OXIDATION/CARBURIZATION BEHAVIOR OF HIGH TEMPERATURE ALLOYS

BY

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بسم الله الرحمن الرحيم

{سبحانك لا علم لنا إلا ما علمتنا إنك
أنت العليم الحكيم}

Dedicated

To

My Parents

and

My Family

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All Praise and Glory to Allah The Almighty Who Alone made this small objective to be accomplished. I feel honored and privileged to Glorify His name and gave due reverence to only Allah The Almighty for bestowing me with spirit, strength, patience and health to complete this work. Peace and Blessings of Allah be upon his Prophet Muhammad.

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ABSTRACT

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The aim of this investigation is to explore the behavior of newly-developed and promising Ni- & Fe-based alloys Haynes 214 and Incoloy 803, respectively, under mixed oxidizing/carburizing environment. Prepared samples were exposed isothermally at 800°C to three different environments ranging from purely oxidizing in air to carburizing environment, using 2%CH_4-H_2 gas mixture, containing trace amount of oxygen impurity (maximum of 100 ppm).

Thermogravimetric measurements were used as a primary criterion for performance evaluation. Analytical techniques (SEM/EDS/XRD and X-Ray Mapping) were extensively used to explain the kinetic behavior of both alloys. Haynes 214 exhibited better oxidation resistance than Incoloy 803 in air, because Al_2O_3 (formed on Haynes 214) grows at a slower rate than Cr_2O_3 which form on the surface of Incoloy 803 under the same condition. This is mainly due to the relatively high Al concentration alloy Haynes 214. In case of carburizing environment with oxygen impurity (100 ppm), the behavior is totally reversed. The causes of this behavior are primarily due to the ability of Incoloy 803 to form protective Cr_2O_3 layer, where Haynes 214 is incapable of forming neither Al_2O_3 nor Cr_2O_3 protective layers. Finally, steam has been introduced in the gaseous (carburizing) environment to provide further understanding of the role of oxygen in carburization resistance under mixed environment. The results are some what similar to those obtained in purely oxidizing environment in air, primarily due to the high oxygen partial pressure provided by the steam.

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ملخص الرسالة

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العنوان: تأكسد\تكربن السبائك عند درجات الحرارة العالية

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الهدف من هذه الرسالة هو إكتشاف سلوك سبيكتين حديثتين تحت تأثير بيئة مكونة من غازات مؤكسدة ومكربنة. وهاتين السبيكتين هما (هاينز٢١٤) وهي مكونة أساساً من عنصر النيكل، والسبيكة الأخرى (إنكولوي٨٠٣) والمكون الأساسي لها هو عنصر الحديد. وتتضمن الدراسة تعريض العينات لثلاث ظروف مختلفة عند درجة حرارة ٨٠٠ درجة مئوية. هذه الظروف تتفاوت من حالة أكسدة نقية الى حالة كربنة وذلك باستخدام خليط غاز من ميثان وهيدروجين محتوياً على جزيئات من الأوكسجين.

وسيكون تقييم أداء هذه السبائك بناءً على إكتسابها للوزن الإضافي جراء تفاعلها مع الغازات الموجودة في البيئة المعرضة لها، والسبيكة الأفضل هي التي تكتسب وزناً أقل. وتم إستخدام العديد من الأجهزة التحليلية في هذا البحث لتوضيح أسباب إكتساب الوزن. وبعد التحليل والدراسة إتضح أن السبيكة الأولى (هاينز٢١٤) هي الأفضل عند تعريضها لبيئة مؤكسدة نقية. وهذا بسبب مقدرتها على تكوين طبقة "أكسيد الألومونيوم" التي تمنع أي تفاعلات مع الغازات الموجودة في البيئة، ويعزى هذا إلى إحتواء السبيكة على تركيز عالي من عنصر الألومونيوم. وأكسيد الألومونيوم ينمو بصورة أبطأ من تلك التي ينمو بها أكسيد الكروميوم الذي يتكون على السبيكة الثانية (إنكولوي٨٠٣). وفي حالة تعريض هاتين السبيكتين إلى بيئة مكربنة تحتوي على جزيئات من الأوكسجين نجد أن سبيكة (إنكولوي٨٠٣) تكون هي الأفضل وذلك لمقدرتها على إيجاد طبقة عازلة من أكسيد الكروميوم التي تحمي السبيكة من التفاعل مع الكربون. بينما نجد أن سبيكة (هاينز٢١٤) في هذه الحالة لم تستطع تكوين طبقة أكسيد عازلة تحميها من التفاعل مع الغازات الموجودة في البيئة. وفي المرحلة الأخيرة من هذا البحث تم تعريض هاتين السبيكتين لبيئة تحتوي على بخار ماء وميثان وهيدروجين لإيضاح دور الأوكسجين في الحماية من تفاعل المواد مع البيئة المحيطة. ولقد إتضح أن زيادة الأوكسجين في هذه البيئة مفيدة حيث أنها ساعدت على إيجاد أكاسيد عازلة للسبيكتين للتقليل من تفاعل المواد مع جزيئات الغازات الموجودة في البيئة عند درجات الحرارة العالية.

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CHAPTER 1

INTRODUCTION

1.1 GENERAL

High temperature corrosion represents a great proportion of corrosion problems encountered in industry. When an alloy is exposed to an environment rich in any reactive gas (O, C, etc.), reactions between the gas molecules and the alloy ingredients will result in the formation of new reaction products (oxides, carbides, sulfides, etc.) which will change the behavior and characteristics of the alloy significantly. Alloys which are selected for specific properties, to serve in high temperature environments, will no longer be able to withstand in that environment because their properties have changed with the new reactions or they may get consumed by the corrosion process. High temperature corrosion has many modes depending on the reactive gas species present into the environment. Oxidation is the general term for high temperature corrosion and if other gases are present in the environment, other modes of high temperature corrosion will occur; if carbon is present then carburization will occur, etc. Oxidation is the most common high temperature corrosion mode, and it is observed when any material or alloy is heated at elevated temperatures with excess air or at an O_2-rich environment. However, even when the O_2 content is fairly low in the environment (reducing environment for some elements) oxidation may still occur.

Oxidation is observed in countless number of applications including: gas turbines, nuclear applications, heat-treating furnaces and chemical vessels when they are heated in air. The other common mode of high temperature corrosion is carburization which is widely observed in heat-treating equipment (which are the components used for case hardening of steels by gas carburizing), chemical processes equipments, refinery equipment and many more. It is also common in petrochemical industries where ethane and naphtha are considered as petroleum feedstock, and cracking them is the major step in getting ethylene. Also, carburization failures can be found in internal combustion engines, waste heat boilers, and in some nuclear reactors. After all, oxidation and carburization are considered to be important major failures if they occur separately for a long periods of time and at very high temperatures. However, if more than one mode of high temperature corrosion occur at the same time, it is likely that the situation becomes even worse, but in some cases oxidation may help in retarding carburization. Figures (1.1 (a-b)) show an illustration of an alloy exposed to a high temperature environment containing reactive gas species. The formation of an oxide layer was helpful in combating carburization by preventing the carbon diffusion to the alloy matrix and consequently preventing reactions with alloy ingredients. This is true only in the case of protective oxide formation, since not all oxides are protective.

The diagnosis of oxidation as a separate problem is well established in the literature, while the research in other modes of high temperature corrosion is progressing at a good pace. On the other hand, high temperature corrosion problems in mixed environments did not gain that much of attention because of its complexity

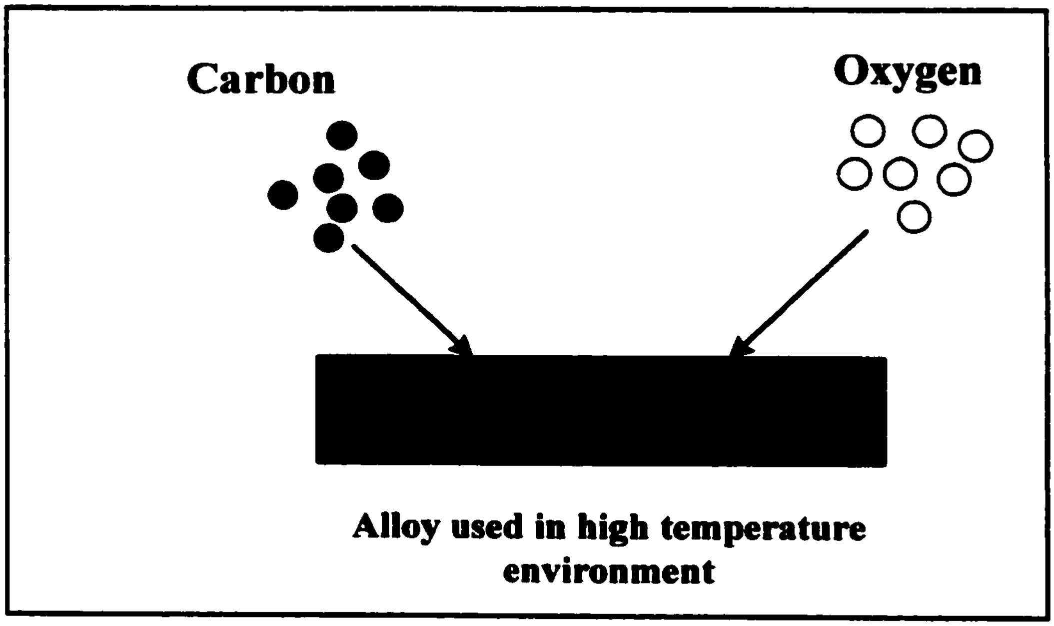


Figure (1.1 a): Hypothetical Alloy exposed to mixed oxidizing/carburizing environment

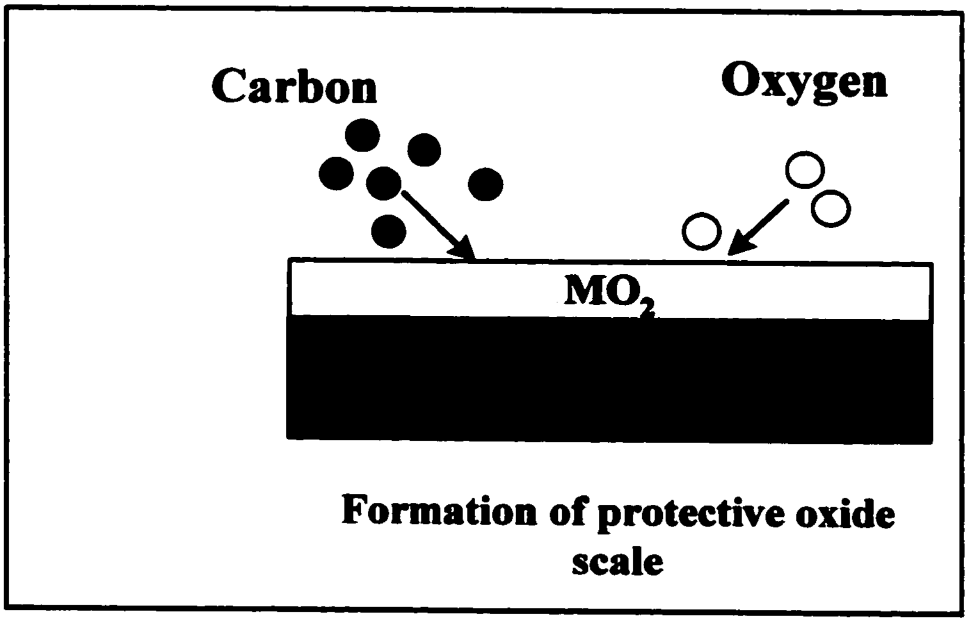


Figure (1.1 b): The formation of a protective oxide layer helped in retarding carbon attack.

and the fact that several high temperature reactions can take place simultaneously. In many applications, more than one mode of high temperature attack could occur, and may result in changes or modifications of reaction kinetics and the types of reaction products, which ultimately affect the life time of the structural metallic components. Mixed environmental conditions are more realistic for the simulation and understanding of such problems occurring in industries.

1.2 PROBLEM STATEMENT

There have been extensive research studies on the oxidation and carburization behavior of binary [1-4] and ternary [5-7] alloys which form the basis of commercial high temperature materials, yet not much attention was given to the commercial materials themselves [8]. Many of these alloys are Fe- and Ni-based with sufficient amounts of Cr and Al to ensure the formation of an external oxide layer that will combat other high temperature corrosion attacks, by blocking the way on any gas species to diffuse in the alloy matrix and cause degradation of the alloy's properties. However, depending on the exposure temperature, partial pressure of oxygen, and the relative amounts of alloy oxide-forming constituents, the development of the oxide layer could be predicted. Also, the presence of minor elements in the alloy composition might improve mechanical properties of the alloy and provide appreciable adhesion of the oxide layer.

Moreover, fewer studies dealt with mixed environments, where more than one form of high temperature corrosion could occur simultaneously. Such investigations were varying between studying pure metals [9] and complex alloys [10-12]. Also, most of the investigations were done on commonly used alloys in high temperature environments such as AISI 310 stainless steel and only few studies considered very advanced alloys such as Ni-based alloy Haynes 214 [12] and other promising superalloys under mixed environments. In the previous study [12] of the advanced alloy Haynes 214, the effect of temperature with two different commercial gas mixtures was studied. In the present investigation, however, the effect of oxygen partial pressure in the mixed environment will be considered, at fixed temperature and gas mixture, on two advanced alloys, namely Haynes 214 and Incoloy 803.

One case is to study the alloys' behavior under purely oxidizing condition (carbon-free environment). Then, studying the behavior of the same alloys when the environment is turned into carburizing environment with trace amount of oxygen. Finally, an intermediate case is considered, where the amount of oxygen is increased in the carburizing environment.

1.3 NEED OF THE PRESENT STUDY

Mixed oxidation/carburization attack is a serious problem that deserves a considerable attention and requires great research work to understand. This mode of high temperature attack might cause severe metal wastage, where a quick replacement action should be taken. In practice, this may lead to plant stoppage and proportional earning of the corroded material loss as well as the added cost of repair, the cost of loss in market position, contractual penalties, etc. The problem of carburization is not yet fully understood after research efforts exceeding half a century. The excellent work by known authorities in the field (most prominent among them is Professor Grabke) has added considerably to our knowledge but the problem still deserves more research work since few questions remain unanswered.

For the mixed oxidizing/carburizing environments, researchers had established extensive thermodynamic studies as an attempt to understand the real behavior of metals or alloys in such conditions. However, since the thermodynamic study is not enough to give final and solid-base (confident) conclusions, experimental studies are performed to confirm the thermodynamic predictions.

Most of experimental studies reported in the literature have dealt with experimental (binary or in rare cases ternary) alloys exposed to mixed gas environments. But in real situations, and especially at very high temperatures, some superalloys are used which contain many constituents reacting in different rates and forming different products. The present investigation aims at studying the behavior of two heat resistant alloys (namely Haynes 214 and Incoloy 803), which are among the best candidates for the use as structural components at elevated temperature in multi-component complex gas systems. Haynes 214 is one of the latest developments in the Ni-based alloys, while Incoloy 803 is selected due to its outstanding resistance to carburizing and oxidizing environments as well as its unique mechanical properties. In all high temperature applications, the alloy to be chosen should contain high Cr concentration in order to help in forming protective oxide layer, but in Haynes 214 the concentration of Al is relatively high, which is rarely observed in high temperature materials.

1.4 OBJECTIVES

1.4.1 General

The overall objectives of the study is to develop a better understanding of the mechanism of failure of the high temperature alloys, namely Haynes 214 and Incoloy 803 under mixed oxidizing/carburizing environments.

1.4.2 Specific

The specific objectives include:

1. Investigating the reaction kinetics in mixed oxidizing/carburizing environments.
2. Determining the effects of exposure on the alloys microstructure under isothermal conditions.
3. Correlating the microstructures of exposed alloys to the kinetic results obtained.
4. Highlighting the role of oxygen partial pressure at carburizing environments.

1.5 BACKGROUND

1.5.1 Oxidation

Oxidation, in general, means the reaction of any metal used at high temperatures with gas constituents present in the environment. Many reaction modes may occur like: carburization, nitridation, sulfidation and all of them can occur besides the occurrence of oxidation. Different metals will react with oxygen to form oxides differing in their stabilities and protectiveness to the metal surface (oxides of Fe and Ni are less thermodynamically stable than oxides of solutes like Cr, Al and Si). By increasing temperature, the rate of oxidation increases which has deleterious effects on the metal [13,14]. Generally, if an alloy is used in a temperature range which exceeds its capability, then high temperature problems will occur. Scaling and internal void formation are examples of the consequences of oxidation processes. In many applications, the selection of materials is mainly based on the corrosion resistance of the alloys used and their mechanical properties; thus in severe situations the selection can be limited to superalloys and some steels (steels for their reasonable cost).

Excessive or uneven firing in furnaces may cause the temperature to rise more than the equipment limitations. For instance, in applications where materials are exposed to temperatures in the order of 1100°C, an alloy containing (35Ni/25Cr) is recommended since it can sustain the mentioned temperature, but if (25Cr/12Ni) which has a temperature limit of 1050°C is used, excessive oxidation is found to occur [15]. Another common example in the case of some bolt assemblies used in reactors that are made of mild steels operating at severe conditions, where the presence of CO_2 will allow the reactions with steel to form magnetite (Fe_3O_4) layers on the washers. These washers will push the assemblies apart causing failure. In boilers, the oxide layers may form and exfoliate; this may cause failure of the turbine, since fragments will be carried by the steam causing erosion of the blades. Moreover, scaling will affect the heat transfer properties and may act like a barrier which stops the heat from going out, thus causing over-heating of the component. [16]

On the other hand, oxidation can become a beneficial process which helps in combating other modes of high temperature corrosion. Most metals and alloys rely on the formation of oxide layers (Cr_2O_3, Al_2O_3, etc.) that will act like a barrier preventing gas molecules from penetrating the scale and reaching the hot metal surface underneath and allowing further reactions. The degree of protection that is provided by the oxide layer depends mainly on the continuity and adhesion of the scale to the metal surface; the more the imperfections present in the scale the more the diffusion paths become available for the gas molecules to reach the base metal.

1.5.1.1 Thermodynamic Considerations

From thermodynamic analyses, reactions can be predicted based on the temperature and the partial pressure of the reactants. If the partial pressure of oxygen in the environment is greater than that necessary to form the oxide, then the oxide will form, but the only proof for that is the experimental observation. Thermodynamically, oxides of Fe and Ni are less stable than oxides of solutes (Cr,Al,Si, etc.), and if the amount of solute is low, internal oxidation would occur, whereas if a high amount is present it will turn into external oxidation [13]. Oxygen can be admitted into the environment by many reactions, like:

$$2H_2O \Leftrightarrow 2H_2 + O_2 \qquad (1)$$

$$2CO_2 \Leftrightarrow 2CO + O_2 \qquad (2)$$

From Gibb's energy equation, the equilibrium partial pressure of oxygen in the environment can be calculated from:

$$P_{O_2} = e^{\frac{-\Delta G^0}{RT}} \left(\frac{P_{H_2O}}{P_{H_2}} \right)^2 \qquad (3)$$

$$P_{O_2} = e^{\frac{-\Delta G^0}{RT}} \left(\frac{P_{CO_2}}{P_{CO}} \right)^2 \qquad (4)$$

In reducing environments where O_2 potential is low, oxygen partial pressure is controlled by P_{H_2} / P_{H_2O} or P_{CO_2} / P_{CO} (eqns.3 and 4). The development of a protective oxide layer might be very slow since lateral growth is needed. In dealing with thermodynamics, it is assumed that the metal and metal oxide are at unit activity, and the partial pressure of O_2 in equilibrium with the metal and metal oxide is controlled by the temperature; however this is not always true. Also, it is assumed that "the activity of all oxidants within the bulk of the alloy is effectively zero" [16].

Now, consider the reaction of the metal with oxygen to form metal oxide:

$$M + O_2 \Leftrightarrow MO_2 \qquad (5)$$

From Gibbs free energy:

$$\Delta G^0 = -RT \ln \left(\frac{a_{MO_2}}{a_M . P_{O_2}} \right) \qquad (6)$$

Assuming the activities of the metal and the metal oxide are unity, equation (6) becomes:

$$P_{O_2} = e^{\frac{\Delta G^0}{RT}} \qquad (7)$$

Note that the partial pressure of oxygen can be controlled by temperature only, since R and ΔG^0 are constants.

1.5.1.2 Kinetics

If diffusion through the lattice defects is the only means of transport across the oxide layer, then the oxidation reactions can proceed either by the inward diffusion of oxygen in the scale (the scale is n-type semiconductor) or the outward diffusion of the metal constituents through the scale (p-type semiconductor) to meet oxygen at the surface and form the oxide, i.e. the growth of the oxide layer in the first case happens at the bottom of the oxide layer, while it is at the top of the oxide layer in the second case.

The kinetics of oxidation can be described by the nucleation of the oxide on the metal surface and then spreading laterally till the entire surface is covered by the oxide layer (provided that the metal or the alloy has sufficient amount of the oxide forming constituent to form the continuous oxide). This is true in pure metals exposed to an environment rich in oxygen, but in the case of alloys the story is totally different. If an alloy has two constituents, where one of them forms a more thermodynamically stable oxide than the other, it is not necessary that this stable oxide will form till enough flux of that constituent is provided to the surface of the alloy to satisfy the needed amount to form the continuous and external oxide. If the surface activity (partial pressure) of this constituent falls below the limit for the oxide (partial pressure needed to from the oxide) then, from thermodynamics, another type of oxide will form, even though it is not the stable phase [16]. The formation of voids at the interface region between the alloy and the oxide is associated with the intergranular penetration of Cr_2O_3, i.e. condensation of cation vacancies at the metal oxide interface or precipitation of vacancies at the grain boundaries [8].

1.5.1.3 Catastrophic Oxidation

Oxidation is a common problem in industrial applications such as oil refining, inorganic chemical production and petrochemical processes. It has two major forms; scaling due to overheating and catastrophic oxidation failures. Catastrophic oxidation is characterized by the accelerated rate of oxidation after the metal had encountered severe oxidation for a long time. For instance, carbon steels that are widely used in high temperature applications may suffer catastrophic oxidation when heated above 1000°C [13].

Catastrophic oxidation may occur in situations where stagnant or moving fluid is present in the environment but at very high temperatures. In such cases no protective oxide layers are observed and a linear oxidation rate is possible. To account for such conditions, the addition of 2% Mo in some alloys (like 316 stainless steels) will prevent the catastrophic oxidation to occur at continuously circulating fluid conditions at temperatures up to 900°C, but in stagnant fluid conditions it can occur even at temperatures as low as 760°C [15].

1.5.1.4 Failure of Oxide Layers

Oxide layers that provide some protection to alloys used at high temperatures might fail due to one of the following reasons [16]:

1) While oxides are forming, pores are developed in the alloy/oxide interface. This is often encountered in situations where the metal diffuse outwardly to form oxide scales more than oxygen diffusing inwardly. When the oxide layer gets thicker, these pores grow and join together to form large voids. This will cause the oxide to rupture after a number of thermal cycles because the oxide layer is completely disconnected from the metal.
2) The existence of a thermal expansion coefficient differential between the oxide scale and the substrate. Thus, with thermal cycling, the scale might get separated from the substrate causing failure of the oxide.
3) An overall degradation of the mechanical strength of the system.
4) Fracture strength of the oxide is less than the fracture strength of the metal. Thus, acceptable elastic deformation of the metal may cause fracture of the oxide.
5) Erosion (caused by impingements of high velocity hard particles) may cause the removal of the protective oxide.

1.5.2 Carburization

When CO, CH_4 or any other hydrocarbon gas is present at elevated temperatures, structural materials become susceptible to carburization. When carbon diffuses into metals and alloys, it reacts with active metal constituents to form internal carbides, thus causing embrittlement (the metals or alloys becomes brittle) as well as other forms of mechanical properties degradation. The cause of embrittlement is attributed to the formation of hard carbide particles that will act like obstacles in the movement of the dislocations; thus providing some hardness with considerable loss in ductility.

In petrochemical industries, and especially in the production of ethylene where thermal cracking of hydrocarbons in a steam-hydrocarbon mixture at 1100°C is done, carburization is the major mode of high temperature corrosion. Also, when natural gas is converted into CO and H_2 with the help of catalysts and when overheating occurs or there exists high carbon activity in any high temperature environment, carburization could occur.

In terms of protection, silicon oxidation is very beneficial in reducing the carburization depth, but Si uses are rather limited because of its adverse effects on mechanical properties and weld-ability. A suitable amount of Si should be added to the metal (about 1.5-3%wt) to help in making a more or less continuous SiO_2 layer beneath the Cr_2O_3, and since SiO_2 is thermodynamically more stable than Cr_2O_3, it is not attacked by C [17]. However, the oxide layer can be destroyed by the carbon growth beneath the scale, creep, and conversion from oxides to carbides. Also, Nb and W additions will act like carbide stabilizing elements.

