by pitting attack in the localized areas or no internal attack underneath the pit. A high partial pressure of  $\text{SO}_3$  in the gaseous phase is required for the

LTHC reactions to occur, as compare to HTHC (Wright, 1987). Rapp and Zhang, 1994 [17] suggested that in type II hot corrosion the non-uniform attack in the form of pits, with only little sulphide formation close to the alloy/scale interface and little depletion of Cr or Al in the alloy substrate. No chromium depletion is generally observed in type II hot corrosion [18-19].

#### **Hot Corrosion Progression of the Superalloys**

The hot corrosion of superalloys take place in two stages termed as i) initiation stage ii) Propagation stage [20-21]

##### **(i) Initiation Stage**

It is the starting stage and during this stage the alloys behave much the same way as they would have behaved in the absence of the deposit. The hot corrosion elements in the alloy are oxidized and transferred from metallic atoms to the reducible substances in the deposit. A reaction products protective barrier is formed in between the alloy and deposit salt. The alloy remains in the initiation stage until the protective reaction products are stable state. As soon as the reaction products become unstable the hot corrosion enters into the propagation stage. Pettit and Meier (1985), during isothermal oxidation of Ni base superalloys at 1000°C with  $\text{Na}_2\text{SO}_4$  deposit, observed that a Ni-30Cr-Al alloy remained in the initiation stage for over 300 hours, but after less than 40 hours, sulfides were detected in this alloy, the amount of sulfides increasing with time. Thus, they proposed that superalloys are preconditioned by the deposits in a way that determines the time after which selective oxidation is no longer possible and which also determines the type of corrosion product scale that forms as the alloy enters the propagation stage. According to them, this fact is responsible for the variety of hot corrosion processes that have been observed when superalloys are exposed to different environments. Further Pettit and Giggins (1987) [22] suggested that the hot corrosion degradation sequence is not always clearly evident. In some conditions the initiation stage does not exist at all and the hot corrosion process directly enters into the propagation stage. Time for which the reaction products are in stable condition depends upon number of factors [23]. Therefore to develop resistance to hot corrosion one should try to set the factor such that alloy should remain in the initiation stage as long as possible.

##### **(ii) Propagation Stage**

During the propagation stage of the hot corrosion sequence the corrosion rates are much higher than that in the initiation stage therefore it is better to remove the superalloy from service [24-25].

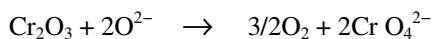
More amount of sulphide particles are found to be present in the alloy beneath the protective reaction product barrier. Sometimes small holes are present in the protective reaction product barrier where the molten deposit begins to penetrate. Finally the protective barrier formed via selective oxidation is turned into ineffective, and propagation stage of hot corrosion starts.

### Salt Fluxing

The deficiency of oxide ions in the processes by which the reaction product barrier becomes non-protective due to the formation of species, which are soluble in the liquid deposit, are called "fluxing" reaction. Fluxing of the oxide layer, results in the loss of protection efficiency [26]. The fluxing reaction may be basic or acidic in nature.

#### (i) Basic Fluxing

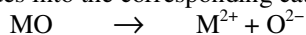
The basic fluxing occurs by combination of oxides with  $O^{2-}$  to form anions. Bornstein and DeCrescente (1969) [27] suggested the initial concept of basic fluxing. In case of basic fluxing, the concentration of oxygen ions available is limited by the amount of deposit present upon the surface of the superalloy. Therefore basic fluxing reactions are not self-sustaining and require a continuous source of  $Na_2SO_4$  in order to precede this type of fluxing for longer times [28-29]. According to Eliaz et al (2002) [30], the hot corrosion of the superalloys with high contents of aluminium and chromium is often reported to occur according to the basic fluxing mechanism. For example the protective oxide scale of  $Cr_2O_3$  can combine with  $O^{2-}$  and destroy the protective properties of the scale.



Rapp and Goto (1981) [31] reported that the basic fluxing can take place in the gases having acidic components.

#### (ii) Acidic Fluxing

The acidic fluxing occurs with the decomposition of oxides into the corresponding cations and  $O^{2-}$ .



The acidic fluxing is self-sustaining in nature, since the displacement of the salt from stoichiometry does not become progressively more difficult as the reaction proceeds [32-33]. Therefore, acidic fluxing is more severe as compared to basic fluxing. The hot corrosion of alloys with high contents of tungsten, molybdenum and vanadium is often reported to follow the acidic fluxing mechanism [34] but when these elements oxidised in the presence of  $Na_2SO_4$ , deposit on superalloys causing catastrophic self-sustaining hot corrosion [35].

## CONCLUSIONS

Hot corrosion is very serious issue for the engineering components working at high temperature. Hot Corrosion is of two types depending upon whether the deposit is in the liquid state right from the beginning or the solid deposit turns into liquid during the exposure to the environment. Hot takes place first through initiation stage followed by propagation stage in case of superalloy. It is better to remove the components before propagation stage starts. The Salt fluxing is of two types basic and acidic fluxing. The acidic fluxing is more dangerous as it is self-sustaining in nature.

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