



# Effect of Air Pre-Oxidation on High Temperature Air Oxidation Behavior of Carbon Steel and Stainless Steel

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**Abstract** — In this paper, air pre-oxidation technique was developed in order to improve the oxidation resistance of carbon steel (0.131 wt% C) and stainless steel (304L). The oxidation behavior of carbon steel and stainless steel specimens with and without pre-oxidation was studied over the temperature range 450 to 550°C for up to 120h. The discontinuous oxidation behavior of the selected experimental materials was tested in static air. The use of pre-oxidation at 450°C for 5 hours to carbon steel and at 500°C for 5 hours to stainless steel showed considerable improvements to the oxidation kinetics for both carbon steel and stainless steel, especially at relatively low temperatures – 450°C and 500°C. Generally, air oxidation kinetic data of carbon steel showed rapid increase of weight compared with stainless steel throughout the selected temperature range. The formation of Cr<sub>2</sub>O<sub>3</sub> layer improved the oxidation resistance of stainless steel. Cr<sub>2</sub>O<sub>3</sub> layer acts as a diffusion barrier to the reactive species. Also, the oxidation process of carbon steel was found to be controlled by the formation of relatively thin and adherent layer of Fe<sub>2</sub>O<sub>3</sub>, especially at low exposure temperature (e.g. 450°C). Whereas, at higher temperatures (e.g. 550°C), the pre-formed Fe<sub>2</sub>O<sub>3</sub> layer failed to protect carbon steel from further oxidation even for short exposure time. The scale formed on carbon steel at 550°C severely cracked and spalled off especially, at places of sample corners. Results of this research revealed that, alloying elements in stainless steel were more beneficial to oxidation resistance than pre-oxidation to steel, throughout the whole range of time and temperature of this study.

**Index Terms:** air oxidation, pre-oxidation, high temperature, carbon steel, stainless steel, reaction kinetics.

## I. INTRODUCTION

The attack of environment on materials can take different forms. At high temperatures, metals get oxidize, polymers react with oxygen and degrade, ceramic refractories may be dissolved by the liquid they are in contact with. With increasing use of alloys at high

temperatures and the use of fuels containing impurities such as vanadium, sodium and sulfur, the problem of oxidation has become increasingly important[1].

Oxidation involves reaction between metal or alloy in air and/or oxygen especially at high temperature, usually in the absence of moisture[2]. High temperature corrosion is a form of corrosion that does not require the presence of a liquid electrolyte. Sometimes, this type of damage is called "dry corrosion". When a metal or alloy is oxidized at relatively high temperature, a stable oxide or other compound generally covers and coats the exposed surface. Thus, the corrosion products layer may act as a barrier between the underlying metal and the corrosive environment. As the temperature is increased, the importance of metal oxidation resistance also increases in applications[2].

If the scale formed is continuous, adherent, and limits access of the corrosive gas to the underlying base metal, a considerable measure of protection may occur. The oxide layer to be protective it must possess good adherence to the substrate, a high melting point, a low vapor pressure, high-temperature plasticity to resist fracture, and low electrical conductivity or low diffusion coefficient for metal ions and oxygen[2].

Oxidation is a diffusion-controlled processes, and usually proceeds by the diffusion of metal ions and electrons through the oxide layer. The resistance to oxidation of any material at elevated temperatures is dependent on the nature of the formed oxide scale. If the scale is porous then, oxidation will continue and the scale will thicken until ultimately the complete section of metal will be oxidized. If, on the other hand, the oxide scale is adherent and non-porous, then the thin film first formed will act as a protection to the underlying metal or alloy. As the scale becomes more voluminous, cracking and spalling often occur with consequent increase in rate of oxidation[3, 4].

Alloys respond to environments containing gases differently depending mainly on the alloying elements present and the temperature. At low temperatures (below 200°C), iron oxides to a negligible extent to form a thin layer of magnetite, Fe<sub>3</sub>O<sub>4</sub>. At temperature range (200 –

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570°C), a second oxide, hematite,  $\text{Fe}_2\text{O}_3$ , is also produced and form the outermost layer of the scale. Within the temperature range (200 – 570°C), iron oxides to hematite and magnetite according to a parabolic rate law. At 570°C another iron oxide, wustite  $\text{FeO}$ , becomes thermodynamically stable. If the barrier is not very effective, oxidation can and will continue at a relatively higher rate[5].