1.5.2.1 Thermodynamics

Carburization occurs by the reaction between carbon molecules into the environment and the material exposed to high temperatures to form different carbides. Because the concentration of carbon in the environment is greater than that in the metal, carbon diffuses in and reacts with the constituents of the alloy. If the carbon activity in the environment exceeds the value necessary to form the carbide, then, thermodynamically, that carbide is expected to form. The carbon ready for the reaction can be obtained from one of the following reactions:

$$CO + H_2 \Leftrightarrow C + H_2O \qquad (8)$$

$$2CO \Leftrightarrow C + CO_2 \qquad (9)$$

$$CH_4 \Leftrightarrow C + 2H_2 \qquad (10)$$

The activity of carbon (a_c) in the above equations can be calculated respectively from the Gibbs energy equations by:

$$a_c = e^{\frac{-\Delta G^0}{RT}} \left(\frac{P_{CO} . P_{H_2}}{P_{H_2O}} \right) \qquad (11)$$

$$a_c = e^{\frac{-\Delta G^0}{RT}} \left(\frac{P_{CO}{}^2}{P_{CO_2}} \right) \qquad (12)$$

$$a_c = e^{\frac{-\Delta G^0}{RT}} \left(\frac{P_{CH_4}}{P_{H_2}^{\ 2}} \right) \tag{13}$$

The activity of carbon can be controlled by temperature variation, and in reactions (11 and 12) the activity will decrease with increasing temperature. However, in reaction (13), the activity of carbon increases with further increase in temperature. Using CH_4 to produce carbon is somewhat safer since the other two reactions involve carbon monoxide, which is a killing gas that depletes oxygen in the human brain. This is the primary reason for the use of a mixture of CH_4/H_2 to simulate a carburizing environment in this investigation.

Thermodynamic stability considerations cannot fully predict the behavior of metals and alloys in carburizing atmospheres. However, if thermodynamic considerations are considered along with kinetic factors that govern the formation, growth and breakdown of oxide layers on the surface of any metal, then a better understanding of the behavior of the high temperature alloys might be obtained. Also, mechanical and structural factors, which control the transport of carbon through oxides, will contribute to the behavior of the substrate alloy.

1.5.2.2 Kinetics

The rate of carburization for any material or alloy is controlled mainly by the presence of an oxide layer, since the rate controlling process will shift from carbon diffusion through metal matrix into diffusion through oxide the layer. In Fe-Ni-Cr alloy the formation of Cr_2O_3 will provide excellent protection to the metal from carburization attack, though carbon can only diffuse through the pores of the oxide layer and react with the metal underneath. Also, due to the creep of the metal at high temperatures, carbon can penetrate the scale through defects, and with excess carbon diffusion graphite might form at the metal/oxide interface causing cracking of the scale while growing. Moreover, there is a possibility of the transformation of Cr_2O_3 layer into carbides, which occurs at very high temperature ($\geq$ 1100°C) with high C activities [17]. In industrial applications where Fe-Ni-Cr alloys are utilized in the vicinity of high carbon concentrations, the reactions between carbon and alloy ingredients result in the formation of internal carbides.

The steps involved for the kinetics of carburization are:

1. Gaseous diffusion of carbonaceous gas molecules in the gas atmosphere,
2. Splitting of carbon molecules into atoms by means of phase boundary reactions at the surface of the metal,
3. Dissolved carbon atoms diffuse inwardly into the metal,
4. Reaction of carbide-forming elements with carbon atoms in the interior of the alloy.

1.5.2.3 Properties Degradation

Some properties will be adversely affected by the occurrence of carburization reactions; for instance mechanical strength where the base metal almost looses its load-bearing capability [16]. Creep strength will improve with carburization reactions, since the carbides that from and segregate to grain boundaries will provide some resistance to grain boundary sliding at high temperatures. Also, ductility can be reduced significantly by carburization because the formation of carbides will make the motion of dislocations difficult. Removing Cr from the alloy, as carburization progresses will affect the oxidation resistance.

Although carburization improves the thermal conductivity of the metal [17], the formation and growth of internal carbides will impose internal stresses because of the increase in the volume of the metal (Pilling Bedworth Ratio). For carburized samples, the tensile strength and impact strength are reduced with serious embrittlement at room temperature.

The ways in which carbon degrade a certain material exposed to environments rich in carbon [18] are: (1) changing the structure and composition, (2) physically removing the metal, and (3) by both of them. Carbon may also diffuse inside the alloy to form internal carbides in an intergranular network form surrounded by a low strength alloy-depleted matrix.

1.5.3 Mixed Oxidation/Carburization

In some cases the presence of more than one reactive gas in the same environment causes more damage than a single gas. The degree of damage of any alloy used in a mixed environment depends mainly on which reaction happens first. In an environment where both oxygen and carbon are present, and the oxidation reaction of Cr, for instance, is kinetically more favored over carburization, the alloy will form a protective oxide layer which prevents the carbon from diffusing in and reacting with other elements. On the other hand, if the carbon reacts first to form carbides like $M_{23}C_6$, then it is difficult to form a protective oxide layer that may permits some protection to the alloy [16]. Although conversion of carbides to oxides is possible, but only in restricted conditions of temperature and time.

To illustrate the idea more, consider the example when carburization occurs first; the oxidation resistance of Fe-Ni-Cr alloy is decreased because of the precipitation of chromium carbides at grain boundaries causes depletion of Cr in the alloy matrix. If partial carburization occurs, the carbides may oxidize at the alloy grain boundaries, but if the carburization is heavy (carbides are assembled beneath the surface to make dense layer) oxidation may still occur and continuous exposure at oxidizing environment may allow the formation of continuous layer. [17]

In carburizing environments, such as carbon monoxide, methane, ethane etc. the carbon combines primarily with Cr and other elements (e.g. Nb, W, Mo, Ti) to form carbides, which are hard and brittle. As a result of that, the ductility of the metal is significantly reduced with carburization which tends to tie up Cr that will reduce the oxidation resistance. Moreover, stresses will develop on the metal due to the volume change caused by the carbon uptake and carbides formation. These stresses will contribute to mechanical failure of the component. Pores, cracks and any other defects in the scale may provide easy access of carbon to the alloy surface where it reacts with the alloy's constituents. Also, silicon carbide internal particles may act like sites for nucleation of failures [18].

1.5.4 Materials Selection and Development

The increased demand for more efficient gas turbines requires increasing the operating temperatures, i.e. inlet temperatures of the turbines may exceed 1000°C or

1100°C. This dramatic increase in operating temperatures means that more efficient materials should be developed in order to sustain long operating life under these conditions. This argument also applies to other high temperature alloys used as structural materials for other equipment which is utilized in chemical process facilities, refining industry and other industries involving hazardous environments. To develop materials that are capable of resisting high temperature environments, a better understanding is needed for the mechanism of oxidation and carburization, and the alloying elements that will enhance the resistance by the development of protective oxide layers. For most engineering alloys used in high temperature operations, the production of protective layers can be classified basically into Cr_2O_3 or Al_2O_3. Oxides of the base metal always form at the beginning of the exposure before steady-state conditions are established. On the same basis, the developments of Al- and Si-rich surface coatings hold a promise for major advancements in the carburization resistance. However, spalling of the oxides, because of thermal cycling, will allow the substrate to be exposed to more oxygen and thus, the formation of lower stability oxides, since the constituent that forms stable oxide was consumed by oxidation reactions.

High temperature problems can be combated in many industries by choosing the right material for the right operation. Moreover, mechanical properties should be kept in mind in order not to have mechanical failures. Selecting materials for high temperature applications is restricted some times to mechanical design-, operation- requirements, economics and availability of the material. " A complete approach to high temperature corrosion problem solving may often require team work between process chemists, design engineers, operators, material specialists, maintenance planners, purchasing officers and even accountants" [15]. Material selection in high temperature applications represents a great challenge since it is difficult to find materials that show good mechanical properties beside their good corrosion resistance.

For instance, nickel can improve the carburization resistance significantly because it reduces the solubility and diffusivity of carbon in Fe-base alloys [17]. Nickel-based alloys are emerging into industrial applications and especially at high temperatures. On the other hand, high Cr content is crucial to allow the formation of an oxide layer (it should be $\geq$ 20%wt). With the help of some trace elements such as Si or Al, which have higher oxygen affinity than Cr, more oxidation resistance is preserved. The presence of these elements at a level of 1.5%wt or more may allow the formation of another more stable oxide layers beneath the Cr_2O_3, but the addition of theses elements is rather limited because of their adverse effect in the mechanical properties. Also, adding some reactive elements such as yttrium or niobium, in small amounts like 0.1%wt will improve the adhesion of the protective oxide layer [17]. The protectiveness of Cr_2O_3 is lost at 950°C because, at this particular temperature, volatile chromium oxide is formed (CrO_3) [19].

Strengthening procedures are crucial at high temperatures to improve the mechanical properties. This can be done through solid solution hardening, precipitation hardening, carbide or dispersion hardening.

CHAPTER 2

LITERATURE REVIEW

2.1 OXIDATION

2.1.1 General

The study of binary alloys was divided into Cr- and Al-binary alloys to notice the different behavior of these two elements in the oxidation process. For ternary alloys the research efforts concentrated on a base metal with both Cr and Al as alloying elements. One typical example is the design of almost all superalloys used in high temperature operations, which contain appreciable amount of Cr that will participate in forming the protective oxide layer. Bruckman et al. [3] investigated the mechanism of oxidation at 1000°C of several Fe-Cr alloys, using an isotope O^{18}. They found that oxygen transport inwardly during the growth of the inner, heterophase scale layer.

By altering the Cr percent form 44-50wt% in a binary Cr-Ni alloy in a temperature ranging between 800-1100°C, Ecer and Meier [1] found that the Cr_2O_3 growth occurs by the outward diffusion of Cr through Cr_2O_3 and by grain boundary diffusion through the scale. The growth mechanism suggested follows the following steps: (a) growing Ni- and Cr-oxide nuclei, and since NiO has a faster growth rate than Cr_2O_3, it will grow above it and the slowly growing Cr_2O_3 will gradually form near the surface of the metal, (b) once the Cr_2O_3 forms a continuous layer, it will undercut any further transport of Ni to form NiO; thus dominating on the surface. Because of the cation vacancy condensation at the metal/oxide interface, the separation of the metal from oxide takes place (because of voids formation) and further growth of Cr_2O_3 will occur by evaporation of chromium from the metal substrate. Cracking of the scale may occur at the sites of voids, thus allowing molecular oxygen to arrive and react with the hot metal surface forming new inner oxide layer that can grow till it reaches the outer layer. The authors [1] also concluded that any factor that reduces the oxide grain size would result in an increased rate of oxidation, because reducing grain size is associated with increased number of grain boundaries which provides more diffusion paths for atoms to transport to the surface and meet oxygen (p-type semiconductor).

The transport of chromium outwardly through the scale will allow the reaction of more Cr and consequently thickening of the Cr_2O_3 layer or the oxygen may be supplied through cracks in the scale (generated by thermal cycling) at the inner interface resulting in a depletion of Cr at the interface. Irregular interface is established between the metal and the oxide because the diffusion of oxygen along the metal/oxide is faster than diffusion along metal lattice which results in a perturbated interface that is thickening with time. [8]

To study the effect of the level of Al in the alloy oxidation process, Wood and Stott [20] conducted oxidation experiments for Ni-7%Al and Ni-12.5%Al in 1 atm O_2 and at temperatures ranging from 800-1200°C. Their results indicated that the formation of α-Al_2O_3 could be attained very easily at higher Al content and higher temperatures, because the contained Al in the substrate can diffuse to the top of the alloy to form oxides very rapidly. In the case of Ni-7Al, the alloy formed non-protective NiO-rich nucleus and underlying α-Al_2O_3 scale. Nickel oxide (NiO), $NiAl_2O_4$ and the thermodynamically favored Al_2O_3 scales are present, but in different quantities based on the Al content. If the alloy is rich in Al and the environmental temperature is high enough to allow the diffusion of Al to meet oxygen, then continuous layer of Al_2O_3 will form, but if the level of Al is low or the exposure is conducted at low temperature, then a subscale of Al_2O_3 is produced.

Since most materials rely on the formation of oxide scales, Wood and Stott [20] stated that the formation of a steady-state α-Al_2O_3 scale on the alloy surface depends mainly on: (1) grain size, (2) purity, (3) surface finish, (4) degree of cold work, (5) initial oxide present, (6) the oxygen partial pressure, and (7) the method of elevating the specimen to the test temperature.

In Fe-Cr-Al alloys exposed in oxidizing environment at 1200°C [21], the predominant scale was α-Al_2O_3 with some traces of Cr_2O_3 that came up to occupy 5% of the scale, provided that the alloy has sufficient amount of Al. In the presence of small amounts of Al the predominant scale was Cr_2O_3, with α-Al_2O_3 particles growing to form small subjacent islands beneath Cr_2O_3.

Ni-base alloys gained great attention since they represent the primary coating alloys in gas turbines. Oxide maps were developed by Jaffee [21], for an alloy mixture of Ni-Cr-Al, and all possible reactions were included. In a 20%Cr-3%Al alloy, a continuous external layer of Cr_2O_3 was formed with internal oxides of Al_2O_3 forming within the surface zone of the underlying metal substrate. At 1200°C, Al_2O_3 was able to link exactly beneath the Cr_2O_3 layer after exposing the alloy for 20 hrs.

In Fe-Ni-Cr alloys, the presence of 30-46% Ni has a great contribution in improving the oxidation resistance under the isothermal conditions, but an exceptional behavior was observed at 1000°C due to a certain breakaway phenomena.

To characterize the behavior of the widely used Ni-Cr-Al alloys, Stott and Wood [6] studied the isothermal oxidation of Ni-Cr-Al alloys in 1 atm O_2 at 1000 and 1200°C with varying contents of Cr and Al (15%Cr-1%Al and 29%Cr-4 %Al). They found that adding 1%Al to Ni-Cr will improve the oxidation resistance, but it is not sufficient to form a protective α-Al_2O_3 scale. An addition of 4% Al will produce a protective and external Al_2O_3 layer very rapidly. During the initial stages, nuclei of NiO, Cr_2O_3, and Al_2O_3 are formed at the top surface of the alloy and then due to the large negative values of the free energies of formation of the Cr- and Al-oxides compared with NiO, the more stable Al_2O_3 will dominate to establish the steady-state surface scale. Chromium- and Al-oxides compete to form the predominant oxide scale and the other will form internal oxide, but both of them will prevent the Ni from forming any further oxides. If Al is present in relatively high concentrations there will be no chance for chromium to form external oxide layer, but if the content of Al is low then internal oxidation of Al is observed with Cr forming external oxide layer.

Kvernes and Kofstad [5] investigated the oxidation resistance of a variety of Cr-Al-Ni alloys at temperatures ranging from 800-1300°C at 1 atm pressure. They found that the alloys possessing the best oxidation resistance was the Ni-9Cr-6Al alloy due to the formation of external α-Al_2O_3 layer at all temperatures studied. One of their objectives was to alter the composition and the ratios of the alloy to determine an optimum oxidation resistance. At a temperature range between 800-900°C the formation of NiO is the dominant reaction, while the reaction of Al to form a predominant α-Al_2O_3 is more important at elevated temperatures. Nickel oxide (NiO) and Cr_2O_3 will also form along with Al_2O_3 when the oxidation reaction takes place at higher temperatures especially at low oxygen pressures. At a reduced Al content the development of internal oxidation zones by Cr_2O_3 and Al_2O_3 is observed with external NiO. If this alloy is heated up to 1300°C, then three layers will form; an outer layer of NiO, middle layer (with a porosity between the two layers) of Cr_2O_3 which seems to be the main reaction product, and an inner thin layer of α-Al_2O_3.

Regarding the significance of Cr in the performance of high temperature alloys, Wood and Stott [20] stated that in the case of M-Cr-Al alloy the α-Al_2O_3 layer is formed and maintained more than in the case of M-Al alloy, because in the former case the Cr tends to stabilize the α-Al_2O_3 rather than γ-Al_2O_3. Also, α-Al_2O_3 will develop as a continuous layer rather than forming islands above the surface with the help of Cr (since it prevents oxygen from diffusing into the alloy).

For commercial alloys, which contain more elements, some work was done [21] to analyze the behavior of such alloys in oxidizing environments. It was observed that for Fe-based alloys, exposure for short time periods creates a relatively large surface depletion of Cr. In terms of rates, the oxidation rate is parabolic, which is associated with the formation of Cr_2O_3 scale, and above it an outer layer of Fe- & Ni-oxides that are formed during the initial stages, and this depends on the rapid completion of the Cr_2O_3

layer. For most commercial alloys, the adhesion of the scale is improved by the formation of internal oxides of some minor constituents.

For Ni-base superalloys, which contain a moderate Cr and Al, increasing Al content promote the formation of Al_2O_3 as the initial phase of the oxide scale. Subsequent oxidation will result in an overgrowth of Al_2O_3 by Cr_2O_3 that start near grain boundaries and then spread laterally till the entire surface is covered by Cr_2O_3 scale. Jaffee [21] presumed that in the period during which Al_2O_3 is overgrown, the oxidation kinetics are linear and then it change to parabolic with the thickening of the Cr_2O_3 layer. Internal oxidation of Al is observed when the Cr_2O_3 layer becomes continuous, while the external layer of Al_2O_3 had been destroyed because it is almost pushed aside by the growing Cr_2O_3 layer. Also, internal oxides of other constituents make the oxide layer more adherent to the surface.

Wei and Stott [8] investigated the oxidation behavior of some Ni-based and Ni/Fe-based commercial alloys that can form Cr_2O_3 scale at 800°C and 1000°C. They concluded that the amount of Cr should be sufficient to ensure the formation of a protective Cr_2O_3 layer, which will give long-term service at elevated temperatures. They stated that Ni-based alloys or alloys that contain considerable amount of Ni are utilized at temperatures exceeding 750°C due to the strength possessed by these alloys and their metallurgical compatibility with other materials such as Cr, Mo, Fe, W etc. Alloying with 20% Cr will ensure the formation of a Cr_2O_3 layer in which Fe-and Ni-containing oxides will form above it.

On the other hand, Grabke et al [22] pointed out that in steels it is not guaranteed to form a Cr_2O_3 scale at low temperatures, even if the Cr-content is very high in the steel. They stated that any type of surface working applied, such as grinding and sand blasting will introduce dislocations and cause a fine-grained microstructure near the surface which will act like rapid diffusion paths for Cr to transport to the surface and react with oxygen to form a protective oxide. However, Stringer and Whittle [16] mentioned that to form a protective Cr_2O_3 layer, a sufficient amount of Cr should be present depending on the base metal, 20% Cr in nickel-, 13% in Fe-, and 25% in cobalt-based alloys.

To contribute to the study of the effect of alloying elements in the oxidation resistance, Donohue et al [23] oriented the research in another direction when they studied the effect of Cr and Y contents in the TiAlN hard coatings, in an oxidizing environment. They modified the $Ti_{0.44}Al_{0.53}Cr_{0.03}N$ conventional coatings with the addition of Y to form $Ti_{0.43}Al_{0.53}Cr_{0.03}Y_{0.02}N$ coating. The new coating shows

improved resistance to oxidation where it starts almost at 950°C, whereas in the conventional one severe oxidation occurs at 850°C. Also, adding dispersed oxide particles shows to have a beneficial effect on the oxidation resistance [24].

2.1.2 Thermodynamic Studies

A thermodynamic study by Stringer and Whittle [16] treated the situation where an alloy is exposed to an oxidizing environment where all possible reactions might occur. They assumed the exposure of a model Al-Ni alloy in an oxidizing environment where Al_2O_3, NiO, and $NiAl_2O_4$ are the possible products of the reaction. They concluded that there is a very strict condition for the formation of $NiAl_2O_4$ and in practice it should be assumed that either Al_2O_3 or NiO to be the only stable oxide. Also, the amount of Al needed for the Al_2O_3 to be stable is very small. In all cases, such a small amount is not enough to form external scale. So, thermodynamics approach is not sufficient to predict the oxide that forms in practice. From thermodynamics, the change in free energy between the metal and the oxidant is the driving energy for the reaction to occur [25].

Van der Biest et al [26] conducted a thermodynamic analysis and experiments to study the ability to form Cr_2O_3 in 25Cr/20Ni steels in temperatures ranging from 825-1000°C in CH_4-H_2 mixture. The experimental analysis agreed with the thermodynamic predictions in that no Cr_2O_3 can be formed due to the low oxygen activity in the system. However, at low temperatures oxidation of Si is possible, and a continuous layer of SiO_2 is formed which contributed to the protection of the steels.

2.1.3 Kinetics

Research work on oxidation has started seriously after Wanger had reformulated his theory on parabolic growth rates in 1951, that was "based on the independent migration of ions and electrons in local equilibrium within the scale, driven by the free energy decrease accompanying the combination of solid metal with gaseous oxygen to form oxide" [27]. In fact, very little work was done before Wanger's time without his guidance. Earlier work was heavily related to temper colours on steels; i.e. when bright steel is heated at moderate temperatures in air, it will get covered by a thin coloured layer which has a good rusting resistance and good adherence to the surface.

In order to study the mechanism of the oxidation process, it is favorable to start with a pure metal in a single oxidant environment, because the formation of more oxides will complicate the analysis. The first step involved in the oxidation reaction is the adsorption of the oxidant on the surface of the metal, where it diffuses in the metal based on the solubility and diffusivity of the oxidant in the metal. Kofstad [28] stated that at low temperatures the growth of the scale follows a logarithmic type rate equation, i.e. it will reach a situation where the growth becomes constant. As time passes the oxide scale becomes thicker and the reaction rate decreases with time, since reactants and electrons have to travel longer distances. Parabolic rate equations can describe the reaction under many conditions.

Also, Hurlen [29] showed that, starting from the theory of absolute reaction rates, a general oxidation equation can be developed under certain conditions, and further representing it by parabolic, cubic and inverse logarithmic equations. He stated that this analysis is valid for cases in which oxidation is controlled by the transport rate of material in the oxide film, assuming that the areas which are oxidizing are constant with time.

Jaffee [21] and Kofstad [28] studied the oxidation process starting with pure metals, binary alloys and ternary Fe-Ni-Co based alloys. In pure metal oxidation, parabolic rates were noticed according to:

$x^n=k_p.t$

where x: distance; n=2; t: time; and k_p: is the parabolic rate constant, which, for different metals the oxidation rate came to be in the order of Fe>Co>Ni at 1000°C.

Because of the importance of Cr in forming a protective Cr_2O_3 scale Lillerud and Kofstad [25] studied the mechanism of the formation of Cr_2O_3 and its growth between 1000-1200°C at an oxygen pressures of $1\text{-}10^{-7}$ atm. They concluded that the transport processes of Cr and O is accomplished by the diffusion through lattice, grain boundaries, and microcracks present in the scale. With the help of O^{18} traces, they found that oxygen is diffusing inwardly through Cr_2O_3 scales to react with Cr. Although they noticed a great change when the oxidation temperature is altered, they concluded that "no significant changes in the oxidation rate on change in the oxygen pressure" [25].

In terms of diffusion, it can occur through grain boundaries, lattice (interstitially and vacancies) or any other diffusion path. Cavities and pores may develop into the scale along with growth stresses (due to the volume change associated with the formation of the oxides), which will cause plastic deformation or cracking of the scale [28]. In the case of Cr-oxide, studies indicate that the Cr vacancies are the defect type in Cr_2O_3 layer at high partial pressures of oxygen (P_{O_2}), and Cr interstitials at low P_{O_2}. Wolf et al [2] did not detect any Cr depletion zone beneath the scale in the case of Fe-Cr alloys in the range between 12.5-20%Cr. At this range of Cr content, the diffusion of Cr ions in the alloy is the rate controlling process at the beginning, whereas in the latter stages, diffusion of Cr into the scale will be the rate controlling process.

Wood and Stott [20] listed the important factors to determine how the steady-state scaling is developed at the alloy surface (gas/metal interface). These are:

1. The free energy of formation, which means that the more negative is the Gibbs free energy the more thermodynamically favorable product, and it came in the order α-Al_2O_3, Cr_2O_3, FeO, etc.
2. The content of Al in the alloy, i.e. whenever Al content is high there is more chance of having α-Al_2O_3 external scale.
3. The diffusivity of oxygen varies depending on the base metal, though oxygen has less diffusivity in Fe than in Ni and greater solubility in Ni than in Fe.

4. Growth rates will have great effects on the oxide formation, and it is in the order FeO, NiO, Cr_2O_3, α-Al_2O_3 $1:10^{-1}:10^{-3}:10^{-5}:10^{-6}$ to 10^{-7} respectively, because of the diffusivity differences between various components.

2.1.4 Initial Stages

The initial stages of oxidation were not given enough attention despite their recognized value of determining the mechanism of oxidation. Most studies dealt with the oxidation for longer time periods where it is assumed that "a plane and homogeneous growth is possessed and the isotherms can probably be described by the laws pointed out in the classical theories of oxidation" [30]. On that basis, Ronnquist [30] studied the oxidation of Cu at temperatures ranging between 150-500°C for durations longer than 5 seconds. He noticed that the higher the oxidation temperature the earlier the nucleation starts. Also, the author compared his results on the early stages of oxidation with previous work and concluded that oxide layers form and grow through three consecutive stages: (1) incubation of nuclei, (2) growth of nuclei, and (3) growth of a continuous film.

