

# High Temperature Corrosion and Protection Methods: A Review

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**Abstract:** *High temperature corrosion is a worldwide problem in many manufacturing processes such as, mineral and metallurgical processing, electric power generation, waste incineration and heat treating. High temperature corrosion involves the chemical attack of solid materials subsequently leading to the degradation of the desired properties. The material reacts with a gaseous environment consuming the material of interest, usually forming disagreeable reaction products. This paper covers forms of high temperature corrosion and several methods to prevent high temperature corrosion.*

**Keywords:** metal dusting, halogen corrosion, molten metal corrosion, molten salt corrosion, oxidation, sulfidation, nitridation, thermal spraying, weld overlay, thermal barrier coatings.

## 1. Introduction

Numerous commercial processes operate at temperatures exceeding 500°C. In industry these processes include refinery plants (500 °C), pulp and paper production (700 °C), nitric acid production (900 °C), and heat-treatment (1000 °C). In the power sector they include waste incinerators (500 °C), coal gasification systems (600 °C), fuel cells (800 °C), and gas turbines (1000 °C). Materials used in high-temperature structures have design constraints additional to those of materials used at or near room temperature. Three important additional constraints are time-dependent inelastic strain (creep), thermal stability of microstructure, and high-temperature corrosion. (1) The term high temperature corrosion refers to material degradation at temperatures higher than the ambient temperatures, when exposed to corrosive environments. The material degradation due to the reaction with environment increases many folds with increase in temperature. (2)

## 2. Forms of High Temperature Corrosion

Some important forms of high-temperature corrosion to be considered are:

### 2.1 Metal Dusting

Metal dusting is a catastrophic form of corrosion affecting iron, low and high alloy steels and Ni- or Co-based alloys exposed to reducing, highly carburizing gases (carbon activity  $a_c > 1$ ) at elevated temperatures (400-800°C). Deposition of carbon on and within these metals is accompanied by disintegration of the substrate. The coke formation impairs heat transfer efficiency, and reduces metal catalyst lifetime, as well as damaging structural materials.

The phenomenon of metal dusting has been studied for decades. However, the mechanism of this process is still not well understood, although several mechanistic models have been proposed. The most widely accepted theory for Fe-based alloys can be described in the following reaction steps (1-3): (1) rapid transfer of carbon from the gas atmosphere into the iron leading to the growth of a surface cementite

layer which acts as a barrier for further carbon transfer; (2) graphite nucleation and deposition, lowering the carbon activity to unity at the Fe<sub>3</sub>C/graphite interface, and initiating cementite decomposition into graphite and iron, which is said to diffuse outwards through the graphite to the graphite-gas interface; and (3) precipitation of iron particles in the coke where they act as catalysts for further graphite deposition. The metal dusting of Ni and Ni-based alloys is considered to follow a similar mechanism to Fe-based alloys, but without forming the metastable intermediate M<sub>3</sub>C. In this case, the nickel atoms have been suggested to diffuse via graphite intercalation, and form nano-scale nickel particles which catalyse further carbon deposition.

The mechanisms described above involve carburisation and subsequent cementite formation (for ferritic alloys) due to carbon super saturation of the metal. However, the suggested cementite decomposition and formation of metal particles has been questioned.

The new finding that the dust nanoparticles are cementite rather than ferrite is at odds with the earlier theory, which required instead that iron in contact with graphite should remain stable after cementite decomposition. Furthermore, the proposal of iron/nickel atoms migrating between graphite planes and accumulating to form fine particles on the graphite surface is difficult to understand, due to the apparent lack of a driving force. The older theory is also inconsistent with the recent observation of ferrite particles or a ferrite layer formed at the cementite/graphite interface.

Because the iron comes from cementite decomposition, the older model proposes instead that it should dissolve in and diffuse outwards through the graphite layer, to form particles at the graphite/gas interface. Mechanical forces generated by the volume changes accompanying graphite deposition will play a role in the metal dusting, and some authors assume this is the only way in which nanoparticles are produced. (3)

### 2.2 Molten Metal Corrosion

Liquid metals are often used as heat transfer media (the use of liquid sodium in nuclear reactors, for example). The

containment material, which is in contact with the molten metal, is subject to molten metal corrosion. It is best to consider how molten metals will react with the material in the containment system. For example, molten aluminum attacks iron-, nickel- and cobalt-base alloys. Molten zinc or lead reacts with nickel-base alloys, but molten lead may be contained by cast iron, steels, and stainless steels.(4)

### 2.3 Molten Salt Corrosion

Many industrial components operate at high temperatures, in which severe corrosion is found because of the aggressiveness of the environments. When the surface of a metal or alloy undergoes accelerated oxidation due to the presence of a thin film of high temperature molten salt, the formation of a crust of porous non protective oxide can be developed, so it is said that materials suffer a hot corrosion attack. In addition to the attack by reactive gases, materials used in these environments containing combustion products of fossil fuels are also attacked by salt deposit. The presence of molten salt deposits can lead to accelerated oxidation and hot corrosion, whose corrosion products comprise internal oxides and sulfides; therefore, under these conditions a rapid material degradation is observed.