Stainless steel is another common alloy containing at least 10.5 wt% chromium (Cr) and other alloying elements with a balance of Fe. Stainless steel is essentially a low carbon steel. Addition of chromium gives the steel corrosion resisting properties. The chromium content of the steel allows the formation of a compact, adherent, corrosion resisting chromium oxide film on the steel surface. The corrosion resistance and other useful properties of the steel are enhanced by increased chromium content and the addition of other elements such as molybdenum and nickel[6].

The major characteristic of stainless is its ability to form a thin layer of protection called a "passive film" on its outside surface. This film results from a continual process of low-level oxidation, so oxygen from the atmosphere is needed for the passive film to exist[7]. Once the oxide is formed, it prevents further oxidation or corrosion from occurring. Even if the oxide layer chipped or scratched, a new passive film on stainless will form. The corrosion resistance of stainless steel arises from a "passive", chromium-rich oxide film that forms naturally on the surface of the steel. Although extremely thin (1-5 nm thick), this protective film is strongly adherent, and chemically stable (i.e. passive) under conditions which, provide sufficient oxygen to the surface[1].

Forming an oxide on an alloy surface will probably provide resistance against further oxidation. However, the parameters to form that oxide should be chosen carefully, and this is called pre-oxidation. Pre-oxidation is a technique based on exposing the base metal or alloy to an oxidizing atmosphere at a selected temperature and exposure time.

This selection depends on the type of the alloy on one hand and the nature of the subsequent environment on the other hand. The role of pre-oxidation primarily is to build up a thin layer of oxide on the surface of the material in order to protect the base metal from further corrosion. The advantage of this technique is that, it is easy to perform and also cheap compared to other surface modification techniques, such as, coatings, ion implantation, ..., etc. There has been general agreement in the literature about the beneficial effect of high temperature barrier coatings. Unfortunately, coatings in general tend to spall especially in thermal cycling applications. This drawback limits the use of such technique. Pre-oxidation has become a promising alternative technique for a wide range of high temperature applications for various reasons mentioned above. Conventional high temperature alloys rely on the formation of an adherent, protective oxide film, e.g.  $\text{Cr}_2\text{O}_3$ , to prevent excessive metal degradation[3, 4]. However, in many of the environments in gasification process, which can be relatively aggressive in nature, such films may not form or break down quite soon after

formation. Under some conditions, many such alloys undergo very rapid, often catastrophic corrosion. While it may be possible to develop alloys which are more oxidation resistance, it would be advantageous to utilize existing conventional alloys for applications involving exposure oxygen containing gases at high temperature. On exposure to aggressive environments, the presence of a  $\text{Cr}_2\text{O}_3$ -rich scale results in an initial incubation period. The length of the incubation period depends on the thickness and integrity of the  $\text{Cr}_2\text{O}_3$  scale with the substrate[8]. Pre-oxidation has been used on several alloys at various temperatures in order to improve their oxidation/corrosion resistance and performance at aggressive environments[9-21].

M. F. Pillis and L. V. Ramanathan[10], Ryoung Sohn and Toshio Narita[11] and Belma Talic (et al.)[13], investigated the effects of pre-oxidation (in Ar- $\text{O}_2$  atmosphere) on the oxidation/sulphidation behaviour of Fe-chromia alloys. They reported a beneficial effect of pre-oxidation to their corrosion resistance. Spinel oxides of  $(\text{Fe,Cr})_3\text{O}_4$  in contact with a thin oxide layer of  $\text{Cr}_2\text{O}_3$  were detected, voids at oxide/alloy interface on these alloys were also observed after pre-oxidation in (Ar- $\text{O}_2$ ) atmosphere. Qing Li (et al.)[16] and Zehao Chen (et al.)[17] studied the influence of pre-oxidation on high temperature oxidation and hot corrosion of Ni-base (coated and uncoated with Al) alloys. They concluded that the preformed oxide layer prevents the rapid formation of CrS, cavities of pre-oxidized Al-coated samples were not observed.

Despite all of these efforts to utilize the significant effect of pre-oxidation in controlled (Ar- $\text{O}_2$ ) atmosphere, very limited work has been carried out on the effect of air pre-oxidation especially to air oxidation behaviour of carbon steel in comparison to low alloy steels at relatively high temperatures for prolonged exposure time in air.

This paper aimed at studying the oxidation behavior and mechanism of carbon steel (0.131 wt% C) and (304L) stainless steel at relatively high temperatures (450°C-550°C) for up to 120hrs. Moreover, the effect of pre-oxidation on further air oxidation behavior of these alloys was investigated.