For the Ni-9Cr-6Al oxidation, initial stages occurs at 900°C by the formation of an outer NiO layer, a second layer containing Cr_2O_3 followed by a spinel phase of $Ni(Al,Cr)_2O_4$ plus γ-Al_2O_3. Further exposure results in the formation of ternary layer with NiO followed by Cr_2O_3 and α-Al_2O_3. At 1200°C and at the beginning of the oxidation, an outer layer of NiO is observed, followed by a mixed Al_2O_3+ Cr_2O_3 layer in between and a spinel of $Ni(Al,Cr)_2O_4$. With further exposure, the only dominant layer is the α-Al_2O_3

and nothing with it. This highlights the effect of exposure temperature in the domination of the more stable oxide. [5]

2.1.5 Trace Elements Effect

The effect of trace elements on the oxidation behavior of high temperature alloys has been the subject of intense efforts due to their importance in determining the oxidation characteristics [21]. These trace elements include Mg, Si, Y, Nb, and rare earth as well as other elements which may improve the adhesion of the Cr_2O_3 and Al_2O_3 protective layers with good reduction in oxidation rate. The widely used alloying element Si has a very stable oxide and improves the oxidation resistance, but it rarely forms a complete surface oxide (SiO_2). This is due to the slow growing nuclei of this oxide and the continuous competition of other oxides that may not allow the formation of a continuous layer but forming only semi-continuous film at the scale base [21]. In the case of Y, it can form discrete particles of Y_2O_3 and either $YAlO_3$ or $YCrO_3$, and it is present mainly as grain-boundary internal oxides. Yttrium has its own effect on the formation of α-Al_2O_3, and it may dissolve uniformly into the α-Al_2O_3 or may segregate at lattice defects such as dislocations. Wood and Stott [20] mentioned that 0.82%Y added to the alloy will be enough to prevent lateral growth of voids at the oxide/metal interface and provides pegs between the α-Al_2O_3 and the substrate of the alloy. For the rest of trace elements and rare earths it is known that these elements provide improved oxide scale adherence and in some cases reduced oxidation rate.

Minor elements like Al and Si have beneficial effects on the oxidation behavior, especially under thermal cycling conditions, while manganese can have detrimental effects because of the establishment of the outer $MnCr_2O_4$ and scale fracture. After all, alloying with Cr plus either Al or Si is necessary to form protective oxide scales.

2.2 CARBURIZATION

Perkins [18] explained carburization problems (existing since the mid-1940's) in petrochemical processing equipments, when the material degrades by the reaction with carbon. In the early days, the modification in design to improve the heat resistance of alloys followed the classical way to combat carburization problems. The work was conducted by varying systematically all the constituents of the alloy under study to assess the relative contribution of each one in the carburization behavior. Then by balancing the composition of the constituents, a material with the needed resistant to the attack will result with useful mechanical properties.

In practice, and especially in steam cracking of hydrocarbons to produce ethylene, carburization is the most dominant form of high temperature attack. Carbon diffuses inwardly into the metal matrix forming precipitates of carbides $M_{23}C_6$ and M_7C_3 where (M=Cr, Fe, Ni). Rahmel et al [31] and Grabke et al [17] stated that $M_{23}C_6$ form at low carbon concentrations, and later on it will convert to M_7C_3, forming two different precipitation zones. The main constituent that reacts with carbon is chromium but in high carbon activities more Fe and Ni can participate in the reaction. As carburization progresses, cracking of the interior wall of the cracker (furnace) is resulted and failure occurs as a result of cooling when the component is shutdown (thermal cycling).

Carburization is observed in the industrial furnaces for steel heat treatments and in the reformer tubes in steam reforming of natural gas. Rahmel et al [31] mentioned that in the temperature range between 800-1000°C, the diffusion of carbon-bearing molecules through pores and channels of cracks on the oxide layer is negligible, if a tight adherent oxide layer is formed on the alloy.

To have a more realistic diagnosis of the industrial carburization, Lopez-Lopez et al [32] studied failed components (tubes) from residual oil-fired boilers operating in electric power plants. A carburization process is noticed at the superheater and reheater boiler zones as well as normal fireside-corrosion to contribute to material degradation on the external surface of the tubes. They noticed also that when carbon diffuses into the steel matrix it forms $M_{23}C_6$ precipitates, which may cause hardening of the steel.

It is recommended to add Cr up to 30% and Ni to at least 35% to improve the carburization resistance [33], since the solubility of carbon in nickel is very low and the inability of Ni to form stable carbides. Harrison et al [33] mentioned that the prior cold working and surface finish of the specimen may influence the rate of carburization. They detected, also, that the carbide formed at the surface of a Fe-Cr alloy would be $Cr_4Fe_3C_3$.

Moreover, Grabke et al [22] recommended increasing Cr-content in order to improve the ability of the material to resist metal dusting, i.e. $a_c>1$ (severe form of carburization where the carbon activity in the environment exceeds unity). Also, surface finish will allow (Cr, Mn, Si, etc.) to diffuse outwardly to form layers that ingress carburization. In contrast, etching specimens without any surface deformation does not enhance the Cr diffusion outwardly because there is not much diffusion paths, and protective layer cannot be formed at intermediate temperatures.

In high temperature applications, creep becomes the most important property of the material and in carburization, creep resistance increases with the fine precipitate formed at the grain boundaries. In a situation where excess carburization or large amount of carbides is formed, the creep resistance decreases, thus the time to rupture decreases (in case of small carbides precipitating into grain boundaries the creep resistance of the alloy increases). Grabke and Wolf [17] noticed that the addition of Nb will improve the creep resistance and ductility because of the formation of NbC that precipitate into the matrix of the material and cause the resistance of the material to improve (because these precipitates will prevent grain boundary sliding at high temperatures).

2.3 MIXED OXIDATION/CARBURIZATION

2.3.1 General

Giggins and Pettit [34] conducted a comprehensive study to understand the behavior and mechanism of attack of pure Ni, Fe, Co and alloys of these metals containing Cr and Al at different concentrations. They exposed these alloys to mixed gases containing carbon-oxygen, sulfur-oxygen, nitrogen-oxygen at temperatures of 600 and 900°C. Upon exposure to carburizing/oxidizing environment, they indicate that 15 wt% Cr at these conditions is not adequate to form a continuous layer of Cr_2O_3 and protect the substrate during exposure in CO_2 gas. On the other hand, alloying alloy Fe-15Cr with only 4wt% Al showed a great protection in C-containing environments since a layer of Al_2O_3 was formed during oxidation, which prevents the carbon induced effects from penetrating the alloy.

To measure the carbon penetration through chromia (Cr_2O_3) layer, Wolf et al [2] and Demel et al [35] performed a study to characterize the porosity of the oxide scale. A radioactive tracer (C^{14}) method was used to determine the distribution of carbon after exposing preoxidized samples into an H_2-H_2O-CO-CO_2 atmosphere. They observed that carbon up-take into different Fe-Cr alloys decreased with increasing Cr content to a minimum amount of 12.5-20%Cr. This amount was enough to form an adherent Cr_2O_3 layer with low porosity. They observed, also, that porosity increases with increasing Cr content of more than 20% of the alloy.

For the research on ternary alloys, Perkins and Goldberg [36] exposed some Fe-Cr-Ni and Ni-Cr-Al alloys in CH_4/H_2 and CO/CO_2 atmospheres at various temperatures up to 900°C. They studied the formation and deterioration of oxide films with various preoxidation treatments. It has been found that Fe-Cr-Ni-C alloys exposed to high temperature carbonaceous gases will develop three distinct layers: (1) Cr_2O_3 layer "predominant", (2) sublayer of oxides and/or carbides, and (3) region of general and/or grain boundary carbide precipitation in the base alloy. When the temperature increases the thickness of theses layers increases. Carbon penetration of the alloy cannot be eliminated by preoxidation, but at best reduced. In both preoxidized and bare alloys the carbon attack increases with rougher surfaces. At the studied conditions, the NiO layer decomposes with further exposure to carbon-rich environment while Al_2O_3 was not affected, despite the fact that its content in the alloy was not sufficient to form a completely protective film.

In the case of commercially used alloys, Norton et al [10] studied the effect of a very complex gas environment on the behavior of 310 stainless steel, where the environment can be described as oxidizing/carburizing/sulfidizing simultaneously. They maintained the oxygen partial pressure to be $P_{O_2}=10^{-26}$ bar and the carbon activity at $a_c=0.2$ but altering the percent of H_2S gas from 0.4-1%. The samples were exposed at 600°C for 1000 hrs at different percentages of H_2S to investigate whether rapid sulfidation or protective oxidation kinetics will ensue. They observed that at low H_2S gas mixture, oxidation dominates the reaction kinetics, even though sulfur managed to penetrate through the surface. But at high sulfur atmospheres, preoxidizing the samples did not improve the protection of the alloy against sulfur attack.

The influence of Si and Al on the behavior of Fe-based alloys was investigated by Liu and Chang [7] who exposed two experimentally prepared austenitic Fe-Mn-Al alloys, where the differences are in the Si contents; one alloy contains 1.27%Si and the other contains no Si. They exposed them in an atmosphere containing 50%CO+50%Ar for 5 hrs, at temperature ranging between 900-1070°C. They found that at the specified temperature range and carbon monoxide atmosphere, internal oxides mixture of $MnAl_2O_4$ and Al_2O_3 is present with internal perovskite carbide having a formula $(Fe,Mn)_3AlC_{0.5}$. The oxidation and carburization reactions occur in the following sequence: CO dissociation, transport of O and C atoms, internal oxidation of Al (selective oxidation) and Mn, then carbide formation and decomposition.

In the case of low oxygen and high carbon activities, protective oxides cannot be formed. A preoxidation experiment was done to examine whether the oxide layer formed is protective or not when exposed to carburizing conditions. Samples of alloy 800 were oxidized in air for 2 hrs, at 1255°K and a dense and adherent Cr_2O_3 scale was formed on the surface. Once it is exposed to a low oxygen activity in an $Ar\text{-}10CH_4$ atmosphere for 48 hrs, at 1123°K, there were a conversion process of the oxide to Cr_7C_3 and heavy internal carburization occurred. If the equilibrium oxygen partial pressure in the carburizing gas was above that required to form the Cr_2O_3 layer, the layer will be maintained on the surface. [18]

For the protectiveness of Cr_2O_3, Agarwal et al [37] stated that the protective layer of Cr_2O_3 is not useful at temperatures around 950°C since Cr_2O_3 is liberated at this temperature. Also, the addition of rare earths will reduce the cracking and spalling of the protective oxide layer.

2.3.2 Thermodynamics

Hemmings and Perkins [38] conducted a theoretical thermodynamic study of alloys exposed to mixed environment; to find all possible reactions and products in different cases. This is done because industrial environments could be oxidizing, carburizing, sulfidizing, nitriding or mixture of more than one of these. At the beginning, potentials of the gas mixtures were calculated and then the relative thermodynamic stabilities of all possible metal oxides, carbides or sulfides were established at these potentials. Then, identification of the phases that would be in stable equilibrium with the gas was made and the relative reactivity of the alloy under the specified conditions was estimated. This led to the establishment of stability diagrams, which show the possible products of certain metal exposed to mixed environment at specified temperatures where the potentials of the gases present govern the products. At specific partial pressures of mixed reactive gas species the identification of all reaction products is possible.

In the mixed environment where two or more gases are present, a possible dissociation of the components to formation of new chemical species will introduce new reaction sites, but since these species will be present in low concentrations, they can be disregarded as possible reactions.

As a practical example, in steam reforming gas, the dominant mode of corrosion is internal and surface oxidation. Quadakkers [39] depicted that Ti has the largest influence on the corrosion rate. Also, at high temperatures carbon can react with Cr_2O_3 according to the reaction:

$$3C + Cr_2O_3 = 3CO + 2Cr \qquad (14)$$

leading to decarburization and destruction of the oxide scale. The author [39] stated that decarburization of the scale is a phenomenon, which occurs only in atmosphere with very low H_2O levels; fortunately this is not the case in steam reforming atmospheres, since H_2O is present at high levels which prevents carburization and decarburization from occurring.

In a thermodynamic study of the behavior of alloys in an environment containing more than one reactant, Meier et al [40] concluded that in mixed environments it is less favorable to develop a selective oxide barrier than in pure oxygen. The reason is that in the mixed environment the formation of products of the second reactant often has adverse effects on the development of selective oxidation barrier. However, they commented that the use of the two-dimensional stability diagrams is restricted to the assumption that the corrosion products are insoluble in one another; otherwise a three-dimensional graph should be used for each pair of constituents.

2.3.3 Kinetics

In the absence of an oxide layer, Perkins [18] stated that the rate of carburization is controlled by the diffusion of carbon into the alloy and the difference in concentration between the alloy and carbon content on the surface. If an oxide scale is present at the surface of an alloy it restricts the carburization process, thus control its rate. However, in the absence of a surface oxide the diffusion and precipitation processes are the rate controlling of the carburization reactions provided that surface reactions are sufficiently high. [38]

If a protective oxide layer is present, carbon atom should diffuse through pores or cracks of the oxide layer to reach the oxide/metal interface. However, it is not possible for carbon to penetrate or permeate through the oxides themselves since the solubility of carbon in oxides is very low. Grabke and Wolf [17] stated that diffusion of carbon into the matrix will control the carburization reactions, whether or not a non-protective oxide is present and a parabolic law is valid for the mass increase which is given by:

$$\left(\frac{\Delta m}{A}\right)^2 = 2kt \qquad (15)$$

Where: Δm: the change in mass with exposure; A: area; t: time; and k: parabolic rate constant.

In the case of complex alloys kinetics, Tjokro et al [41] performed experiments on some commercial alloys under carburization and cyclic carburization/oxidation conditions (4 hrs carburization and 2 hrs oxidation). They found that a parabolic rate of growth is observed which follows: $x^2 = 2k_p.t$ for carburization, and a parabolic growth rate in the cyclic carburization-oxidation in the form: $x^2 = 2k_p.t + c$. They noticed that while changing the conditions from carburization to oxidation, the carbon, which is deposited on the surface, would penetrate till the external carbide scale is consumed by oxidation. Also, the previously formed Cr_7C_3 may dissociate to form $Cr_{23}C_6 + C$, where this carbon will precipitate through grain boundaries to from internal carbides.

Removal of the material is observed in the case of mixed oxidants, like in the case of oxygen and carbon. The steps involved in the carbon transport are: (1) carbon is adsorbed on the alloy surface, and (2) carbon diffuses inwardly through bulk material or grain boundaries. In order to control the carburization reaction, blocking carbon from entering the alloy from the surface would be the best way by forming a stable and continuous oxide layer. because carbon will continue to diffuse whenever there is a difference in concentration between the metal and the environment.

In the presence of perfect and dense oxides, no detectable solubility of carbon is observed; oxides like FeO, Fe_3O_4, MnO, or Cr_2O_3 will not permeate carbon through them. If carbon succeeds in penetrating through any of the oxides, this is an indication of the presence of pores, microchannels or fissures.

Wolf et al [2] gave three mechanisms of the pores and microchannels formation:

1. Dissociation of the scale, especially at grain boundaries
2. Imperfect joining of the growing crystals
3. In thickening the scale, the growth stress will crack the layer.

2.4 PROPOSED SOLUTIONS

J. Stringer [42] believed that failure of industrial components used at high temperatures is due to the departure in the process form normal conditions, which drives the system to work beyond its limitations. Failure analysis is an important factor of the development and understanding of any process and failed components should be studied immediately before loosing much of their values. He summarized the methods of improving the high temperature corrosion resistance in industrial applications as follows:

1. Using more resistance alloys,
2. Using protective coatings,
3. Modifying the process conditions to make it less harmful,
4. Modifying the design to move the parts which are susceptible to corrosion to a less demanding location,
5. Improve the life prediction methods.

Also, it is commonly believed that inhibiting surface catalysts to reduce the surface concentration and adsorption of carbon will help in combating carburization. Inhibition can be performed either by injecting sulfur in a gaseous phase or by using it in alloying, thus controlling the carburization process. If surface inhibition is not possible, pre-oxidation may produce some protection, provided that O activity is sufficient to prevent the reduction of the oxide layer (conversion from oxides to carbides). Also, balancing Ni:Fe ratio in the alloy can be used to reduce the carbon diffusivity in the alloy, (4:1 shows to be the optimum). Also, adding 3%Si may retard carburization by forming an oxide layer. [18]

When the protective Cr_2O_3 layer converts into non-protective carbides (when $a_c=1$ and temperature >1050-1100°C), severe failure may occur. When carbon activity is unity ($a_c=1$), Al_2O_3 or SiO_2 produce good protection to carburization and they may form an inner layer beneath Cr_2O_3 layer.

CHAPTER 3

EXPERIMENTAL WORK

3.1 EXPERIMENTAL PROCEDURE

Table (3.1) shows the chemical compositions of the two alloys under study. Both alloys were precipitates-free and consist of single phases in the as received condition. Before exposure to test conditions, samples were cut from 3-4 mm thick sheets into approximately 20X20 mm coupons. These coupons were cleaned by Acetone to remove any contamination and then dried.

Typical exposure conditions for the conducted tests are shown in Table (3.2). In each case the corresponding partial pressure of oxygen and carbon activity are calculated. In carburizing conditions a commercial methane-hydrogen gas mixture is used with a level of oxygen impurity of approximately 100 ppm (parts per million).

Test specimens were isothermally exposed for different durations (max. of 500hrs) to the conditions shown in Table (3.2). Measurements of the weight gain after each test run were taken using a sensitive microbalance. Then, these weight measurements were plotted versus the duration of each test. After that, selected samples of both alloys were examined and analyzed using Scanning Electron Microscope (SEM) and X Ray-Diffraction techniques to view the morphologies, determine the elemental distribution and identify the present phases.

TABLE (3.1): Composition of Alloys used in this investigation

Materials	Ni	Fe	Cr	Al+Y	Si	Mg	C	Ti	Cu	Mn	S
Haynes 214	75	3	16	4.5	0.2	—	0.05	—	—	0.5	—
Incoloy 803	32-37	Bal.	25-29	0.15-0.6	max. 1	max. 1.5	0.06-0.1	0.15-0.6	max. 0.75	—	max. 0.015

TABLE (3.2): Typical exposure conditions for the conducted tests

Condition	Oxygen partial pressure(P_{O_2})	Carbon activity(a_c)
Oxidation in air	0.2 (atm.)	No Carbon
2%CH_4-H_2 +Oxygen impurity (100ppm)	1.28×10^{-26} (atm.)	0.226

3.2 WORK PLAN

The aim of the experimental study is to understand the behavior of two alloys, namely Haynes 214 and Incoloy 803, in the following environments: (1) oxidizing, (2) carburizing, and (3) mixed oxidizing/carburizing. Specifically, each of these environments will be simulated in the lab, where specimens will be exposed isothermally for periods up to 500 hrs before conducting extensive microstructural analyses. All experiments will be conducted at 800°C under flowing gas mixture. This temperature was selected since it represents a typical temperature of most industrial operations in chemical and petrochemical industries.

3.2.1 Oxidation Experiments

In these experiments samples are exposed at 800°C in air for different time periods isothermally, and then analyzed using the analytical equipments. Exposure includes initial stages and long exposure to develop steady-state conditions.

3.2.2 Carburization Experiments

In these experiments samples were exposed at 800°C in a mixture of $2\%CH_4$-H_2 for different time periods isothermally, and then the samples were analyzed using the analytical equipments. Exposure includes initial stages for periods ranging from 6 hours up to 500 hrs.

3.2.3 Mixed Oxidation/Carburization Experiments

At this stage of the experiments, samples were exposed at 800°C in a mixture of 2%CH_4-H_2, with Argon gas bubbled in distilled H_2O to control the oxygen potential, and then admitting it to the samples for different time periods isothermally. After that, samples were analyzed using various analytical equipments. Exposure includes initial stages for 6 hours and long exposure (500 hrs) to develop steady-state conditions.

3.2.4 Analytical Facilities

Thermogravimetric data will be obtained by measuring the exposed specimens' weight gains following each run of exposure by using an accurate microbalance. Microstructural characterization will be conducted using SEM, EDAX, XRD and X-Ray Mapping. These equipments are available in Materials Science Laboratory in Mechanical Engineering departments, Material Characterization Laboratory (MCL) of Research Institute (RI) and Chemistry department.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 THERMODYNAMIC ANALYSIS

One of the tasks in studying the thermodynamics of high temperature corrosion is to produce stability diagrams. These diagrams can be generated for each metal at specific temperatures. From these stability diagrams, one can predict the formation of certain phases when a metal or alloy is exposed to an environment containing different reactive gas species, i.e. oxidizing and carburizing environment. In figures (4.1 (a-f)), prediction of phases is possible by knowing the partial pressure of oxygen and carbon activity in the environment. All of these diagrams were generated at the exposure temperature of 800°C. A new complete stability diagram for all metals (ingredients of alloys under investigation) was produced in this thermodynamic study figure (4.1f).

From the complete stability diagram (figure (4.1f)) the dissociation pressure of various oxides (expected to form following exposure to air at 800°C) can be calculated. Table (4.1) lists the values of the dissociation pressures of the oxides and based on the case of oxidation in air, where the oxygen partial pressure is higher than the values listed in the table, all types of oxides are expected to form.

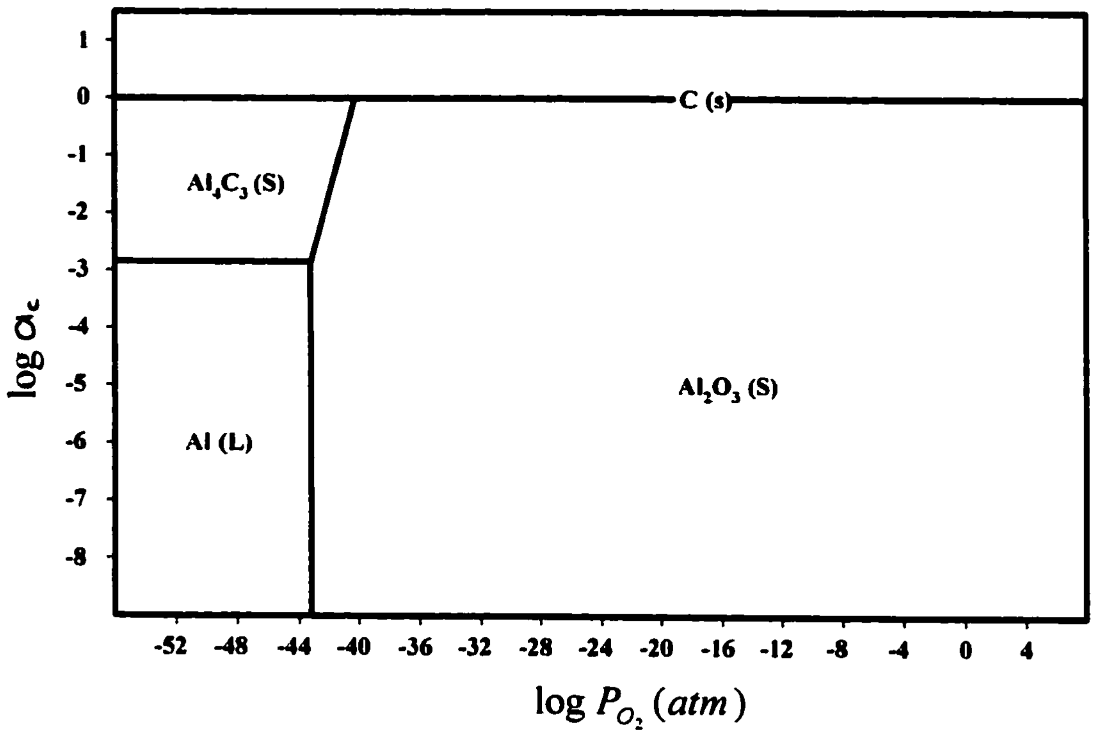


Figure (4.1a): Stability diagram for aluminium at 800°C.

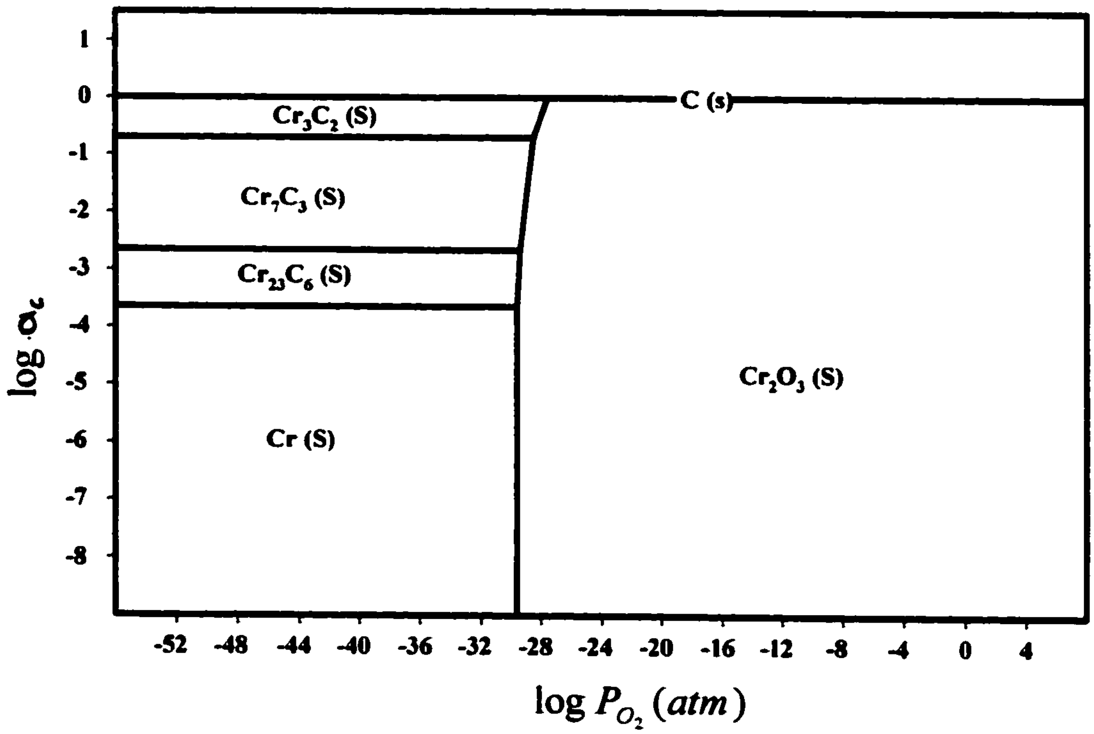


Figure (4.1b): Stability diagram for chromium at 800°C.