It has been reported that the corrosion of metals in molten salts can be explained by the combination of the anodic oxidation of metals and cathodic reduction of the oxidants such as in aqueous electrolytes systems. This phenomenon is caused by the oxidation of the elements forming the alloys, the reduction of oxidant species, and then the formation of compact or porous corrosion films and their fluxing by molten salt mixtures.(5)

### 2.4 Halogen Corrosion

Fluorides, bromides, and iodides, despite being less common than chlorides, are present in various environments of industrial relevance. Stainless steels suffer pitting corrosion in solutions of all halides except fluorides, which can be understood considering that fluoride is the anion of a weak acid. The aggressiveness of the rest of the halides for pitting corrosion is on the order  $Cl^- > Br^- > I^-$  for stainless steels with Mo content below 3 wt.%. Mo is not as effective in inhibiting  $Br^-$  pitting corrosion as it is for inhibiting  $Cl^-$  pitting corrosion. Most of those observations were rationalized based on the effect of anions on pit growth kinetics. Sensitized austenitic stainless steel suffers stress corrosion cracking (SCC) in solutions of all halides, albeit chlorides seem to be the most aggressive. Fluoride SCC is relevant for SCC under insulation of stainless steels, and standards and regulations developed to mitigate this problem consider this ion as aggressive as chloride. For the solubilized stainless steels, aggressiveness toward SCC is in the order  $Cl^- > Br^-$ . The SCC of solubilized stainless steels was not observed in solutions of  $F^-$  and  $I^-$ , and the possible reasons for this fact are discussed.(6)

### 2.5 Oxidation

The term high temperature oxidation, here, refers to material degradation (corrosion) at temperatures higher than the ambient temperatures, when exposed to hostile gaseous

environments. The rate of attack is controlled by many factors including temperature, pressure, nature of corroding species, composition of materials, etc. The attack is invariably initially very fast but may then slow down because a protective layer is formed between the surface and the gas/liquid. Some layers protect better than others and it is the job of the scientist to improve the protective nature of the layer. To do this, it is important that the initial reaction between the corroding molecules and the surface can be identified and that the succeeding layers be well characterised. (7)

### 2.6 Sulfidation

The sulfidation process is generally an irreversible corrosion process in that the sulfur that is released during reoxidation of the sulfides can penetrate the substrate alloy along the grain boundaries, thereby affecting the mechanical integrity of structural components, increasing the corrosion rates on reactors and pipelines based on steel and its alloys.(8)

Iron (Fe) or steel reacts readily with hydrogen sulfide ( $H_2S$ ) to form iron sulfide ( $FeS$  or  $Fe_xS_y$ ). Since  $H_2S$  is a ubiquitous compound in the oil and gas industry, sulfidation of steel occurs under upstream (exploration and production) and downstream (refinery) conditions. Reaction of Fe with sulfur (S) also occurs in power generation during the burning of fossil fuels.(9) Although the mechanism of sulfidation is fundamentally similar to that of oxidation, they differ both in complexity and in rate of attack. Sulfidation is more complex than oxidation due to the occurrence of a larger number of stable sulfides as compared to the oxides. The complexity is further enhanced due to the low-melting-point eutectics formed in many of the metal/sulfide systems. Examples of such eutectic temperatures are: 985 °C for iron; 880 °C for cobalt; and 645 °C for nickel. The maximum temperature for long-term service of metallic materials exposed to highly sulfidizing environments is generally considered to be 600-650 °C. This is because the sulfidation rates of most of the major metallic constituents in conventional high-temperature alloys are generally 104–106 times higher than their oxidation rates, depending on temperature (*i.e.*, the activation energies are different). The sulfidation rates are generally much higher than oxidation due primarily to the higher degree of nonstoichiometry in sulfides compared to the oxides. Large deviations from stoichiometry occur in sulfides because their lattice energies are such that point defects are easily created. A sulfide containing a high density of point defects will evidence a high diffusion rate and, correspondingly, a high growth rate. For example, the sulfides of chromium are very non-stoichiometric and, as a result, the protection from sulfidation achieved by chromium additions is less than that observed for oxidation. The only metals which show superior resistance to sulfide corrosion are the refractory metals (*e.g.*, Mo, Nb, Ta, W, V). For instance, molybdenum and niobium sulfidize at rates comparable to the oxidation rates of chromium under analogous conditions.(10)

### 2.7 Nitridation

In air or combustion atmospheres containing nitrogen, nitridation can take place under certain exposure conditions.