## II. EXPERIMENTAL PROCEDURE

### A. Materials

The chemical composition of the two experimental alloys is shown in Table 1.

Table 1. Chemical composition (wt%) of alloys (Balance Fe).

Element wt%	C	Cr	Ni	Si	Al	Mn
Carbon Steel	0.131	–	–	0.016	0.057	0.509
Stainless Steel	0.03	18	8	1	–	2

### B. Sample Preparation

Rectangular  $15 \times 12(\text{mm})^2$  coupons of 2.5(mm) thickness were cut from stainless steel and carbon steel sheets, using electric cutter. The surface of the specimens were prepared by grinding on metallographic (SiC)

papers up to 1000 grit. As a matter of record and accuracy, the specimens dimensions prior to exposure were accurately measured in three locations using a digital micrometer, followed by cleaning in acetone.

The samples were then weighted before and after exposure on digital balance capable of reading to a resolution of ( $\pm 0.001$ )gram. The total mass gain of the sample was determined by the mass change of the sample plus the spalled scale – if exist – collected in alumina crucible.

### C. Oxidation Procedure

Four different alloys were used in this experiment which are, carbon steel (CS), stainless steel (SS), pre-oxidized carbon steel (P.O.CS) and pre-oxidized stainless steel (P.O.SS). (P.O.CS) was obtained after exposing carbon steel samples to 450°C for 5hours. (P.O.SS) was obtained after exposing stainless steel samples to 500°C for 5hours.

The experimental alloys were exposed to 450°C, 500°C and 550°C for 1, 5, 24, 72, 120hrs. Then, they were cooled in static air. The purpose of this experiment is to determine the role of alloying elements and pre-oxidation on their protection against further air oxidation.

## III. RESULTS AND DISCUSSION

Results of the experiments can be summarized in Figures 1, 2 and 3.

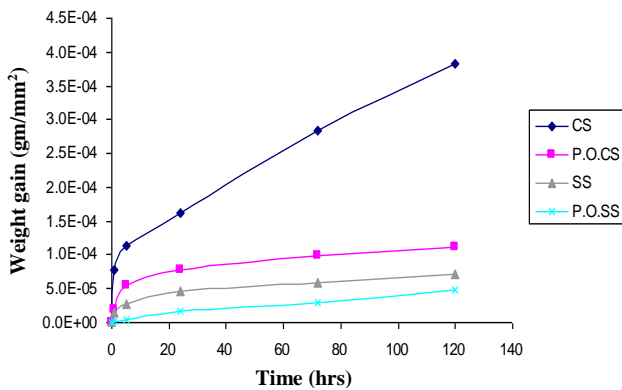


Figure 1. Air oxidation of the experimental materials at 450°C for up to 120hours.

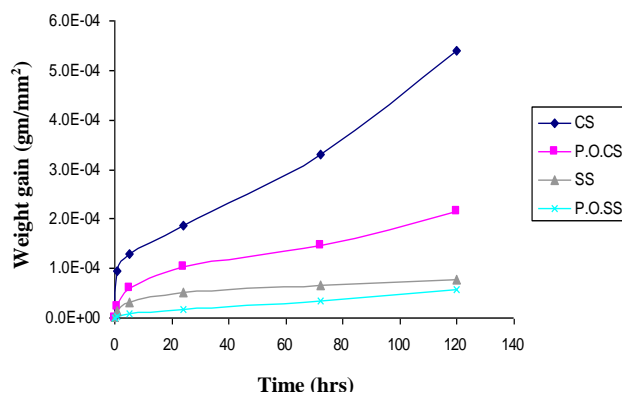


Figure 2. Air oxidation of the experimental materials at 500°C for up to 120hours.

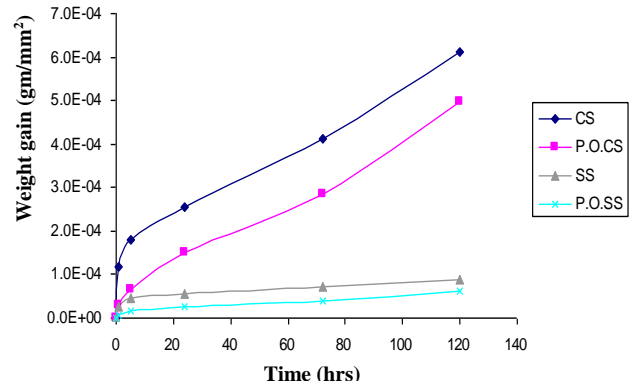


Figure 3. Air oxidation of the experimental materials at 550°C for up to 120hours.