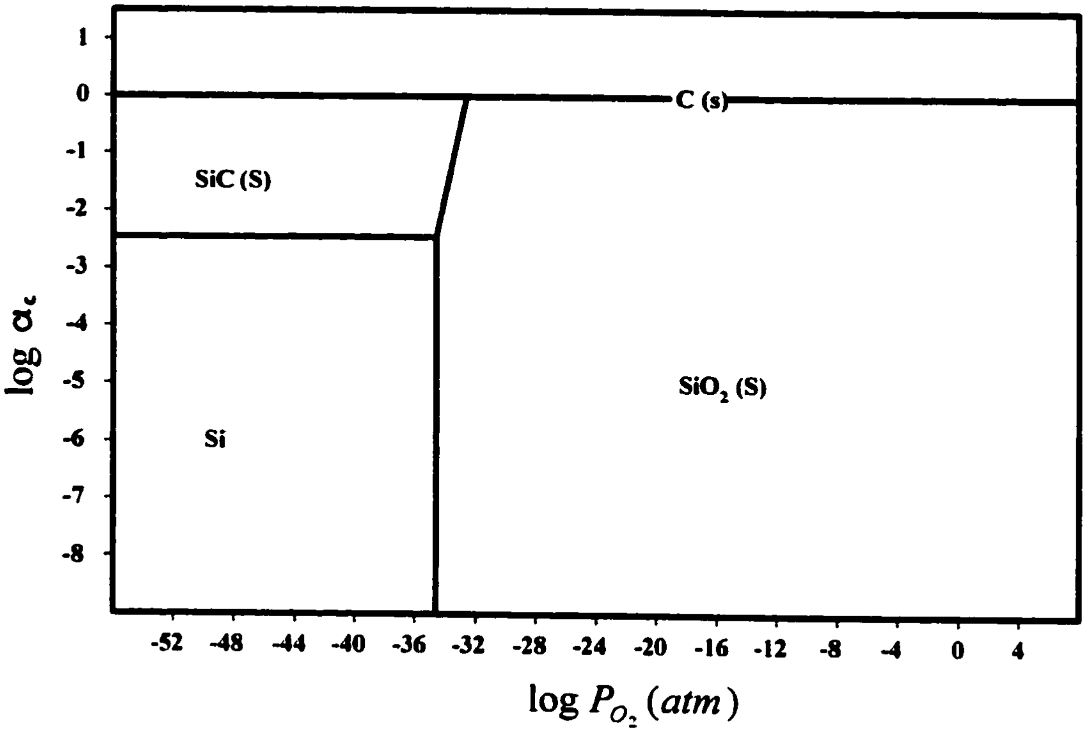


Figure (4.1c): Stability diagram for Silicon at 800°C.

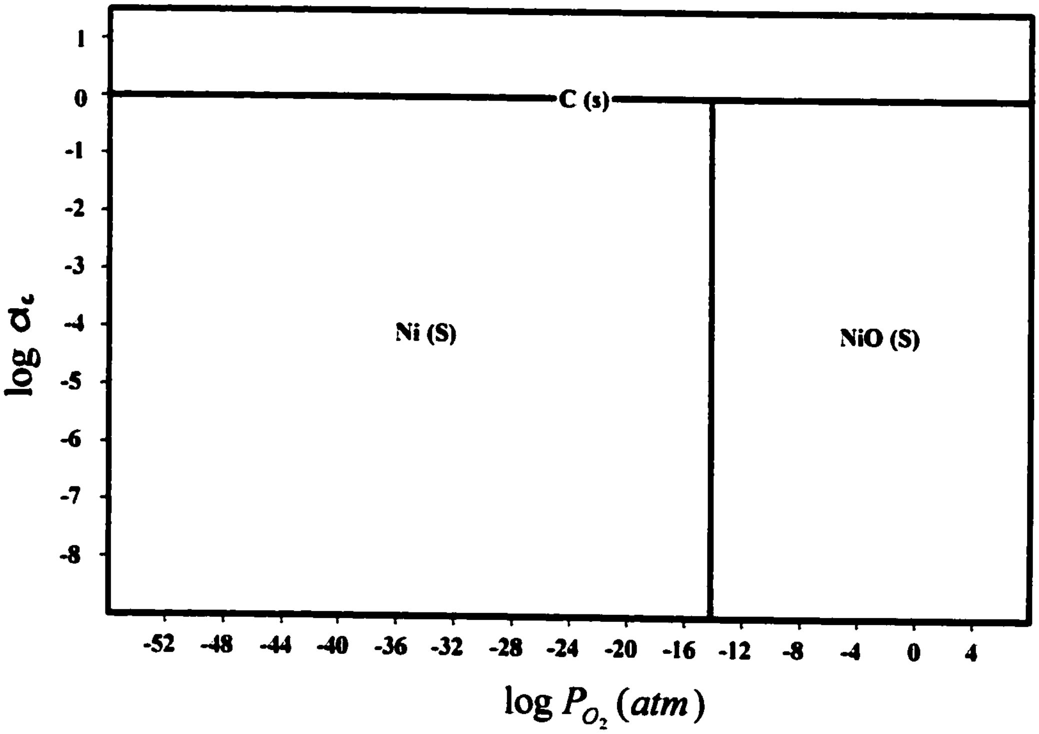


Figure (4.1d): Stability diagram for Nickel at 800°C.

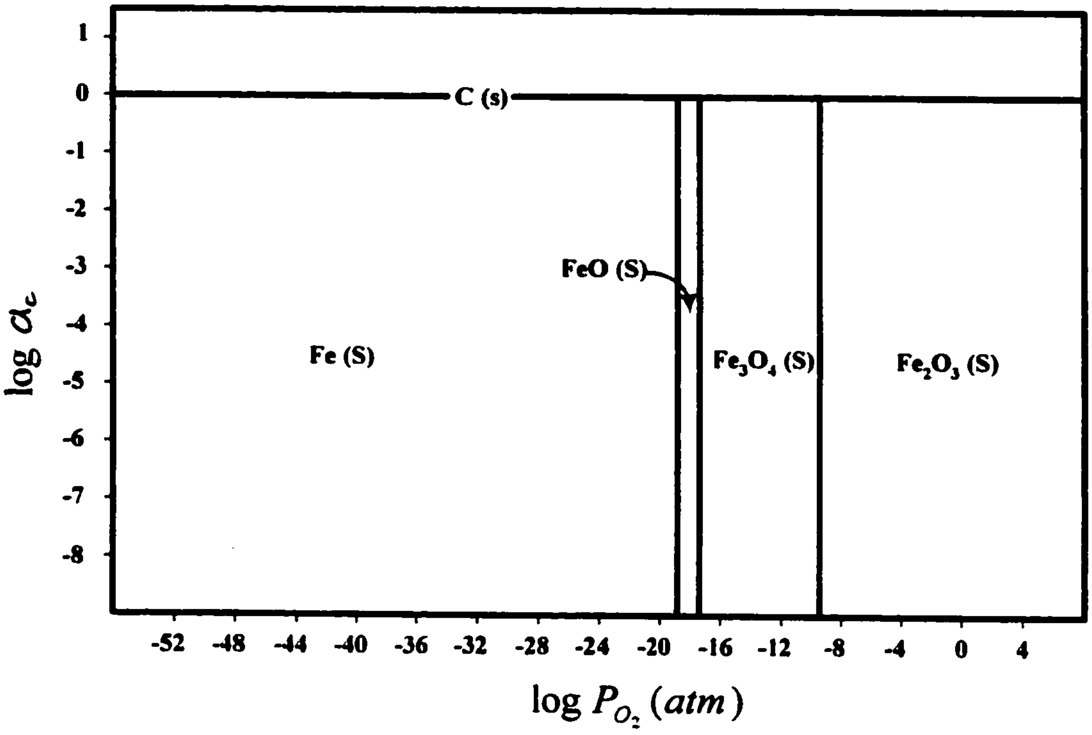


Figure (4.1e): Stability diagram for Iron at 800°C.

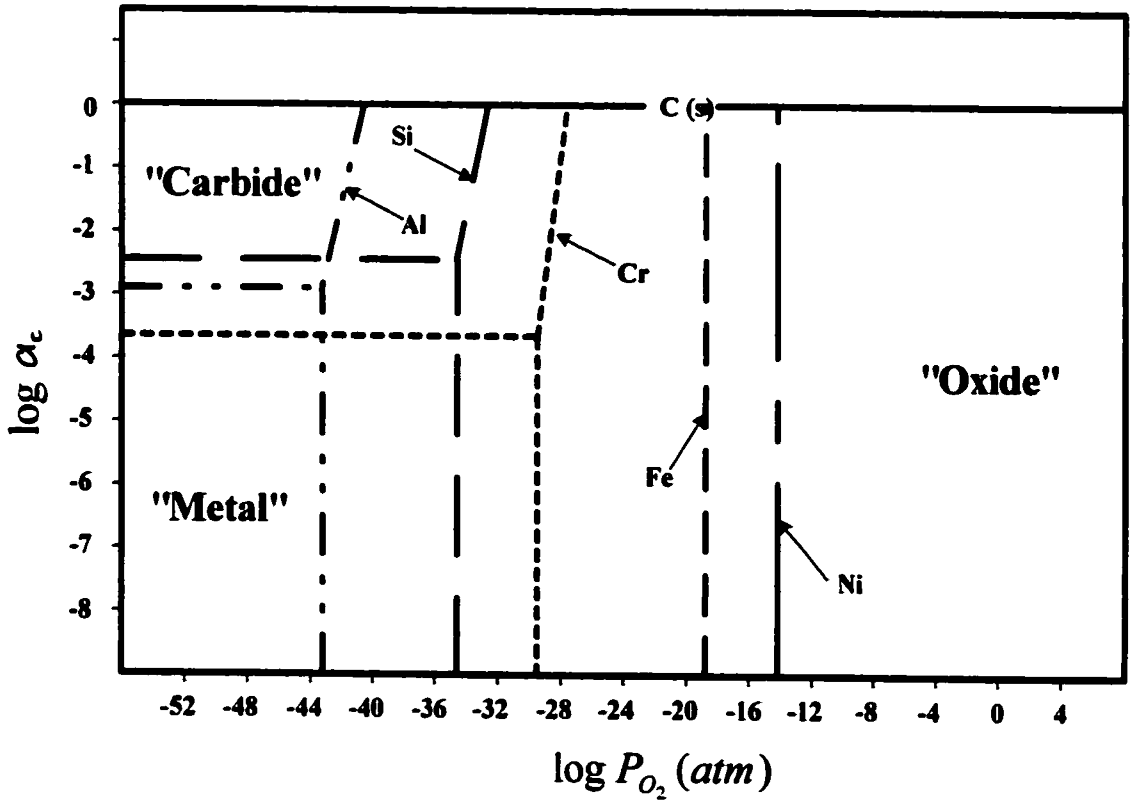


Figure (4.1f): Complete Stability diagram at 800°C.

TABLE (4.1): Dissociation pressures of various oxides

Type of Oxide	NiO	Fe_2O_3	Fe_3O_4	FeO	Cr_2O_3	SiO_2	Al_2O_3
Dissociation Pressure (atm.)	6.87×10^{-15}	2.58×10^{-10}	4.73×10^{-18}	1.1×10^{-19}	1.33×10^{-30}	1.44×10^{-35}	3.9×10^{-44}

4.2 OXIDATION IN AIR

The oxidation rate measurements on two commercial alloys, namely Ni-based Haynes 214 & Fe-based Incoloy 803 were carried out at 800°C. The primary differences between the two alloys are in the Al and Cr contents. Prepared coupons of these alloys were exposed in static air at a specified temperature under 1 atm pressure.

Typical oxidation curves for these alloys were obtained from weight gain versus exposure duration measurements. The oxidation experiments were performed under both cyclic and isothermal conditions (figures 4.2 and 4.3) to show the differences between the two exposure conditions. The figures show that there was no difference in the oxidation behavior of the studied alloys under both cyclic and isothermal conditions. This is primarily due to the absence of spallation (falling) under cyclic condition. The maximum duration was 500 hrs for both tests, which is relatively short to show the deviation between the collected cyclic and isothermal oxidation data. The effect of the heating method will be significant for long exposures, especially when spallation of the oxide layer occur during thermal cycling. The spallation of the oxide scale would be due to the difference in the thermal expansion coefficients between the oxide scale and the base metal underneath [16].

On the other hand, the corrosion products for each alloy can be predicted by conducting thermodynamic analyses. The prediction of these products depends mainly on the test temperature as well as the partial pressure of oxygen into the environment. However, the thermodynamic analysis is not enough to assure the formation of the

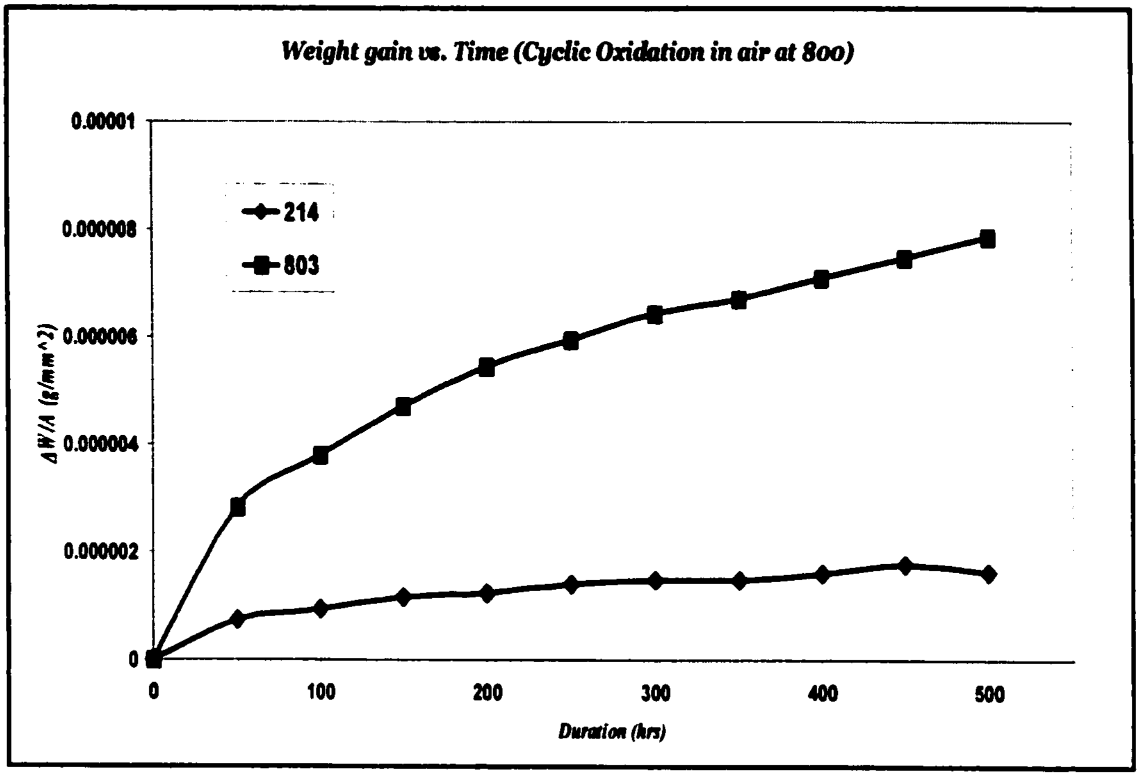


Figure (4.2): Weight gain against exposure time for cyclic oxidation in air at 800°C.

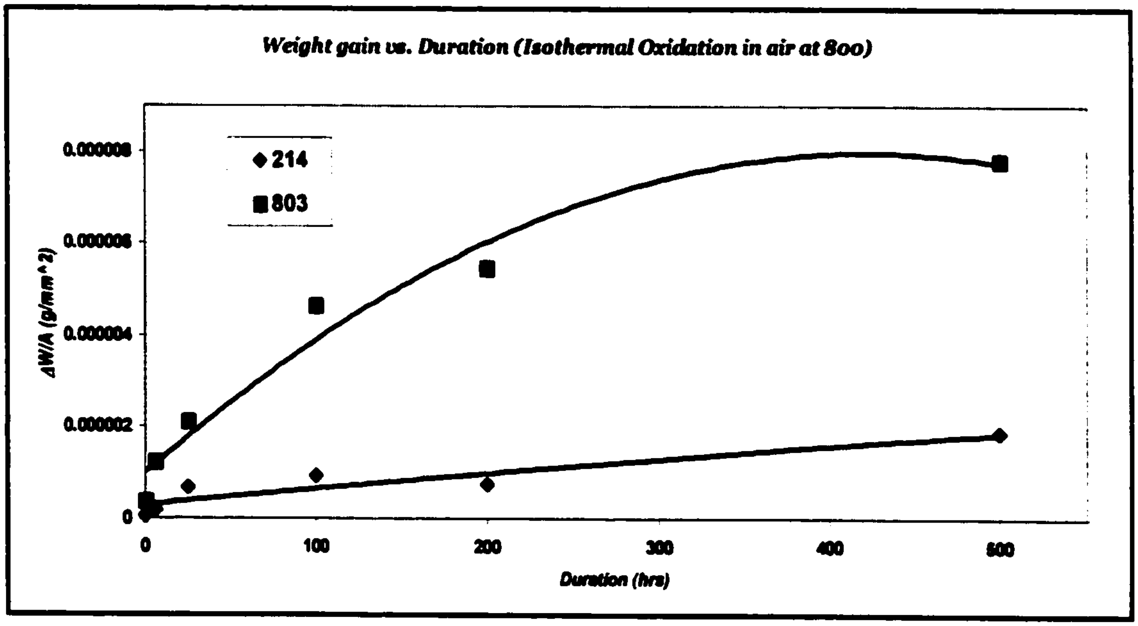


Figure (4.3): Weight gain against exposure time for Isothermal oxidation in air at 800°C.

predicted phases. So, experimental results are important for confirmation of the predictions of the thermodynamic study. Since the partial pressure of oxygen is very high in the test environment, it is very possible from stability diagrams to form all types of oxides of the alloy constituents. The formation of all types of oxides is only true during the initial stages of the oxidation process, where alloy constituents can diffuse freely to the surface to meet oxygen and react with it to form nuclei of different oxides. These oxides differ in thermodynamic stabilities, i.e. oxides of Fe & Ni are less stable than oxides of solutes (Cr, Al, Si etc.) [13]. Then, the more stable oxide will dominate at the surface of the alloy forming and external oxide layer; provided that there should be enough amount of that constituents in the alloy matrix. Once the more stable oxide forms a continuous and adherent layer at the gas/metal interface, it will undercut any further transport of the less stable oxides' formers. If the amount of this constituent is low in the alloy, then internal oxidation is expected to occur.

4.2.1 Ni-Based Alloy (Haynes 214)

From the generated plots for the oxidation rate of this particular alloy, it is clear that the oxidation rate decreases with time. This indicates that the oxide scales formed at the surface of this alloy have protective properties. Alumina (Al_2O_3)is known to be an n-type oxide, i.e. grows by the inward diffusion of oxygen through anion vacancies. It has been well established that Al_2O_3 growth primarily by the inward diffusion of oxygen along oxide grain boundaries. The degree of protection of the oxide layer depends mainly on the continuity and adhesion of the layer, i.e. the more the imperfections and discontinuities present into the scale the more diffusion paths available for other constituents to react with oxygen.

Since oxidation experiments were conducted in air, and this alloy contains a relatively high amount of Al ($\cong$4-4.5wt%), the formation of continuous and external Al_2O_3 layer is fast. This Al_2O_3 layer will seal the surface and blocks the way for other metal constituents to travel to the surface and react with more oxygen to form their own oxides. Also, this alloy contains high amount of Cr which will help and maintaining the Al_2O_3 layer by acting like an oxygen getter [20]. At the beginning of exposure, Cr was able to form chromium oxide islands on the substrate because the growth rate of Cr_2O_3 is more than Al_2O_3. However, the growth of Cr_2O_3 islands is possible till continuous Al_2O_3 is formed, which will prevent oxygen and Cr penetrations to form Cr_2O_3 layer. Once the Al_2O_3 dominates on the surface, the only possible oxidation process is the thickening of the Al_2O_3 layer.

Figures (4.4 and 4.5) show surface and cross-sectional views of specimens following exposure for 100 hrs in air, respectively. They show the formation of oxide islands at the gas/metal interface and a continuous scale at the cross-section. It is clear from the X-ray mapping pictures (figure 4.6) that the dominating scale is Al_2O_3. Other types of oxides were observed like: Si and Ti but in very minute quantities. This is mainly due to the low concentrations of these alloying elements, which is not enough to form continuous layers. No considerable thickening of the Al_2O_3 layer was observed in testing samples exposed to 500 hours (figure 4.7), since diffusion rate across Al_2O_3 is extremely low. However, lateral growth of the scale is relatively fast. In this Ni-base alloy $NiAl_2O_4$ might not be expected to form since the formation of that oxide is very strict [2].

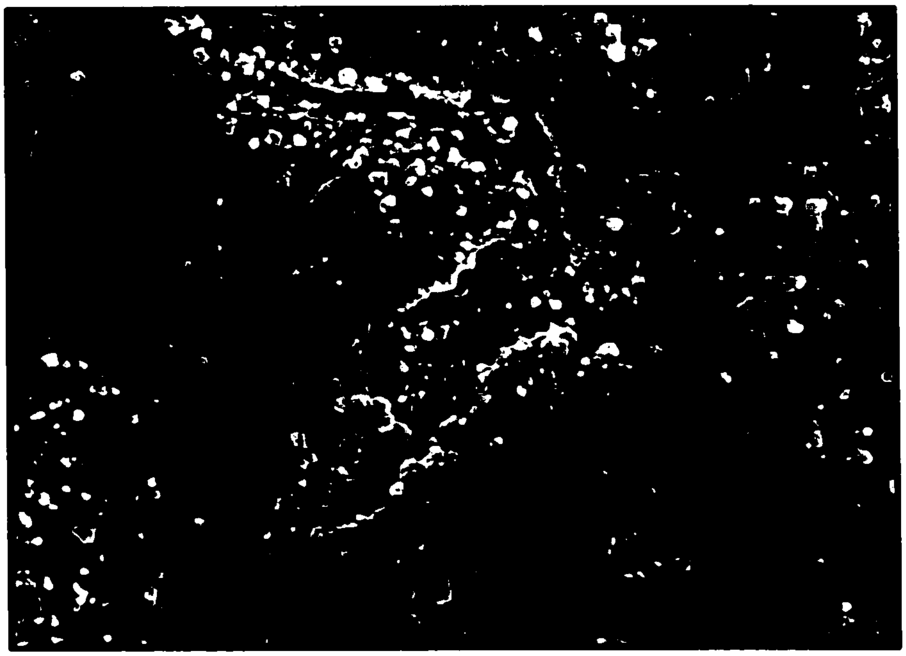


Figure (4.4): Surface morphology of Haynes 214 after 100 hours of exposure in air at 800°C.

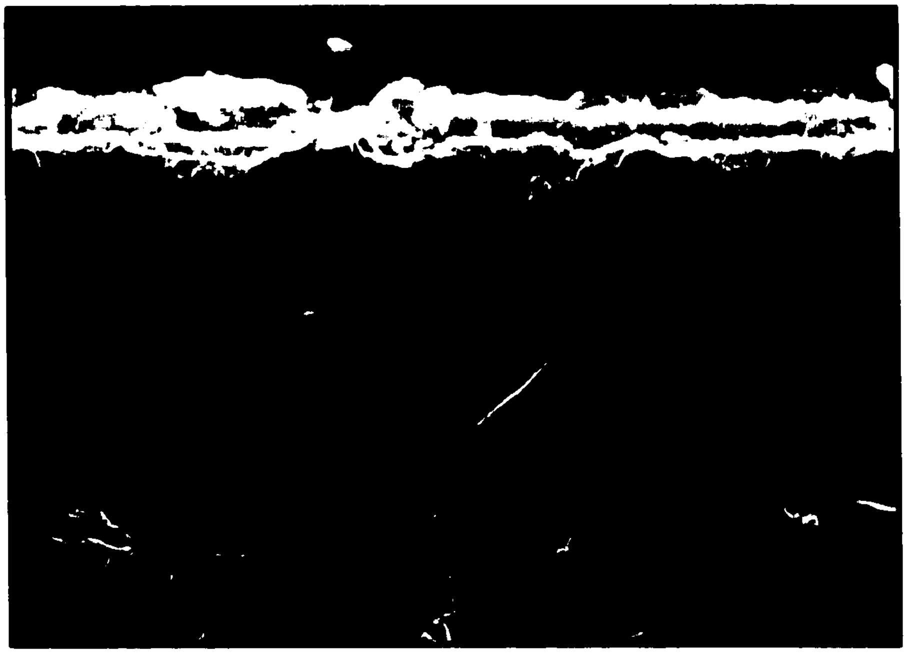


Figure (4.5): Cross-sectional morphology of Haynes 214 after 100 hours of exposure in air at 800°C.