In most cases, oxidation dominates the high-temperature corrosion reaction. However, nitridation can take place for some alloys when oxide scales no longer provide protection. The alloys that are particularly susceptible to oxidation/nitridation attack are those containing strong nitride formers, such as titanium and aluminum. Many high-temperature nickel-base alloys containing both aluminum and titanium are strengthened by  $\gamma'$  phase,  $\text{Ni}_3(\text{Al,Ti})$ . For these alloys, nitridation by forming internal nitrides of aluminum and titanium can deplete the surface layer with aluminum and titanium, thus weakening the alloy. Under a high-velocity combustion gas stream with severe thermal cycling, similar to the conditions in "flying" gas turbines (aircraft engines), nitridation can be particularly severe in oxidation/nitridation attack. In nitrogen-base atmospheres, such as  $\text{N}_2$  or  $\text{N}_2\text{-H}_2$ , metals and alloys can also suffer nitridation attack. This type of atmosphere is often used as a protective atmosphere in heat treating and sintering operations. Molecular nitrogen can be severely nitriding for many metals and alloys, particularly when temperatures are sufficiently high.

Ammonia ( $\text{NH}_3$ ) is a commonly used nitriding gas for case hardening at temperatures from 500 to 590 °C (925 to 1100 °F) (Ref 1). Furnace equipment and components repeatedly subjected to these service conditions frequently suffer brittle failures as a result of nitridation attack. (11)

### 3. Methods to Prevent High Temperature Corrosion

Surfacing Engineering is the most emerging field to improve the surface i.e. corrosion, oxidation and wear resistant depending upon the required service conditions in an economical way. This can be done by depositing a layer of superior material on the substrate of sufficient mechanical strength. Protective coatings used on structural alloys and energy conversion units, prevent surface degradation. Some of the factors that must be taken into account include substrate compatibility, adhesion and resistance to corrosion. The recent development of surface coatings and new methods of coating are available which can provide the desired properties that were previously unachievable. (12)

#### 3.1 Thermal Spraying

Thermal spraying is used to form a coating layer by heating a metal or ceramics to melt or half – melt and spraying it at high speed. Thermal spraying is used for applications such as thermal barrier coatings (TBC) on gas turbine engines and jet engines. The coating layer formation rate is so high that a thick coating layer (100-500  $\mu\text{m}$ ) can be formed in a short time. According to the type of the heat source, thermal spraying is classified into the gas type which includes flame spraying and HVOF and the electric type which includes arc spraying and plasma spraying. (13)

Thermal spray coating is selected in accordance with the workability, the duration of repair, the required lifetime and the total cost performances. As-sprayed coatings are convenient from the viewpoint of working duration and quick application, but durability of such coatings is lower than complete dense coatings due to the existence of open

defects in the layer. It is difficult to completely remove the small size defects such as micro pores and inclusions of oxide. Therefore, it is known that accelerated blister and peel-off formations of the coating layer can occur due to interface corrosion in coating/base material by corrosive gases that have penetrated through such defects. High velocity processes using a relatively fine powder and with a high spraying speed such as HVOF are good for improving bonding strength and durability by reducing of defects. This has led to an increase in use of the HVOF. (14)

#### 3.2 Weld overlays

Corrosion-resistant weld overlays are often used to improve the service life of components made with an otherwise corrosion-prone material. A major concern in an arc welding based overlay is dilution or the extent of change in the chemistry of the deposited metal by the mixing of base metal. Even though some generic information is available on the extent of dilution associated with common arc welding processes, the actual dilution with a particular process itself can vary over a wide range, based on the welding parameters employed. In most cases of overlaying, it is necessary to control the dilution within close limits as an uneven chemistry can reduce the service life. There are a number of variables which affect dilution such as the welding current, the arc voltage, current polarity, electrode diameter, electrode extension, weld-bead separation, welding speed, electrode grinding angle, welding position, shielding gas composition, etc. It is necessary to control each of these variables within limits to get the desired properties on the overlay, for which it is necessary to have a clear understanding of the influence of each of these variables on dilution. (15)

### 4. Summary

Materials deterioration as a consequence of high temperature corrosion is a challenge facing a major sector of elevated temperatures operating industries. Different methods to control high temperature corrosion have been developed and applied to metallic surfaces to offer excellent properties regarding the high temperature operating conditions.

This paper reviews forms of high temperature corrosion and several procedures to enhance the surface properties in order to provide protection from high temperature corrosion.

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