### A. Oxidation behaviour of carbon steel and stainless steel

Oxidation rates of (CS) are higher than that of (SS) with one order of magnitude at all three temperatures. The oxidation rate of (CS) increases parabolically for up to 72h exposure time and change over linear rate with the increase of time at a temperature. The general mode of (SS) oxidation is found to be parabolic throughout the entire range of exposure time and temperature (Figures 1, 2, 3).

Rapid increase of weight gain of (CS) samples (with scale collection of the scale) especially at 550°C and for prolonged exposure time is attributed to the rapid and easy diffusion of the reacting species throughout the formed scale, whereas, at 450 and 500°C (Figures 1, 2), the scale formed on (CS) specimens was relatively adherent to the substrate and worked as a diffusion barrier to the material from the environment. Although, the weight gains of (CS) samples increased with the increases of exposure time and temperature, marginal difference in weight gains of (CS) samples especially at 450 and 500°C throughout the exposure time. Increasing the exposure temperature of (CS) to 550°C (Figure 3), the oxidation rate increases rapidly in response. This might reflect the fact that the air oxidation temperature capability of (CS) is bounded to less than 500°C.

A quasi-parabolic rate “protective” was observed for the oxidation of (SS) coupons at the three temperatures prior to 24h exposure (Figures 1, 2, 3), but the corrosion rate was reduced after prolonged exposure. At the initial stages of (SS) oxidation, rapid formation of adherent, compact “protective”  $\text{Cr}_2\text{O}_3$  expected to be found, especially at 550°C.

These findings are in agreement with the results obtained by M. F. Pillis and L. V. Ramanathan[10] and Ryoung Sohn and Toshio Narita[11] where a very thin  $\text{Cr}_2\text{O}_3$  scale was detected on Fe-20%Cr alloys at relatively higher temperatures 700 and 800°C. The high Cr content in the alloy enables a continuous supply of Cr species to form a compact and adherent  $\text{Cr}_2\text{O}_3$  layer

instead of the formation of less protective spinel of  $\text{Cr}_2\text{O}_3$  and  $\text{NiO}$  or  $(\text{Fe}, \text{Cr})_2\text{O}_3$  and  $\text{NiO}$  on the alloy.

With the increase of exposure time, a continuous spinell (mixed oxides) of  $\text{Cr}_2\text{O}_3$ ,  $\text{NiO}_2$  and  $\text{Fe}_2\text{O}_3$  covers the (SS) samples if compared to that spongy, non-adherent scale formed on (CS) samples [3, 4].

Raising the experimental temperature of (SS) to  $550^\circ\text{C}$ , especially after longer exposure time, promoted the outward diffusion of Fe, Cr, Ni and Si of the substrate and also it activated the ingress of oxygen through the less protective scale of (SS) samples. Although, no spalled scale was observed in the crucible (used for this purpose), however, the kinetic date of (SS) indicated that, the scale formed at  $550^\circ\text{C}$  is no longer protective to the substrate. This is probably due to the formation of spinel of  $(\text{Fe}, \text{Cr})_2\text{O}_3$  and  $\text{NiO}$ . Further investigation to the scale properties and composition need to be clarified using Scanning Electron Microscope (SEM), Energy-Dispersive X-ray (EDX) and X-ray Diffraction (XRD) techniques.

It can be observed (eye observation) the spalled scale of (CS) samples, with increasing exposure temperature led to acceleration of the growth of iron oxides scale. The scale formed on (CS) specimens is expected to be spinel of  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_2\text{O}_3$  especially at 450 and  $500^\circ\text{C}$ , whereas, the majority of it will be  $\text{Fe}_2\text{O}_3$  at  $550^\circ\text{C}$  [3, 4]. The spinell of (CS) samples was relatively protective at the early stages of oxidation, especially at  $450^\circ\text{C}$ . When the experimental temperature increased to  $550^\circ\text{C}$ , the scale grew very rapidly due to the remarkable acceleration of the reactive species to diffuse through the scale formed. After rapid cooling of (CS) samples (from the exposure temperature to room temperature), it is interesting to note that, the spalled scale observed at  $550^\circ\text{C}$ , whereas at  $500^\circ\text{C}$ , it was minimal and hardly seen at  $450^\circ\text{C}$ . Because with increasing the exposure temperature, the scale thickens. Increasing the scale thickness will increase the tendency of the scale to spall off [3, 4]. Furthermore, rapid cooling of the specimen after oxidation will lead to the formation of severe cracks and voids between the scale and the substrate, especially at sample edges (corners). This is due to the difference in thermal expansion coefficient between the substrate and the formed scale [3].