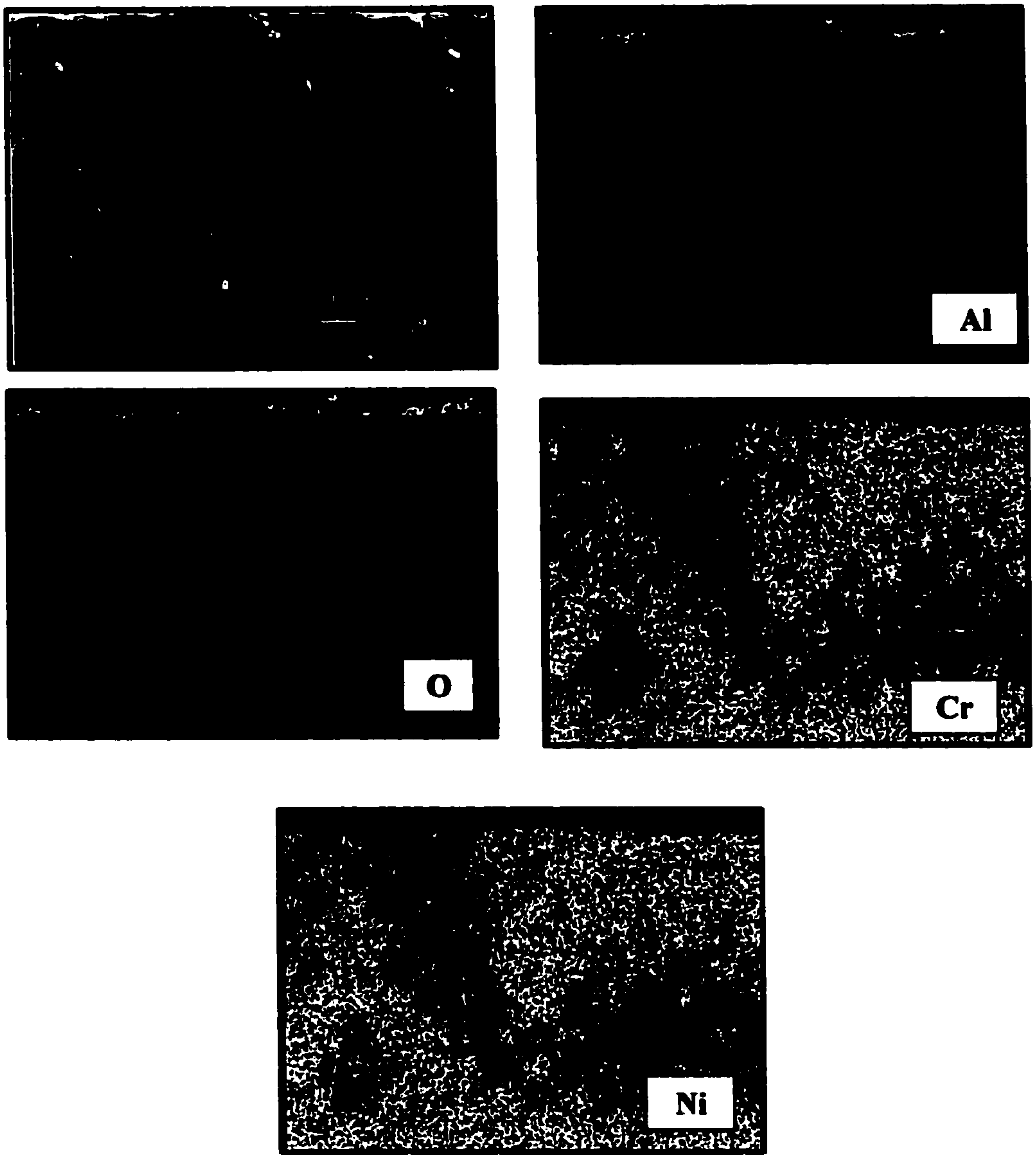


Figure (4.6): X-Ray mapping for Haynes 214 oxidized in air for 100 hours

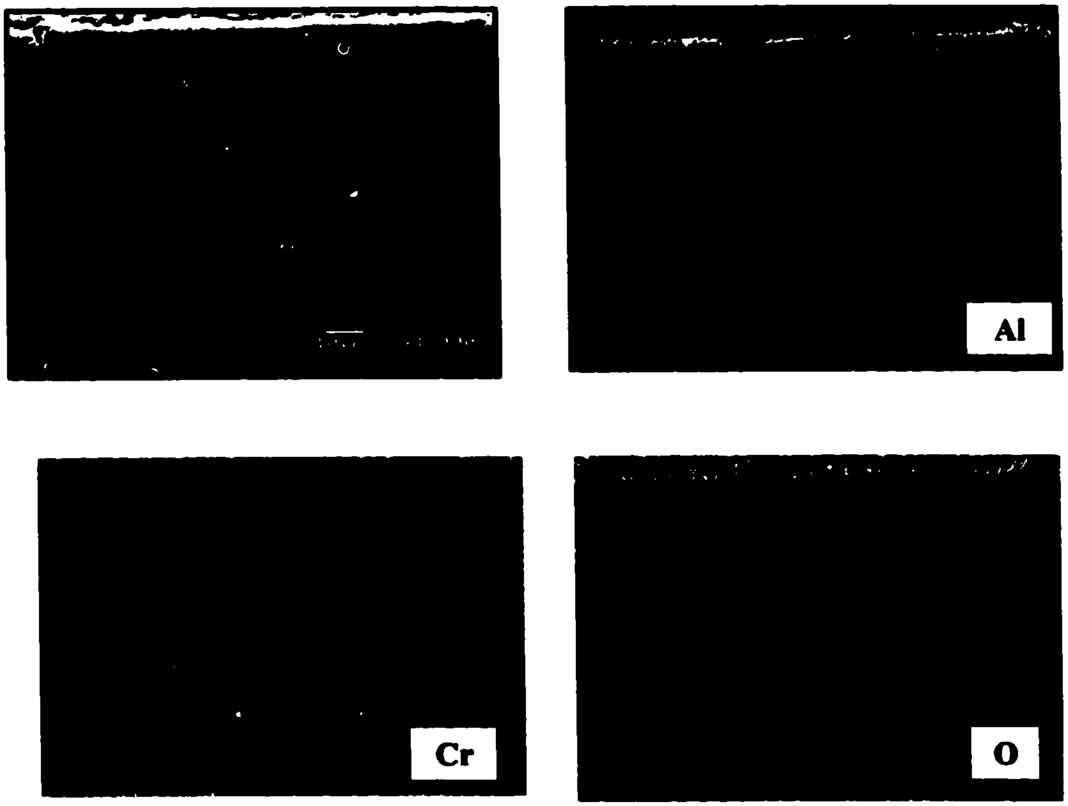


Figure (4.7): Al_2O_3 protective layer at Haynes 214, exposed for 500 hours in air.

4.2.2 Fe-Based Alloy (Incoloy 803)

In this investigation the oxidation rate of this alloy was more than the previous one (Haynes 214). This is due to the formation of a relatively thick corrosion product "oxide scale" as a result of the exposure to the high oxygen partial pressure environment at the test temperature. The major element in forming the oxide in this alloy is Cr. Moreover, the oxidation rate of this alloy is relatively high which indicates that the forming Cr_2O_3 layer was less protective in comparison with Al_2O_3. This alloy contains low amount of Al (0.6 wt% max. with Y) which is not enough to form an external and protective Al_2O_3 oxide layer at the test temperature. By contrast, it contains a high amount of Cr (almost 29 wt%) which is capable of forming continuous Cr_2O_3 layer with subjacent internal discreet particles of Al_2O_3 [4]. The dominating scale in this alloy was Cr_2O_3 which is continuous and thick. Since Cr has faster growth rate than Al to form Cr_2O_3, it will form a dense oxide layer. This explains the increased oxidation rate of this alloy compared with the Al_2O_3 forming alloy Haynes 214. The reason for the faster growth rate of Cr_2O_3 over Al_2O_3 is because of the fact that the former grows by the outward diffusion of chromium while the latter grows by the inward diffusion of oxygen. Chromium diffuses into the scale faster than the diffusion of oxygen.

Surface and cross sectional views of samples exposed to air at 800°C are shown in figures (4.8 and 4.9), respectively. Continuous layer can be observed from the cross sectional view with some cracks and voids along the interface with the metal substrate. Elemental mapping of cross sectional picture (figure 4.10) shows that the dominating layer is Cr_2O_3. This is mainly due to the high Cr-, low Al-contents in the

Figure (4.8): Surface morphology of Incoloy 803 after 100 hours of exposure in air at 800°C.

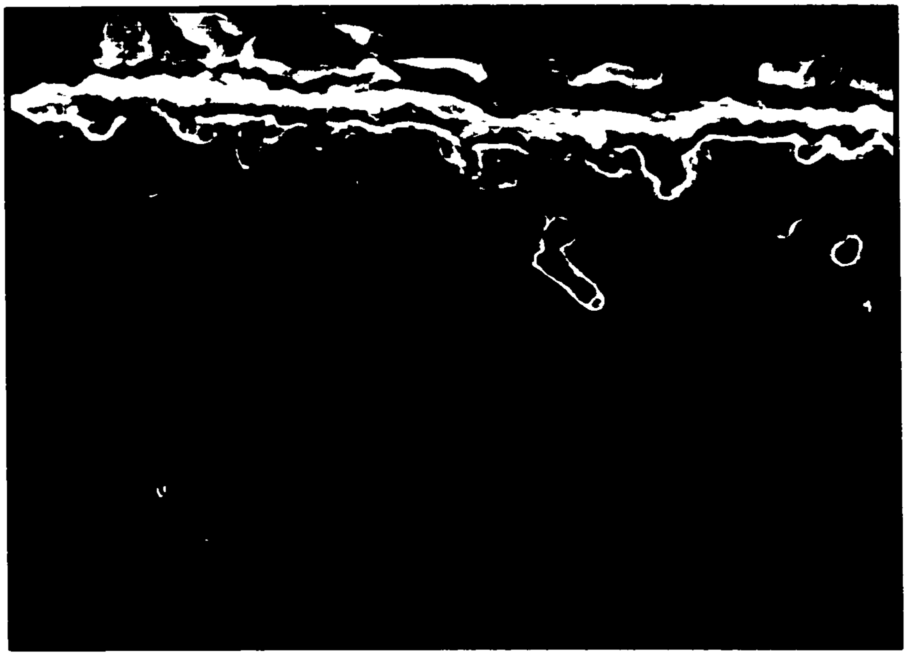


Figure (4.9): Cross-sectional morphology of Incoloy 803 after 100 hours of exposure in air at 800°C.

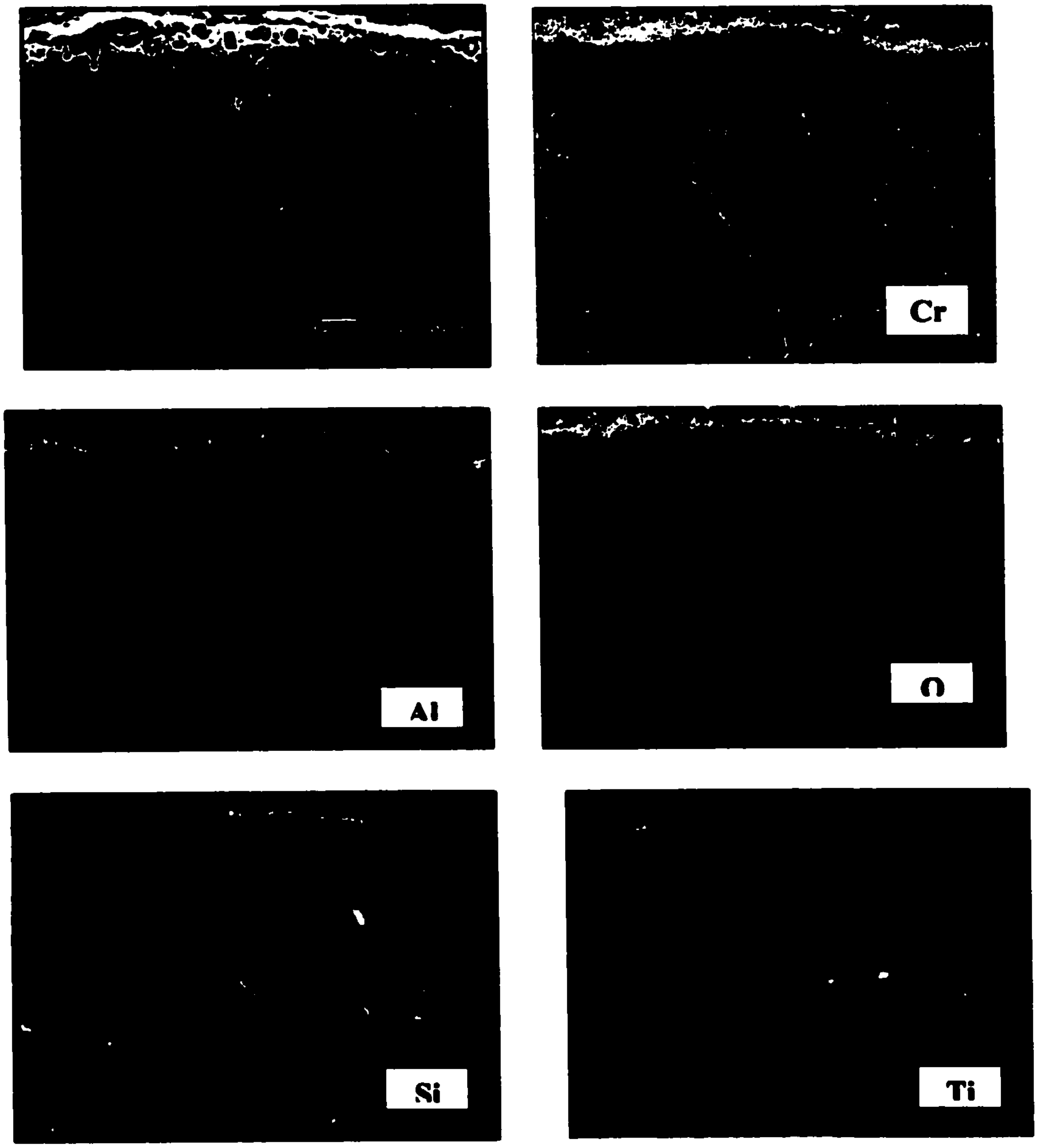


Figure (4.10): X-Ray mapping for Incoloy 803 oxidized in air for 100 hours showing the continuous and external layer of Cr_2O_3.

bulk of the alloy. At the test temperature, Al was unable to form complete external oxide layer, so internal oxidation of Al is observed. It is inappropriate talking about the importance of Al-content in combating oxidation without considering the temperature effect. At higher temperatures Al might be able to form protective and external oxide layer, even though the amount of Al is relatively low [6], due to the fast outward diffusion of small Al atoms into the alloy matrix to form stable oxides.

Trace elements like Ti and Si were able to form internal oxides beneath the Cr_2O_3 layer (figure 4.10) in this alloy. No Cr-depletion zone is observed into this alloy beneath the Cr_2O_3 layer. This is probably due to the high Cr-content in the alloy, which leads to a continuous supply of Cr to the surface. Also, after exposing the alloy to high temperatures Cr tends to segregate to grain boundaries which lead to thickening of grain boundaries, i.e. formation of Cr-rich coarse grain boundary phase.

4.3 CARBURIZATION IN METHANE-HYDROGEN MIXTURE CONTAINING TRACE AMOUNT OF OXYGEN (100 ppm)

4.3.1 Thermodynamics

Carburization attack of metals and alloys is best described by the interaction between carbon species present into the environment with the metal or alloy constituents exposed to high temperatures. It is initiated by the disintegration of carbon atoms (produced by the dissociation of methane molecules at the hot metal surface) from the gas phase to the hot substrate of the exposed metal, and then diffusing inwardly in the metal matrix. Metals or alloys' resistance to carburization depend mainly on the carbon activity in the gas phase, the partial pressure of oxygen in the environment, the total gas pressure, the exposure temperature and the alloy composition [12]. Commercial grade methane (used in this investigation) usually contains trace content of oxygen which plays an important role in the carburization process. Haynes 214 and Incoloy 803 are promising alloys and described to be among the alloys capable of resisting carburization attack, especially Haynes 214 since it contains a relatively high amount of Al that will promote the formation of protective Al_2O_3 layer.

To simulate a carburizing environment a commercial CH_4-H_2 gas mixture was used which contains a trace amount of oxygen to be 100 ppm. Although the level of oxygen impurity in the used commercial gas was 100 ppm, it should decrease to a very low level corresponding to the equilibrium value of (P_{O_2}) determined by Gibbs energy equation (1) for the following reaction:

$$2H_2O \Leftrightarrow 2H_2 + O_2$$

Carbon concentration in the environment can be calculated at the test temperature based on the reaction:

$$CH_4 \Leftrightarrow 2H_2 + C$$

The values of the partial pressure of oxygen and the activity of carbon at the test temperature were shown in Table (3.2). The dissociation pressures of Cr_2O_3, NiO, FeO, SiO_2 and Al_2O_3 at the test temperature were shown in Table (4.1). Moreover, the equilibrium carbon activities for the possible forming carbides (chromium carbides) at the test temperature are shown in Table (4.2).

Comparing the partial pressure of oxygen into the environment with the dissociation pressures of the oxides in table (4.1) leads to the prediction that, from theoretical basis, the oxides of Cr_2O_3, SiO_2 and Al_2O_3 should form and neither NiO nor FeO should form. This is because the value of the oxygen partial pressure in the environment is several order of magnitudes higher than the dissociation pressure of the above oxides (Cr_2O_3, SiO_2 and Al_2O_3). On the other hand, the carbon activity in the environment is also higher than the equilibrium carbon activity of all types of chromium carbides. Therefore, the formation of all chromium carbides will be favorable at the test temperature, due to its higher stability in preference to Al_4C_3.

4.3.2 Kinetic Results

The weight gain measurements versus exposure duration for both alloys Haynes 214 and Incoloy 803 during the isothermal exposure to the 2% CH_4-H_2 commercial gas mixture at a temperature of 800°C is shown in Figure (4.11). By comparing the weight gain results for both alloys, it is noticed that, generally, the weight gain of alloy Haynes 214 is higher than that for Incoloy 803. In terms of rates, it is very difficult at this stage (oxidizing/carburizing case) to specify the rate of the overall reaction. This is due to the lack of knowledge about the rate determining process (slowest process that determines the overall reaction rate). In such complex environments, so many reactions occurring simultaneously, i.e. diffusion of carbon into the alloy matrix, thickening and spreading of carbides as well as formation of internal and external oxides. In case of pure carburization, and in the absence of a protective oxide layer, the rate determining step is the diffusion of carbon into the alloy matrix, while in the oxidation case and in the presence of a protective oxide layer the diffusion through the oxide scale is the rate determining process.

TABLE (4.2): Carbon activity for different carbides

Type of Carbide	Cr_3C_2	Cr_7C_3	$Cr_{23}C_6$	Al_4C_3	SiC
Carbon Activity	0.201625	0.002139	0.000212	0.00168	0.00338

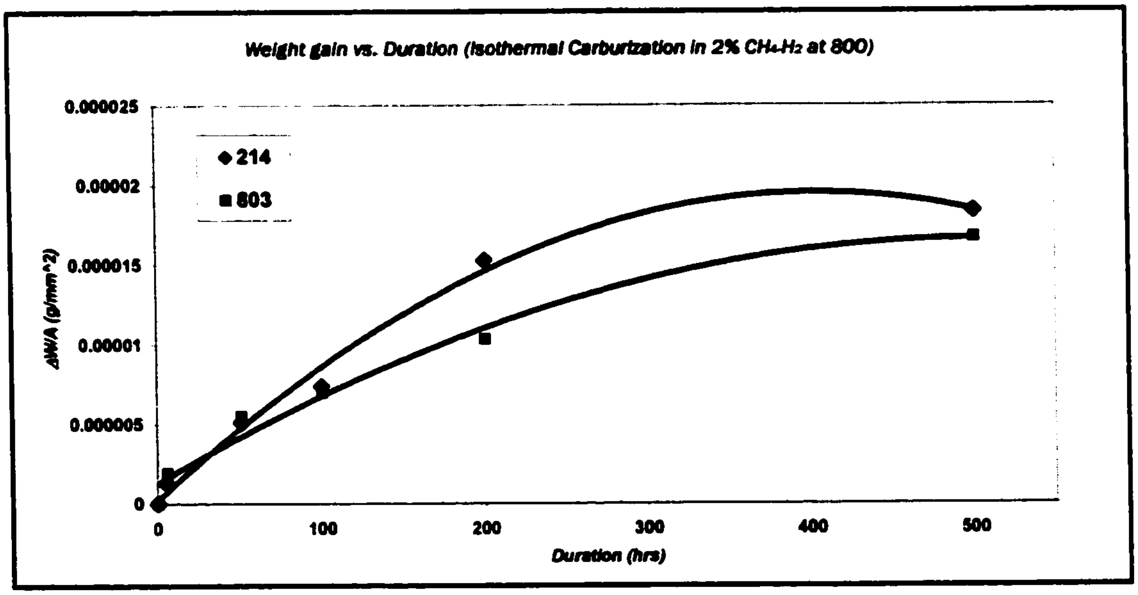


Figure (4.11): Weight gain versus exposure duration after exposing alloys to carburizing environment with trace amount of oxygen.

4.3.3 Microstructural Characterization

4.3.3.1 Ni-Based Alloy (Haynes 214)

Figures (4.12 and 4.13) show the surface and cross-sectional morphologies of the alloy Haynes 214 following exposure to carburizing environment of CH_4-H_2 with oxygen impurity (maximum of 100 ppm) at a temperature of 800°C. As mentioned earlier, the most important feature that governs the behavior of this alloy is the relatively high Al content. This is because of the possible oxidation of Al even though the partial pressure of oxygen in the environment is very low. The oxidation of Al in this particular alloy was internal in the subsurface zone to an approximate thickness of about 8-10 μm. After oxidizing this alloy in air, Al was able to form external Al_2O_3 layer (because of the high oxygen content). However, at low oxygen partial pressure the oxidation of Al becomes internal, while no external Al_2O_3 particle has been observed. The Al ability to form protective and continuous external Al_2O_3 layer at high oxygen partial pressure, highlights the role of oxygen in the environment in combating other modes of high temperature attack. Although the concentration of Al is relatively high in this alloy, it was not enough to promote the formation of external and continuous Al_2O_3 layer at the methane-hydrogen mixture and at a temperature of 800°C.

The oxidation of Al, in this particular alloy, occurs by the inward diffusion of oxygen through the metal as well as the transport of Al from the alloy matrix to the surface through either the bulk of the alloy or grain boundaries. This is shown in the elemental distribution figures (4.14 and 4.15), where Al is clustering along grain boundaries. This is true also at short exposure times (figure (4.16)), where grain

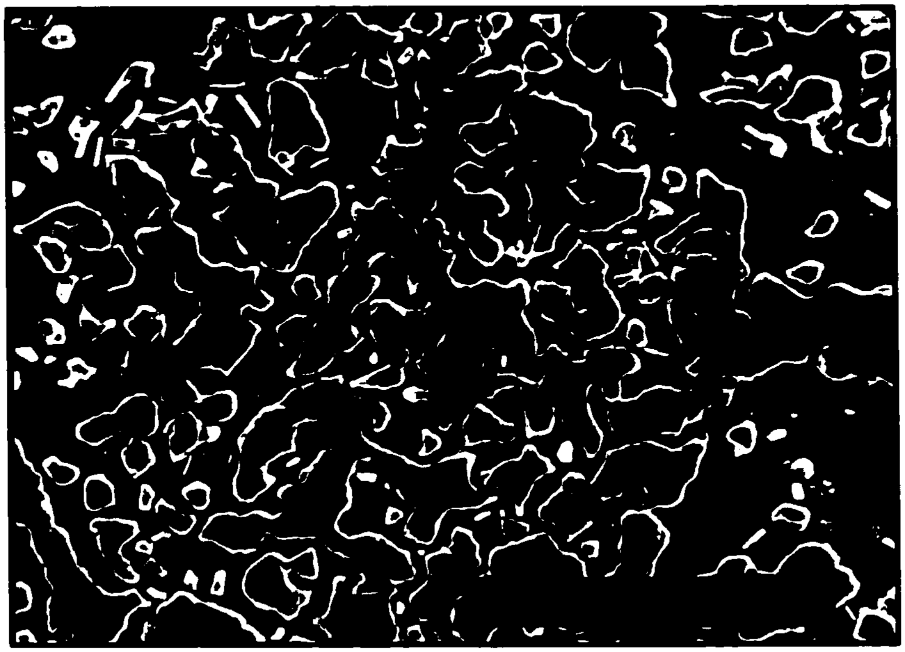


Figure (4.12): Surface morphology of Haynes 214 after exposure to carburizing environment containing trace amount of oxygen.

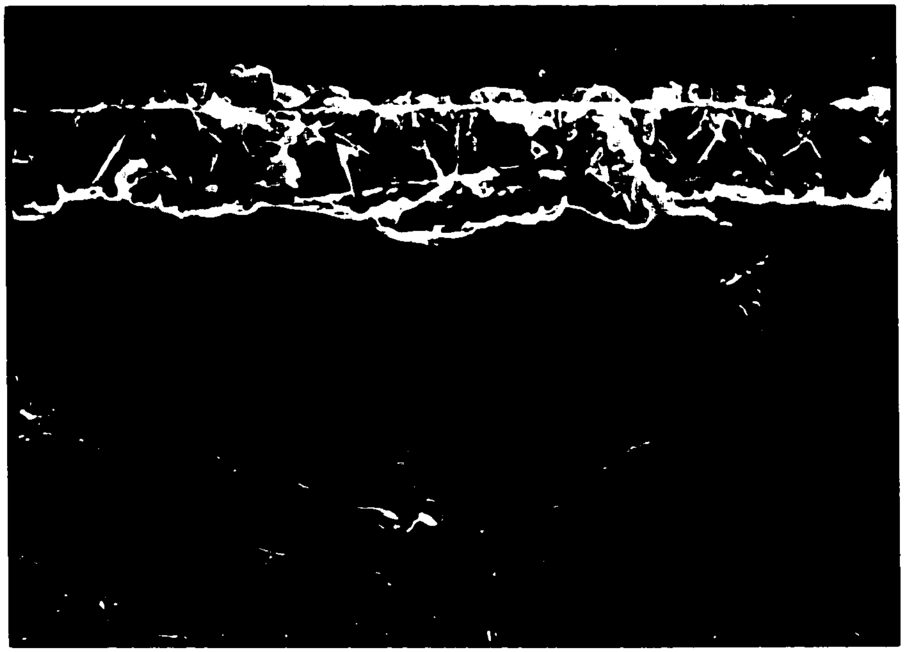


Figure (4.13): Cross-sectional morphology of Haynes 214 after exposure to carburizing environment with trace amount of oxygen.

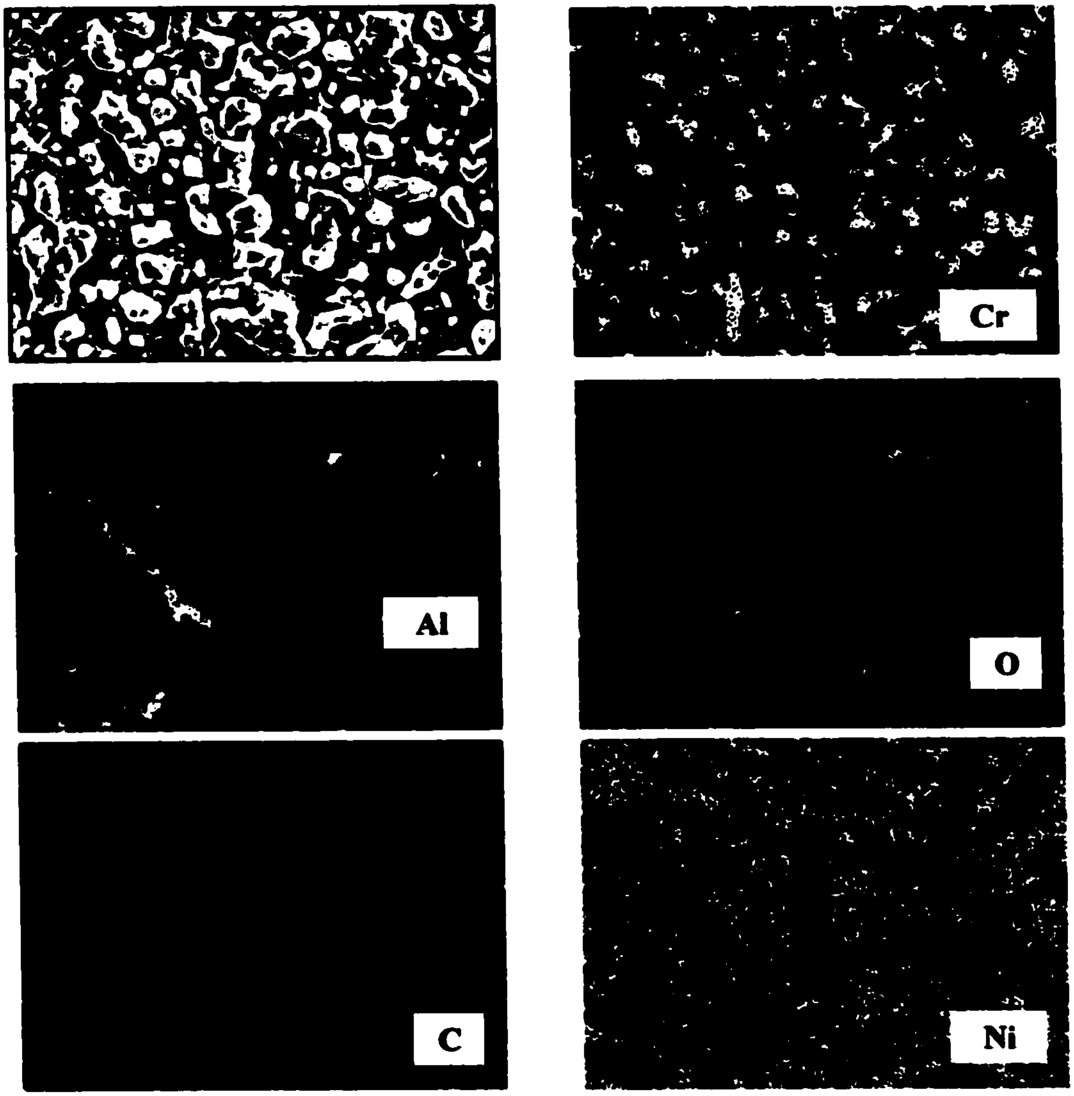


Figure (4.14): Elemental distribution of the Surface of Haynes 214 after exposure for 100 hours.

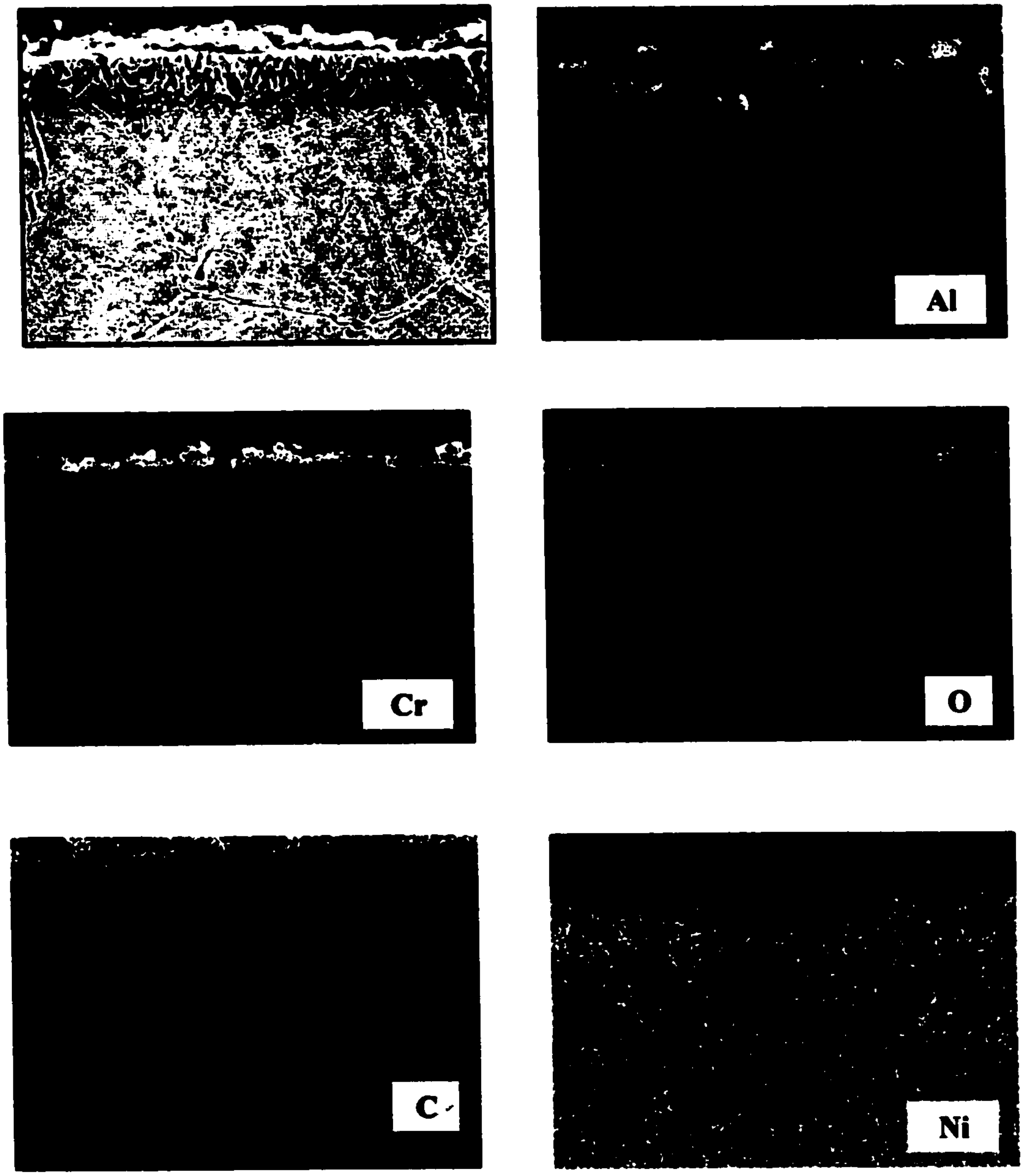


Figure (4.15): Elemental distribution of the cross section of Haynes 214 after exposure for 100 hours.

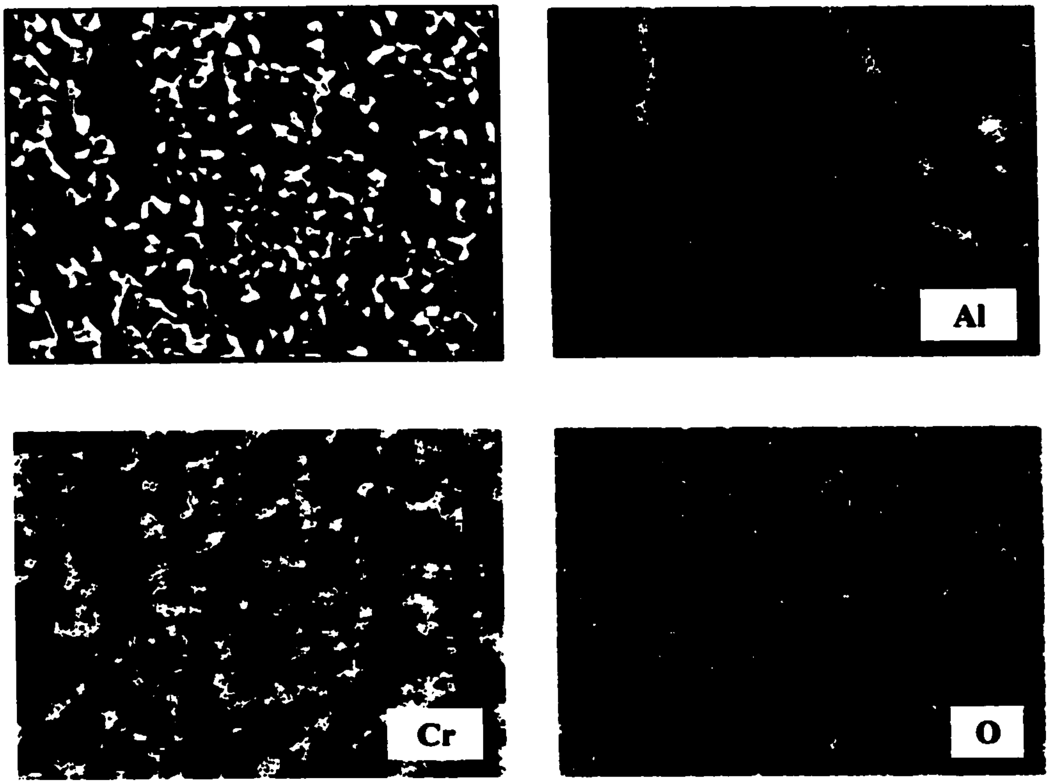


Figure (4.16): Elemental distribution of the surface of Haynes 214 after exposure for 6 hours.

boundaries are rich in Al. However, internal oxidation of Al offers no protection against oxidation or carburization, but increases the weight gain of the alloy. It affects the mechanical properties of the metal surface detrimentally. This alloy contains higher chromium concentration than Al. Moreover, Al_2O_3 is much more thermodynamically stable than Cr_2O_3, besides the higher affinity between Al and oxygen than Cr with oxygen. These two reasons favor the formation of dispersed-internal Al_2O_3 particles rather than the formation of internal Cr_2O_3. Therefore, a semi-continuous Cr_2O_3 layer is observed on the external surface of the alloy at the gas/metal interface.

Also, from the XR-Diffraction and elemental distribution analyses (Table (4.3)), it is clear that islands of chromium carbides (Cr_7C_3 and Cr_3C_2) can be seen on the top of the alloy surface at the gas/metal interface. Chromium carbides are more thermodynamically stable than aluminium carbides. Since the alloy contains higher Cr concentration than Al, carbides of Cr will form on the top surface as discrete islands in preference of Al_4C_3. With continuous exposure of this alloy chromium depletes below the surface of the alloy where Al is oxidized. At high temperatures chromium tends to segregate to grain boundaries in the bulk of the alloy, leading to uneven distribution of Cr into the alloy matrix.

4.3.3.2 Fe-Based Alloy (Incoloy 803)

The surface and cross-sectional morphologies of Fe-based Incoloy 803 after exposure to carburizing environment similar to the previous condition (2% CH_4-H_2 at 800°C) are shown in figures (4.18 and 4.19 respectively) for 500hrs. It is clear that a continuous and external Cr_2O_3 layer was dominating on the surface of the alloy (at the

TABLE (4.3): XRD results for both alloys

Exposure condition	Haynes 214	Incoloy 803
800°C, 2%CH_4-H_2	Al_2O_3 Cr_7C_3 Cr_3C_2 Cr_3Ni_2SiC	Chromium Carbides

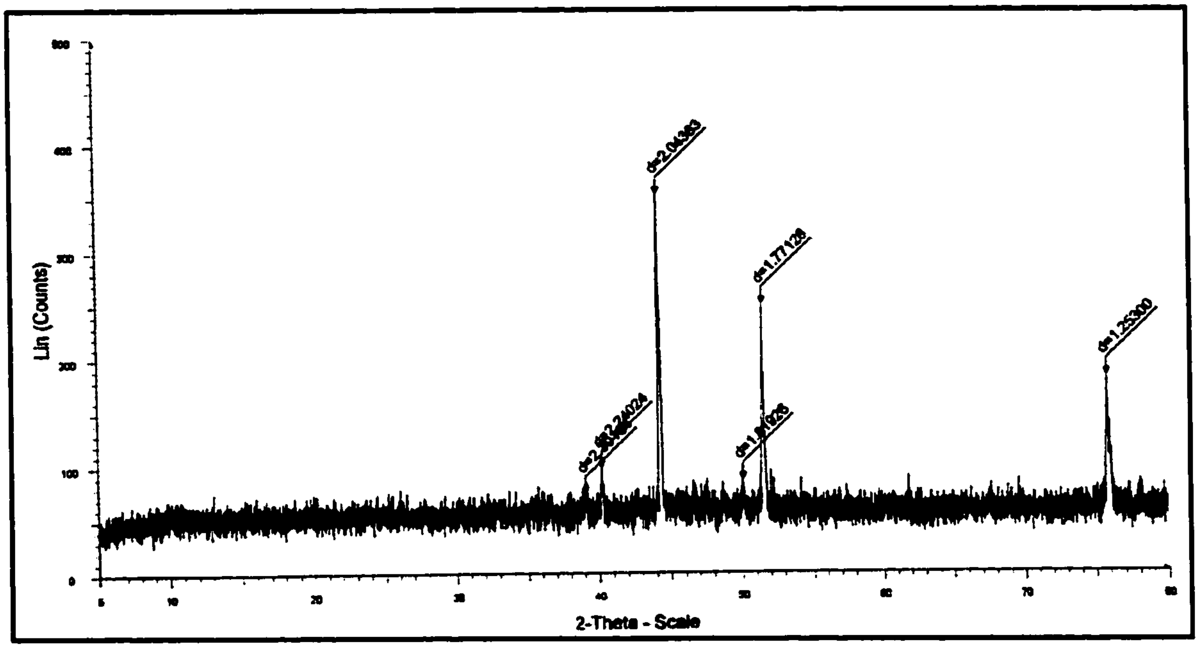


Figure (4.17a): X-Ray diffraction Result for Haynes 214 after exposure for 200 hours

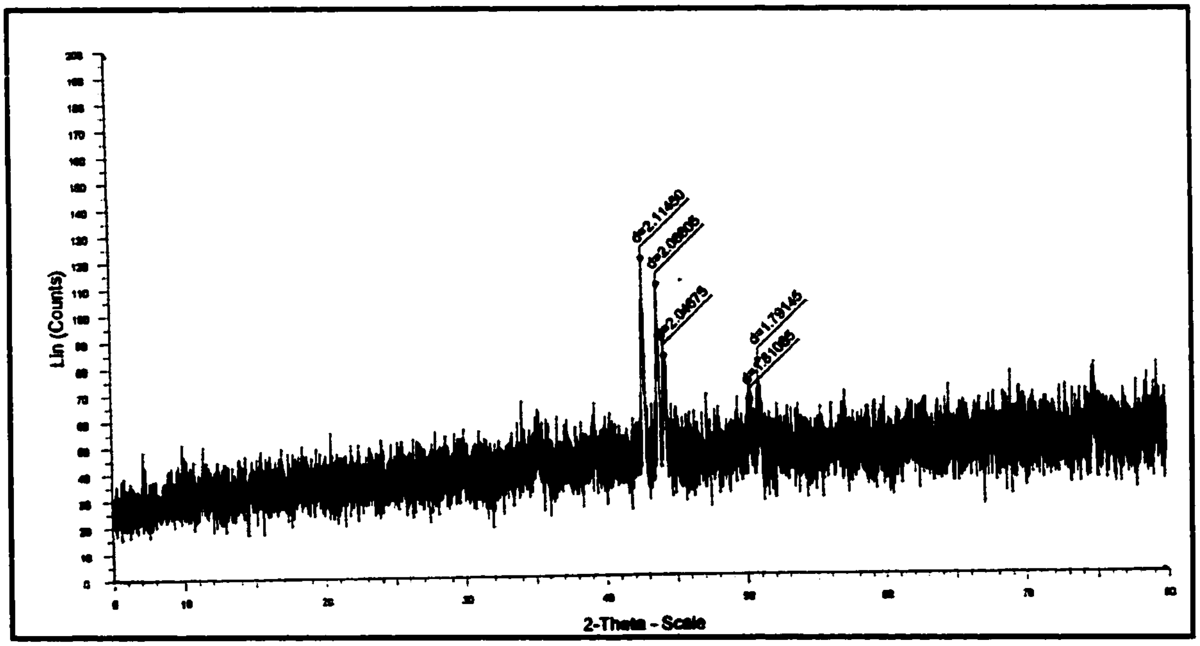


Figure (4.17b): XRD Result for Incoloy 803 after exposure for 200 hours in carburizing gas

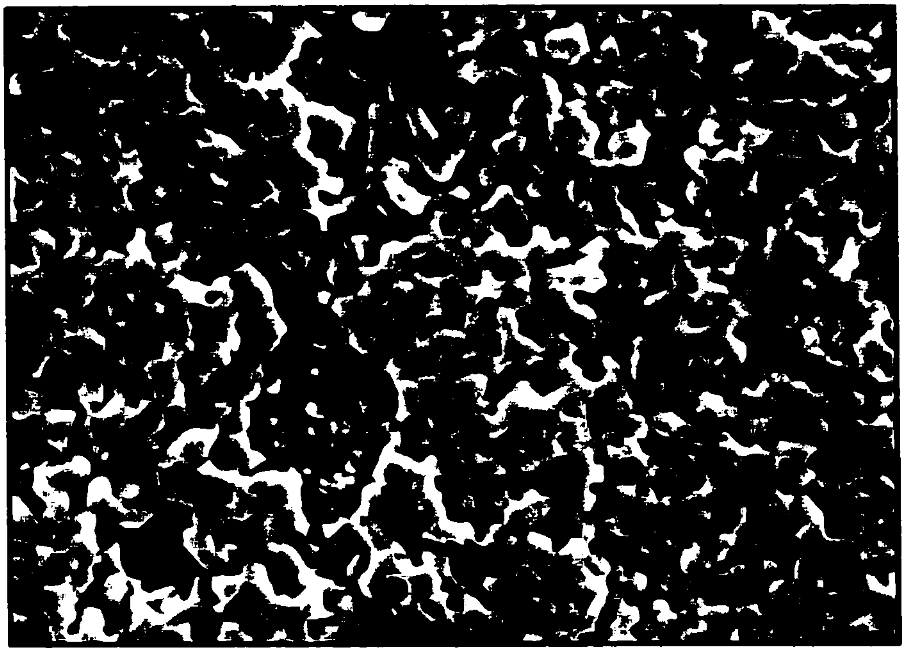


Figure (4.18): Surface morphology of Incoloy 803 after exposure to carburizing environment with trace amount of oxygen.

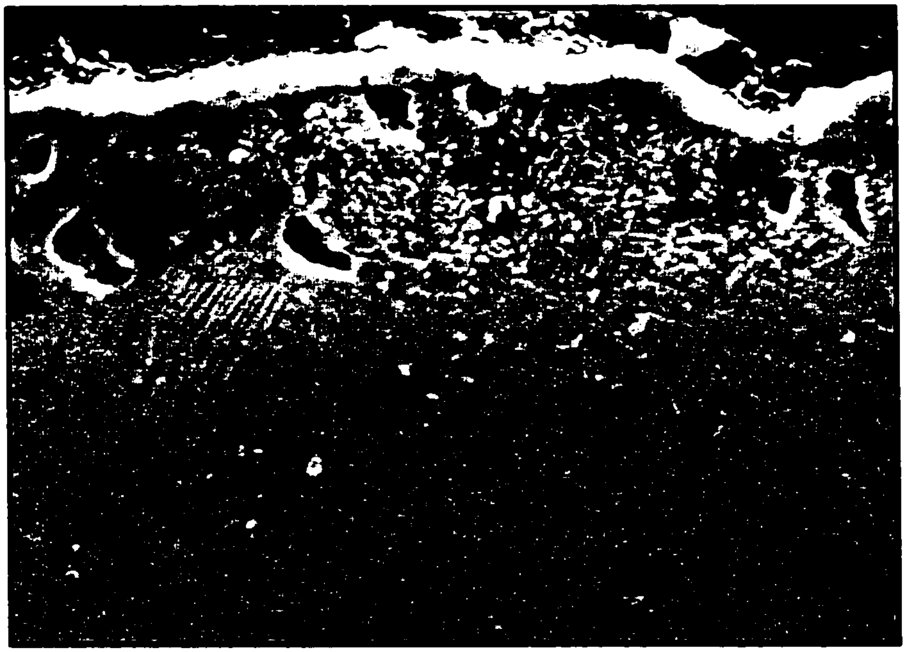


Figure (4.19): Cross-sectional morphology of Incoloy 803 after exposure to carburizing environment with trace amount of oxygen.

gas/metal interface), with an approximate thickness of about 2-3 μm, even though the partial pressure of oxygen was relatively low into the environment. This is shown in the elemental distribution of the selected samples (figure (4.20)). Although oxides of Al are more stable than oxides of Cr, only few discrete Al_2O_3 particles were able to form internally with some SiO_2. This is because the amount of Al in this particular alloy was extremely low in comparison to the previous alloy (Haynes 214).

The formation of a continuous Cr_2O_3 layer was possible at this low oxygen environment due to the high Cr content (25-29 wt %) in the alloy's composition, which is responsible for the reduced weight gain of this alloy compared with Haynes 214 (because of the absence of a similar continuous layer in 214), and hence improved the carburization/oxidation resistance. Discrete islands of chromium carbides were able to form initially on the top of the alloy surface at the gas/metal interface until it is undercut by the formation of Cr_2O_3 layer. Since carbon is generally incapable of diffusing through oxide layers (except through cracks) the presence of such continuous Cr_2O_3 layer will markedly reduce further dissolution of carbon and formation of carbides below the external oxide layer.

In comparison with the previous oxidizing environment for this particular alloy, where the presence of high oxygen partial pressure accelerated the formation of continuous Cr_2O_3 layer in early stages of exposure, much earlier than the carburization case (with trace amount of oxygen). Therefore, once Cr_2O_3 layer forms, its thickening rate will be reduced dramatically due to slow lattice diffusion of Cr in the Cr_2O_3 layer. Despite the high amount of Cr into this alloy, Cr-depletion zone appears beneath the Cr_2O_3 surface layer and its thickness ranges from 10-13 μm. This is shown from the elemental distribution of exposed samples to 500hrs (figure (4.20)). The thickness of the Cr-depletion zone in this case was more than that in the oxidation case due to the early formation of a continuous Cr_2O_3 layer in the oxidation case (see figure (4.10)). Also, in the bulk of the alloy and following exposure to high temperatures Cr segregates to grain boundaries. Grain boundaries become thicker with the continuous coverage of Cr.

4.4 CARBURIZATION IN METHANE-HYDROGEN-STEAM MIXTURE

4.4.1 Experimental Procedure

In this stage of the investigation, the intention is to produce a carburizing environment with a relatively high amount of oxygen. To achieve that, a new system was designed in order to increase the partial pressure of oxygen into the reaction chamber "furnace". Figure (4.21) shows the system designed to produce this highly oxidizing-carburizing condition. This is accomplished by bubbling the commercial grade (2% CH_4-H_2) gas mixture into a water bubbler, which is kept at a temperature lower than 100°C (70°C in this case). Then the (2%CH_4-H_2) gas bubbles were admitted at the bottom of the bubbler to allow complete saturation with steam before the gas is allowed to enter the furnace. The travelled distance by the CH_4-H_2 gas bubbles is at least 150 cm to ensure maximum saturation with steam. Then, the gas-steam mixture is admitted into the furnace at a temperature of 800°C for specific durations. Then the weight gain were measured after each test run, and then plotted against the duration periods in hours.