#### B. Effect of air pre-oxidation on air oxidation of carbon steel and stainless steel

Most of the work undertaken in this paper concentrated on the comparison of oxidation behavior of (CS) and (SS) at the specified range of time and temperature. Pre-oxidation to both materials was also investigated as an attempt to protect the two selected materials from further oxidation. This technique – pre-oxidation – is expected to be useful for many high temperature applications even in severe environment, such as, sulphadizing, chloradizing atmospheres, ..., etc.

For better understanding of the isothermal air oxidation behavior of (P.O.CS) and (P.O.SS), it was found necessary to describe and compare them at a single temperature. As would be expected, pre-oxidation played an important role in protecting both (CS) and (SS) from further degradation. However, from the results obtained, the situation seems to be complicated and needs extensive research. As a matter of simplicity, the explanation of

isothermal oxidation kinetic date of (CS) (pre-oxidized and non-pre-oxidized) and (SS) (pre-oxidized and non-pre-oxidized) will be dealt separately.

The oxidation rate of pre-oxidized carbon steel (P.O.CS) samples follows parabolic reaction law with a rate of the order =  $10^{-5}$  ( $\text{gm mm}^{-2} \text{h}^{-1}$ ) at  $450^\circ\text{C}$ , whereas, the as-received (CS) specimens shows para-linear relation at the same temperature with an order of  $10^{-4}$  ( $\text{gm mm}^{-2} \text{h}^{-1}$ ). It can be clearly noticed that demonstrate that pre-oxidation significantly enhanced the oxidation resistance of carbon steel samples for up to  $500^\circ\text{C}$ . At the early stages of exposure (e.g. 5h), the degree of protection was hardly distinguishable. However, pre-oxidation of carbon steel improvement was observed at prolonged exposure period. The diverging of kinetic curves of (P.O.CS) specimens at  $450^\circ\text{C}$  is similar to that at  $500^\circ\text{C}$ , (Figures 1, 2) but with higher rate especially prior to 72h exposure at  $450^\circ\text{C}$ . At  $550^\circ\text{C}$  (Figure 3), the material behave differently, where, rapid increase of weight gain with increasing time.

Although, the scale of (P.O.CS) specimens remained in contact with the base alloy at  $550^\circ\text{C}$ , if compared to that of (CS) samples, but the pre-formed oxide layer starts to lose its protectiveness from the early stages of exposure to the substrate. The further air oxidation experiment performed on both (SS) and (P.O.SS) revealed that pre-oxidation improved the oxidation resistance of (SS) with one order of magnitude at  $450^\circ\text{C}$  (Figure 1).

The scatter (Figures 1, 2, 3) of the kinetic date of (SS) and (P.O.SS) at the three temperatures was found to be similar throughout the whole exposure time. Rapid increase of weight of (SS) samples exposed to  $550^\circ\text{C}$  can also be observed. Whereas, very similar trend of weight changes of (P.O.SS) samples at the three temperatures can be noticed throughout the whole range of exposure time.

The tremendous effect of both alloying elements and pre-oxidation on the oxidation resistance of (CS) especially at 450 and  $500^\circ\text{C}$  can be easily observed (Figures 1, 2). This improvement becomes minimal with the increase of temperature even after short exposure at a temperature. Another fact can be derived is that, in terms of oxidation resistance, the alloying elements (Cr, Ni, Si) present in (SS 304L) played better role to (CS) if compared to pre-oxidation technique throughout the whole range of temperature and exposure time.

## IV. CONCLUSIONS

1. Stainless steel showed much better oxidation resistance than carbon steel throughout the specific range of temperature and exposure time.
2. Pre-oxidation to CS and SS showed tremendous improvement to their oxidation behavior at high temperature.
3. The beneficial effect of pre-oxidation to carbon steel was found to be up to  $500^\circ\text{C}$ , for short exposure time.
4. The pre-oxidized layer of stainless steel showed degradation resistance even at  $550^\circ\text{C}$  and is expected to survive at higher temperatures and prolonged exposure time.

5. Results revealed that, the alloying elements in SS were found to be more beneficial to the oxidation resistance of CS than its pre-oxidation throughout the whole range of time and temperature.

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