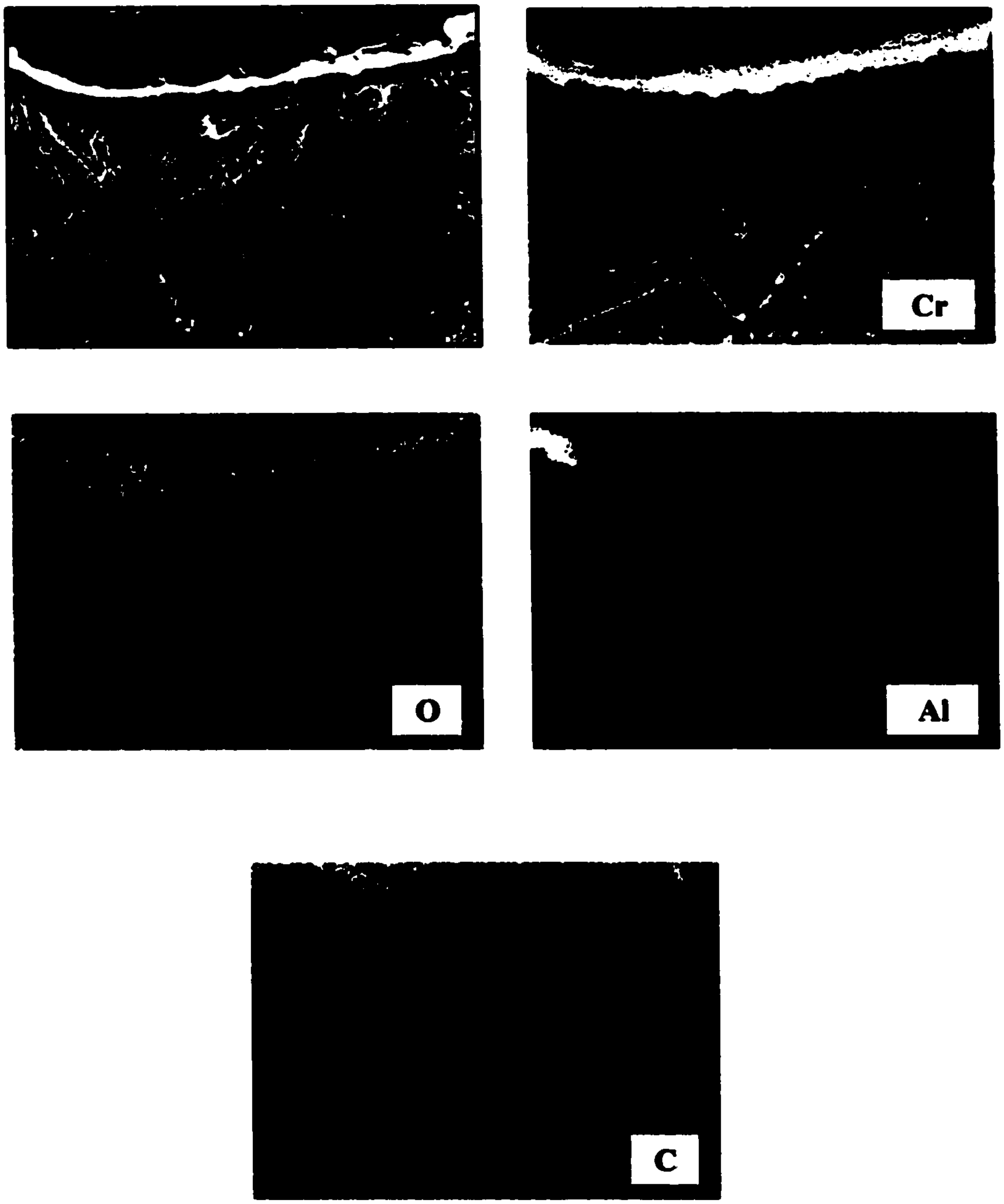


Figure (4.20): Cross-sectional elemental distribution for Incoloy 803 after exposure for 500 hours.

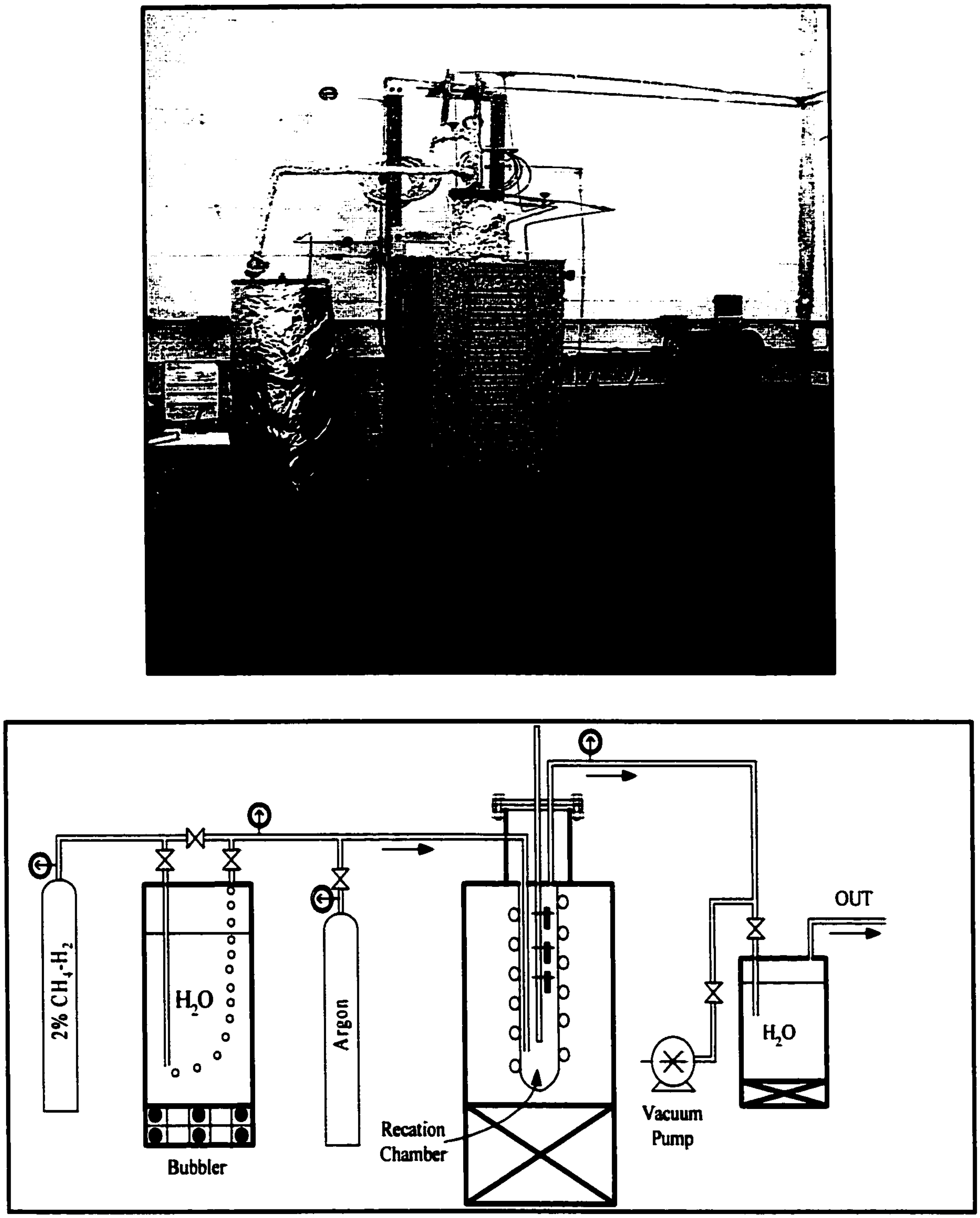


Figure (4.21): Experimental setup used in providing methane-hydrogen-steam mixed environment.

4.4.2 Thermodynamics

In the thermodynamics analysis it is expected to calculate the oxygen partial pressure into the environment as well as the carbon activity. Then, by comparing theses values with the dissociation pressure values of expected oxides and carbides, predictions of these reaction products is possible. This is usually achieved by assuming equilibrium condition to exist inside the reaction chamber at the test temperature, and thus from Gibbs energy equation, characterization of the environment is achieved. However, since the 2% CH_4-H_2 gas mixture was bubbled in the steam bubbler, steam is introduced into the furnace (mixed with the commercial gas mixture). Therefore, an excess amount of steam will be introduced into the system. The experimental condition above is designed such that high and continuous flow of steam is ensured to provide highly oxidizing-carburizing environment compared to carburization case with trace amount of oxygen. This condition cannot be avoided, i.e. experimental condition imposed into the system. In other words, the flow rate of gas mixture into the bubbler should be maintained relatively high in order to continuously provide steam into the system. This, in turn, will shift the gas composition (H_2/H_2O) from equilibrium; therefore, Gibbs energy equation cannot be applied. This is because the environment contains higher partial pressure of steam (P_{H_2O}) than necessary for equilibrium reaction to get established:

$$H_2 + \frac{1}{2}O_2 \Leftrightarrow H_2O$$

The environment should provide higher oxygen partial pressure than the second carburization case with oxygen impurity. Figure (4.22) shows the partial pressure of oxygen in each test environment, where the partial pressure of oxygen in

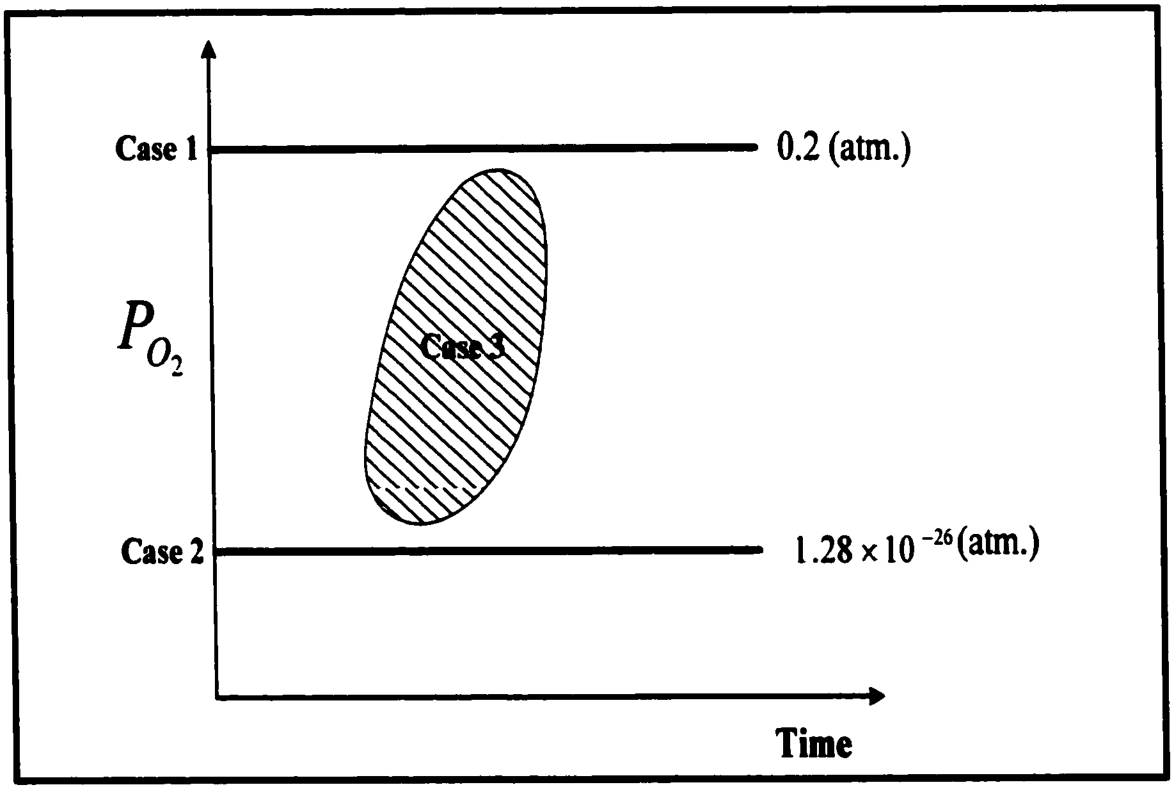


Figure (4.22): partial pressure of oxygen in each case (case(1) Oxidation in air, case(2) carburization with oxygen impurity, and case(3) methane-hydrogen-steam mixed environment).

this case (highly oxidizing-carburizing) shows to be in between the last two cases. This condition approaches a more realistic condition available in industry (steam reforming):

$CH_4 + H_2O \rightarrow CO + 3H_2$ (Steam Reforming)

OR

$CO_2 + 2H_2 \rightarrow C + 2H_2O$ (Carburization reaction)

From the previous discussion, it is clear that the condition inside the furnace is far more oxidizing than what can be achieved at equilibrium, i.e. the environment inside the furnace is highly oxidizing. However, it is less oxidizing than 0.2% oxygen in air. Therefore, a thermodynamic study can not be conducted at this stage to determine the possible reaction products, since the system deviated from equilibrium.

4.4.3 Kinetic Results

Figure (4.23) shows the weight changes measurements against exposure duration for both alloys (Haynes 214 and Incoloy 803) during isothermal exposure to a mixture of commercial gas 2%CH_4-H_2 (with trace amount of oxygen to be 100 ppm) and steam at a temperature of 800°C. From the weight gain results, the weight gain for alloy Haynes 214 under this condition is considerably lower than that of Incoloy 803. The test environment is expected to be strongly oxidizing environment, in comparison

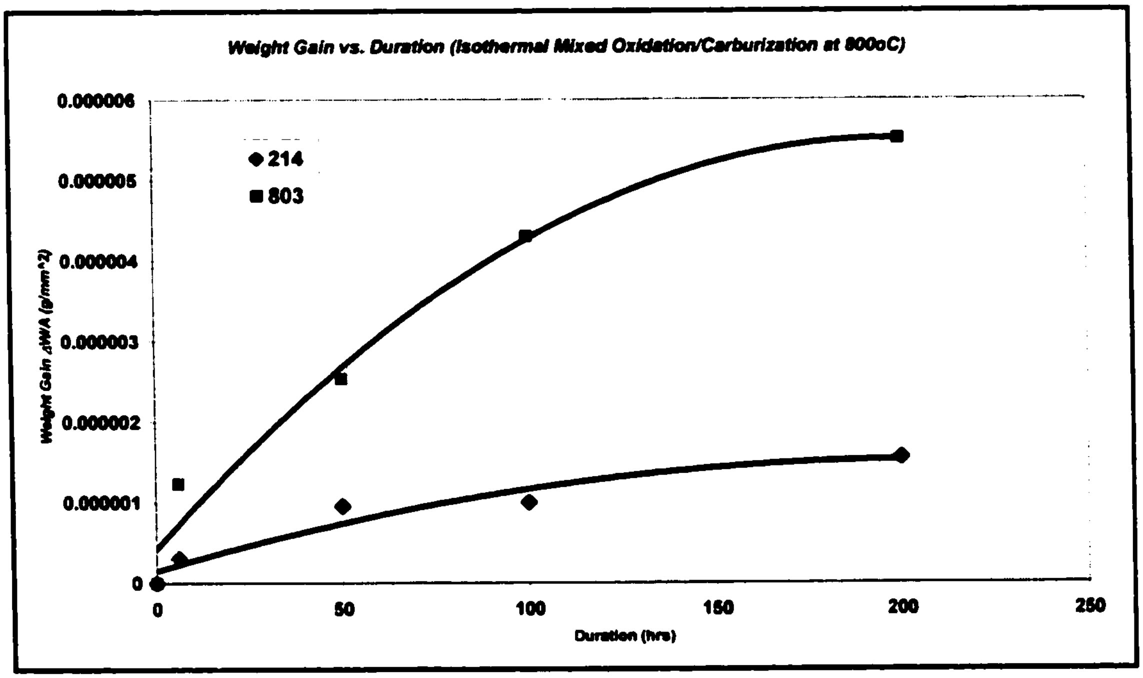


Figure (4.23): Weight gain versus exposure duration for alloys exposed to methane-hydrogen-steam environment.

to case (2) (carburization with trace amount of oxygen), thus the weight gain measurements for samples exposed to this environment look almost similar to those obtained upon exposing the two alloys to air (case(1) more oxidizing). Moreover, the reaction products obtained from this case are greatly similar to those formed during air oxidation Figures (4.6 and 4.10). Table (4.4) summarizes the X-ray diffraction results obtained upon exposing these two alloys for the environment described above.

4.4.4 Microstructural Characterization

4.4.4.1 Ni-Based Alloy (Haynes 214)

Figures (4.25 and 4.26) show the morphologies of surface and cross-sectional views of alloy Haynes 214 after exposure to methane-hydrogen-steam mixture for 100 hours. The test was carried out at a bubbler temperature of 70°C and a furnace temperature of 800°C. Since the environment is highly oxidizing, alloy Haynes 214 was able to form an external and protective Al_2O_3 layer at the gas/metal interface. The formation of this layer is promoted by two parameters: the first is the relatively high Al content in the alloy and the second is the presence of steam which produces high oxygen partial pressure. If one of these parameters is not achieved, internal oxidation of Al would occur. The amount of oxygen is enough at the test temperature to form continuous layer that will undercut any further transport of other alloy's constituents towards the surface to react with gas molecules. Since the amount of steam was relatively high into the environment, oxidation reactions dominate over carburization reactions, since the solubility of carbon into oxides is almost nil.

TABLE (4.4): X-Ray Diffraction results from exposing alloys into methane-hydrogen-steam environment

Exposure condition	Haynes 214	Incoloy 803
800°C, 2%CH_4-H_2-Steam	$Ni_{2.9}Cr_{0.7}Fe_{0.36}$	Cr_2O_3 $Cr_{23}C_6$

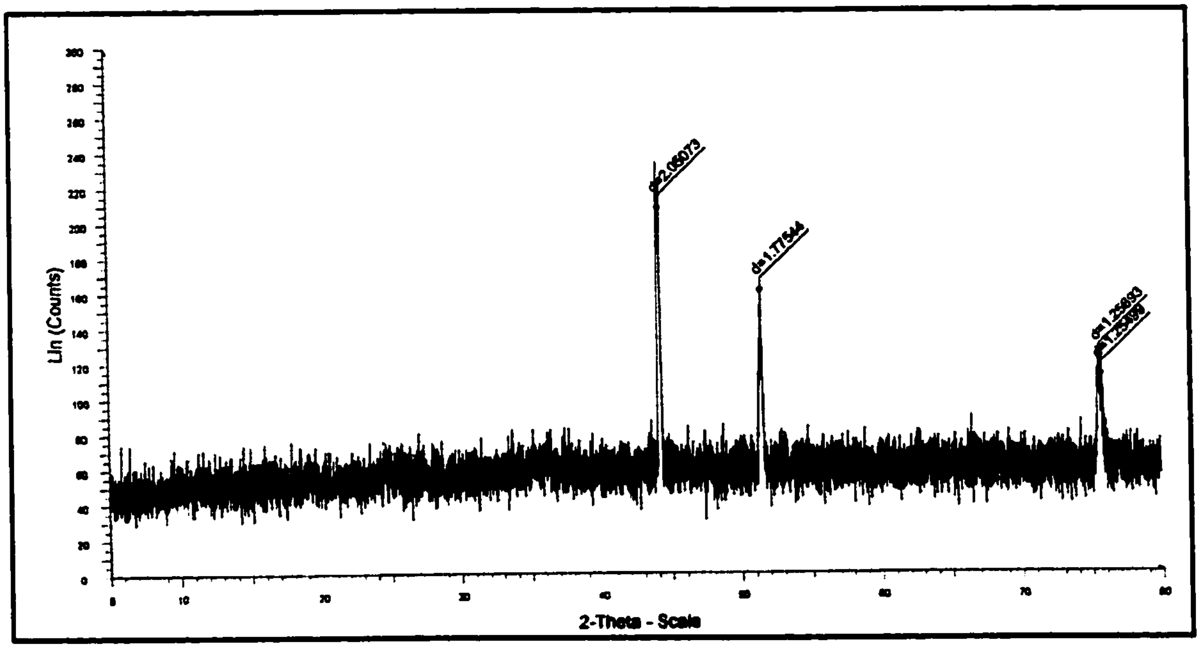


Figure (4.24a): XRD result for Haynes 214

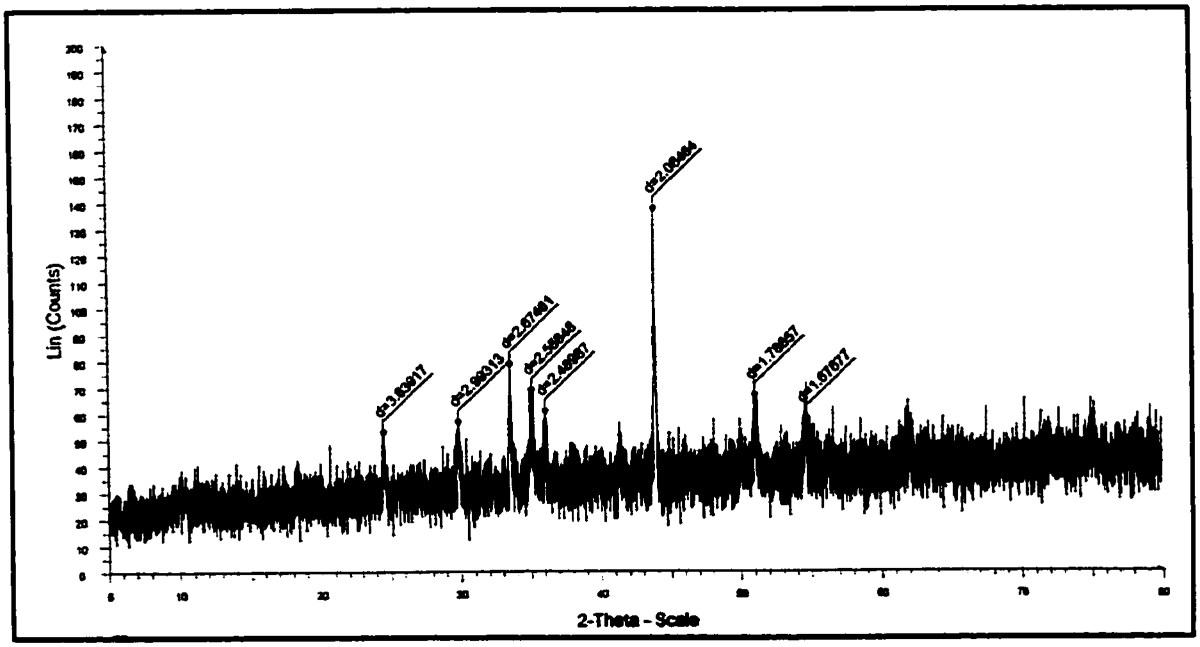


Figure (4.24b): XRD result for Incoloy 803

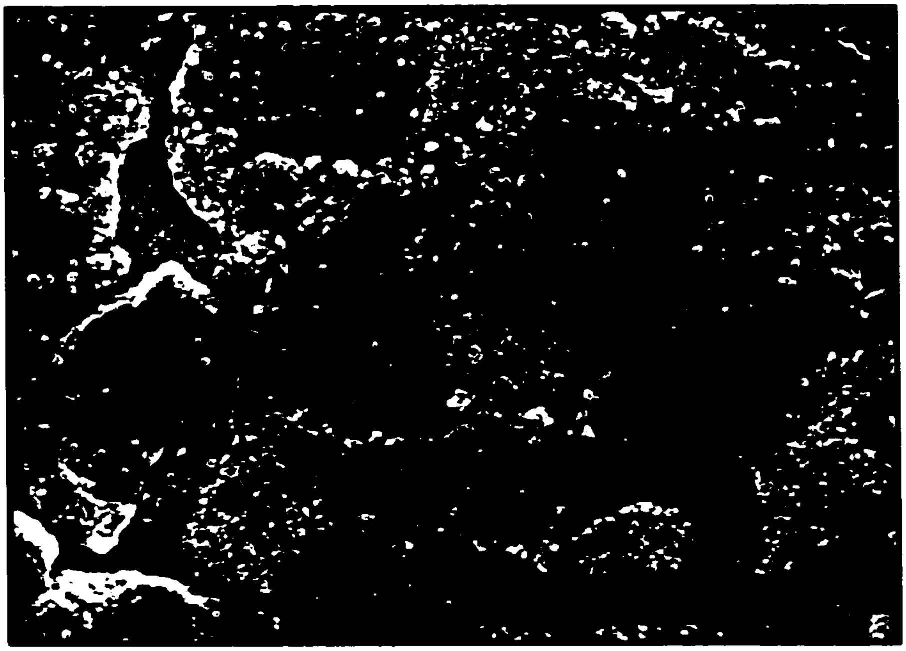


Figure (4.25): Surface morphology of Haynes 214 after exposure to methane-hydrogen-steam mixed environment.

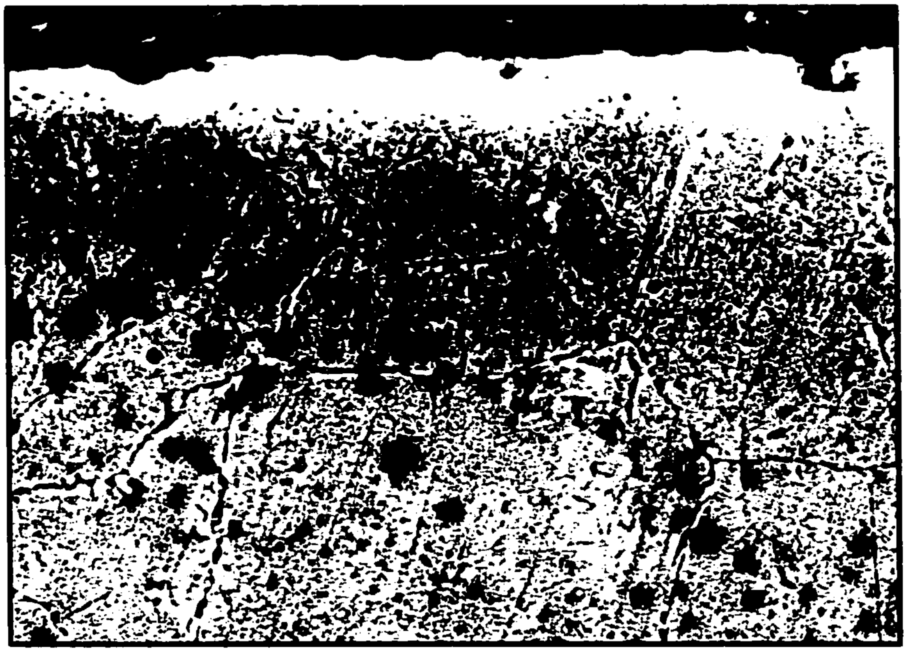


Figure (4.26): Cross-sectional morphology of Haynes 214 after exposure to methane-hydrogen-steam mixed environment.

As shown in the elemental distribution analysis (figures (4.27 and 4.28)), high concentration of Al in grain boundaries is noticed with Al distribution on the top surface of the alloy. Also, Cr-rich islands were noticed on the top surface of the alloy (probably in the form of oxides or carbides). These islands are suspected to be oxide particles at the top surface layer of the alloy (gas/metal interface). On the other hand, elemental distribution for cross sectional views shows a continuous Al_2O_3 layer with discreet islands of chromium carbides at the top surface of the layer formed during the initial exposure. Similar to the case of oxidation in air, the formation of Cr_2O_3 islands is possible in the initial stages, but once the continuous Al_2O_3 layer is formed, no more oxidation of Cr can be reached.

4.4.4.2 Fe-Based Alloy (Incoloy 803)

Surface and cross sectional morphologies of several samples of alloy Incoloy 803 exposed to the mixed CH_4-H_2-Steam environment at 800°C are shown in Figures (4.29 and 4.30). As observed in the case of oxidation in air, a continuous layer of Cr_2O_3 is observed to dominate on the gas/metal interface. This is shown in the elemental distribution Figure (4.10), where a continuous layer of Cr_2O_3 can be seen. Also, EDS analyses for different spots on the surface show clearly that Cr is dominating on the surface layer of the alloy and more specifically in the form of Cr_2O_3 (figures 4.31 (a,b)). The domination of Cr_2O_3 layer on the gas/metal interface is primarily due to the high Cr content in the alloy composition.

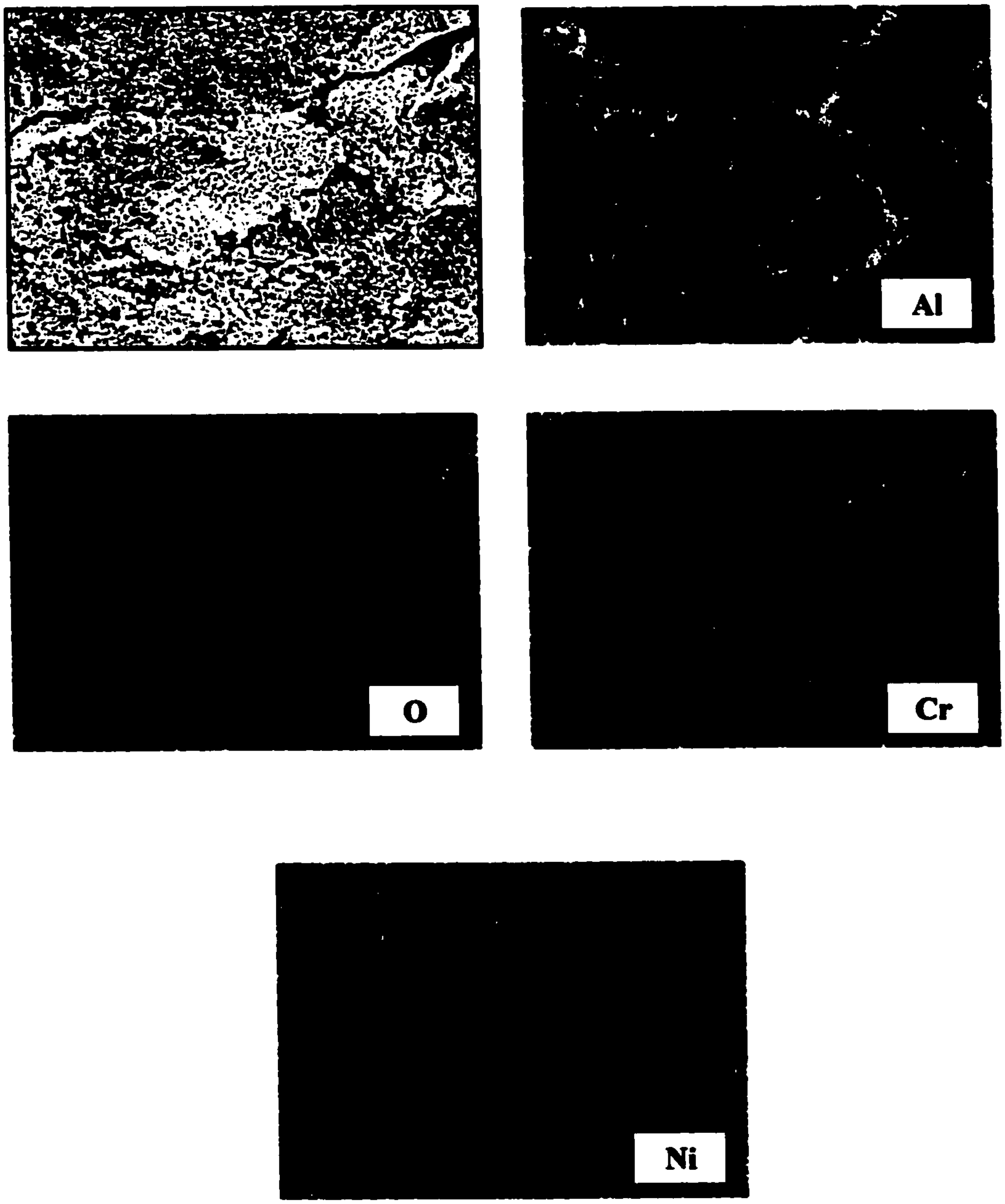


Figure (4.27): Surface elemental distribution for Haynes 214 after exposure for 100 hours.

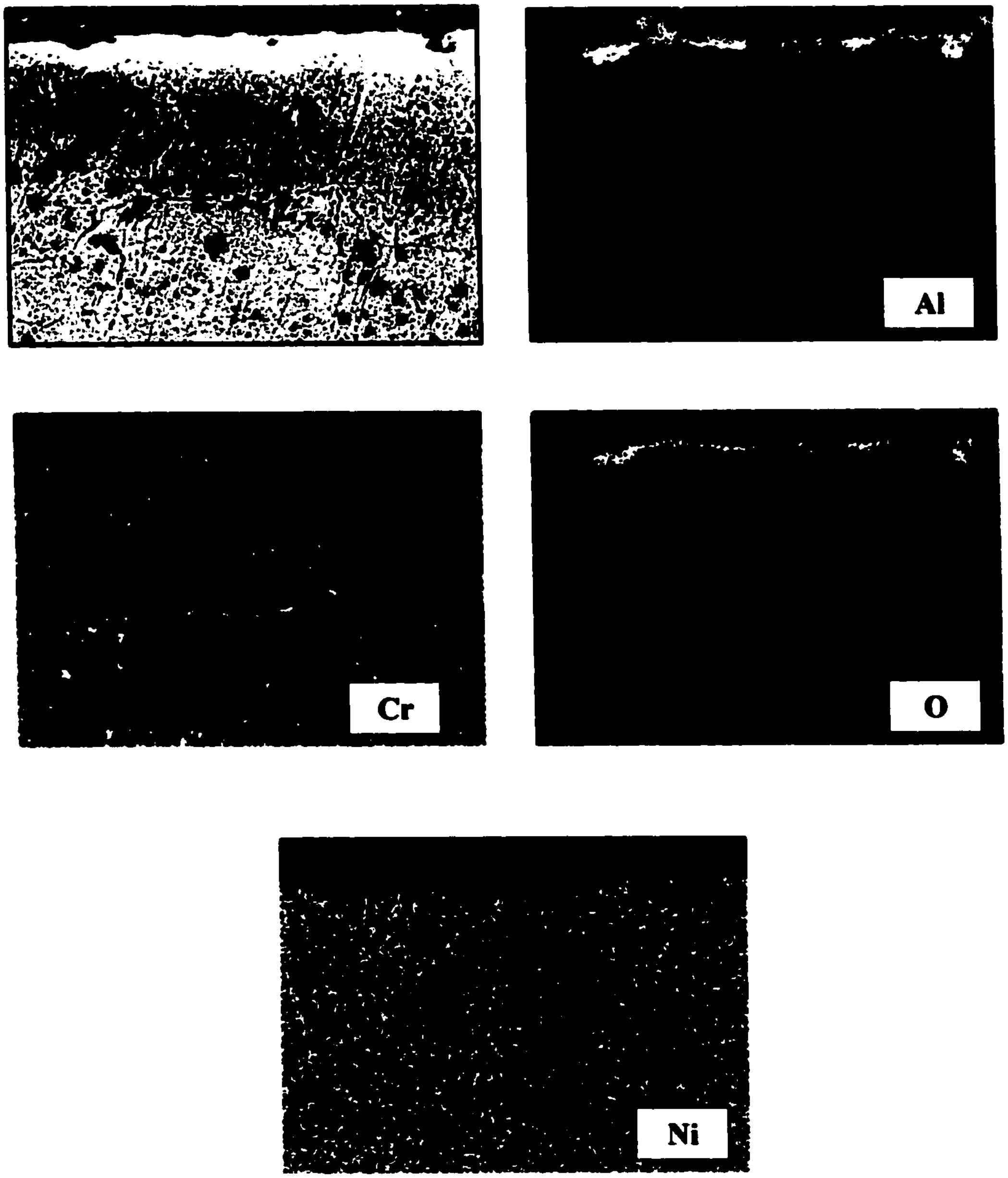


Figure (4.28): Cross-sectional elemental distribution for Haynes 214 after exposure for 100 hours.

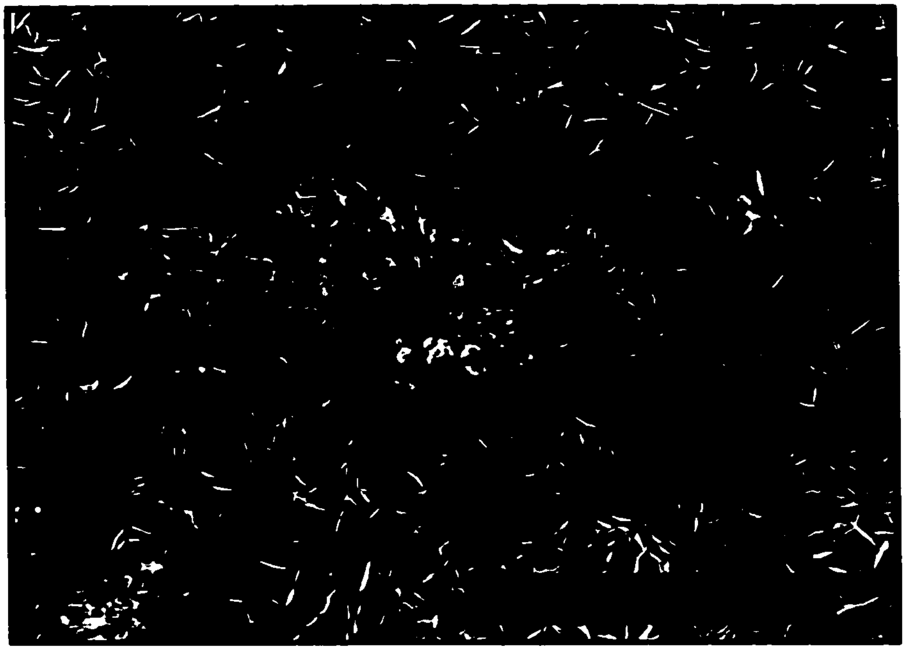


Figure (4.29): Surface morphology of Incoloy 803 after exposure to methane-hydrogen-steam mixed environment.

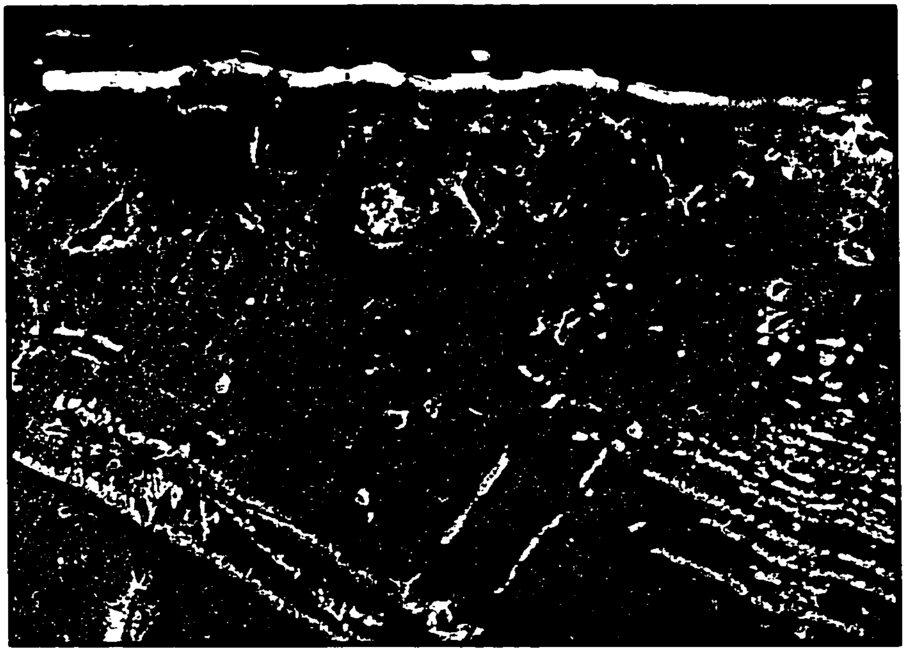
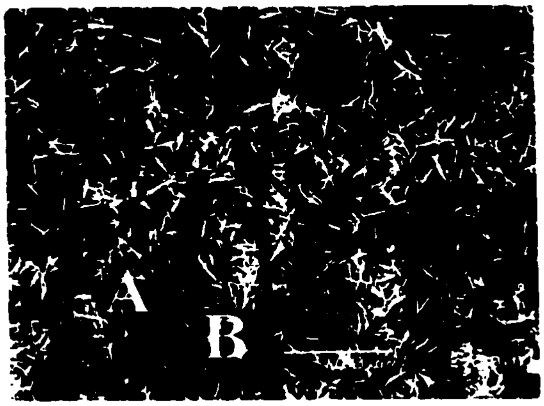


Figure (4.30): Cross-sectional morphology of Incoloy 803 after exposure to methane-hydrogen-steam mixed environment.



Incoloy 803 following exposure to methane-hydrogen-steam environment for 100 hours

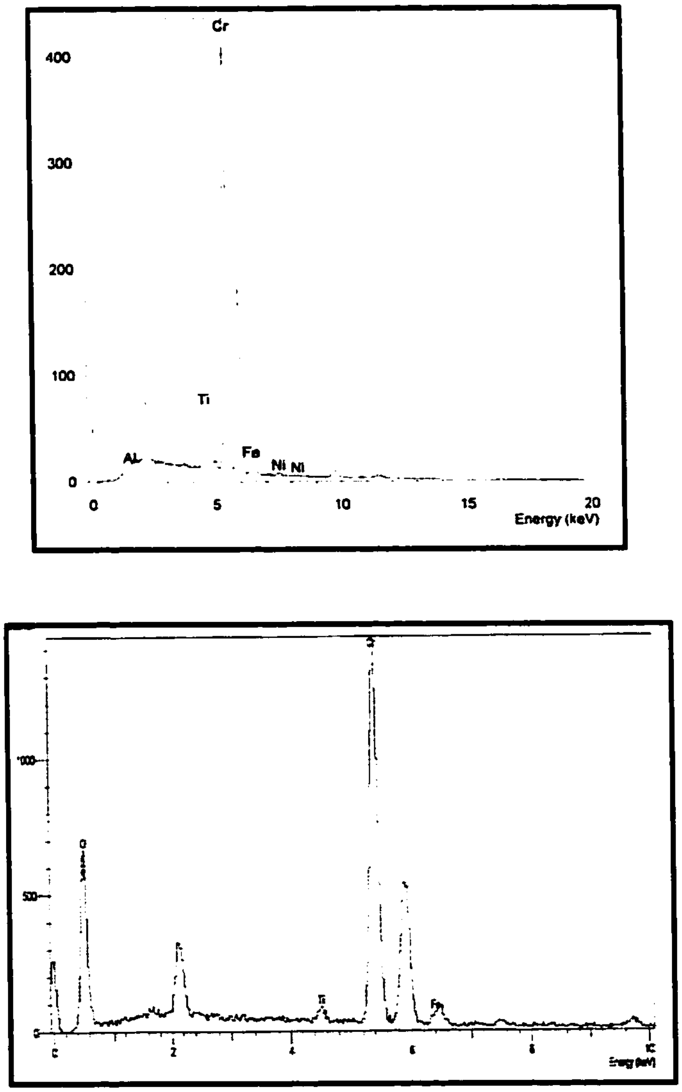
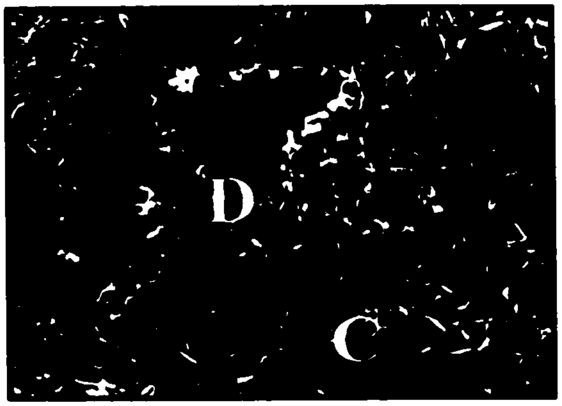


Figure (4.31a): EDS Analysis for points A and B, respectively, in the above picture



Incoloy 803 following exposure to methane-hydrogen-steam environment for 100 hours

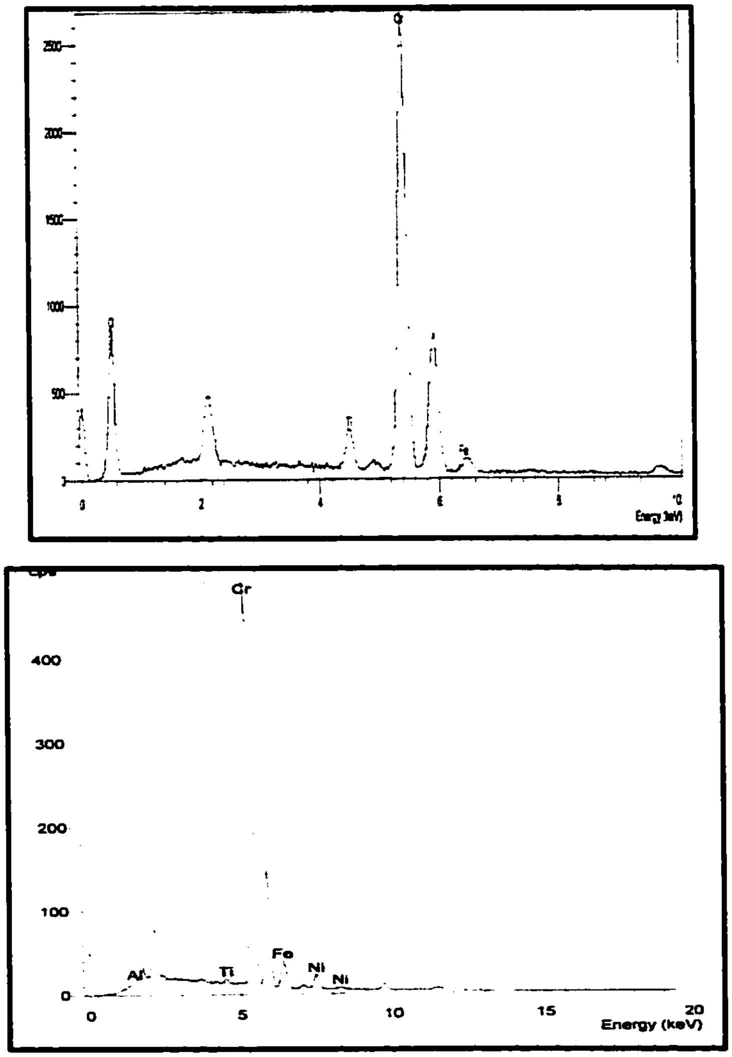


Figure (4.31b): EDS Analysis for points C and D, respectively, in the above picture.

This particular alloy (Incoloy 803) was able to form continuous Cr_2O_3 layer in all test conditions, even though when the amount of oxygen was very low in the previous carburizing environment. From the elemental distribution (figure (4.32)) discreet and internal particles of Al- and Ti-oxides were observed to form beneath the Cr_2O_3 layer. The formation of internal oxides particles is interpreted by the low concentrations of Al and Ti into the alloy matrix (low concentration of active elements).

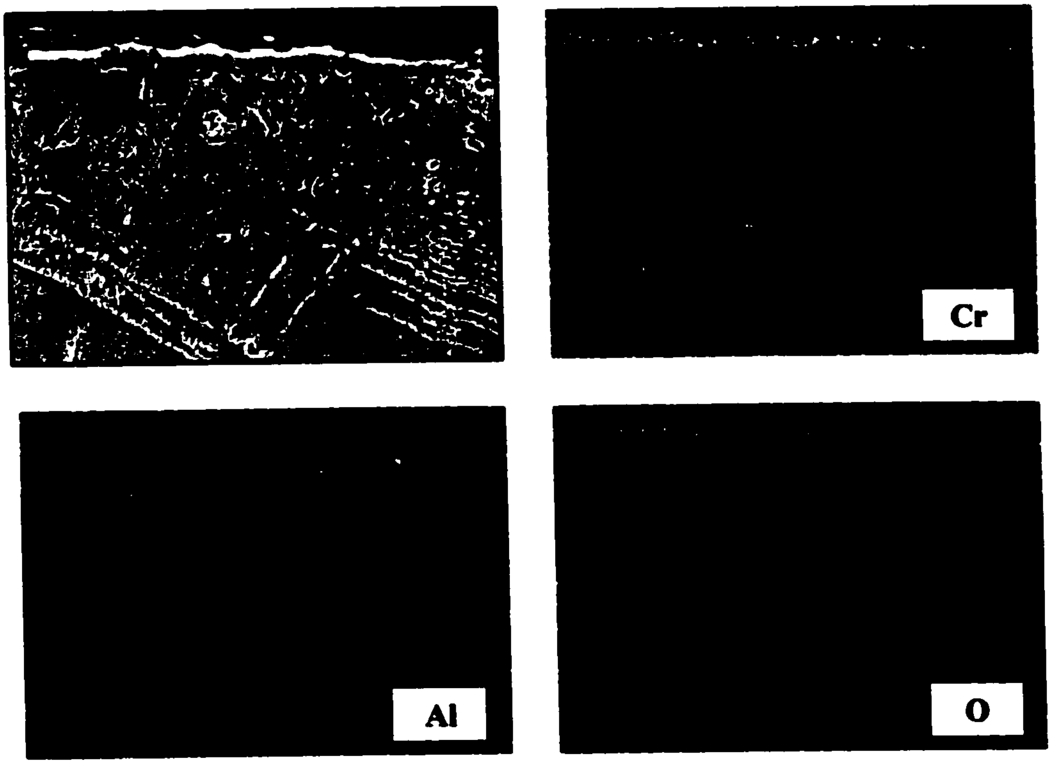


Figure (4.32): Cross-sectional elemental distribution for Incoloy 803 after exposure for 100 hours.

CHAPTER 5

STATISTICAL ANALYSIS

5.1 INTRODUCTION

Performing statistical analyses is very important in experimental work. It gives a quantitative measure of the total trend of the data, especially, in the case of comparison between two candidates (metals or alloys) exposed to harmful environments. In this investigation two alloys (namely Haynes 214 and Incoloy 803) were used to study the behavior of each one of them in three different environments. Two extreme conditions are considered at first, which are purely oxidizing in air and highly carburizing environments, while the last one came between the two extreme cases. The third environment considered in this investigation was highly oxidizing and carburizing.

In the first environment, which is oxidation in air, samples from the two alloys were exposed to a purely oxidizing environment to study the ability of each alloy to form a protective oxide layer that reduces the weight gain. Then, in the second environment, a commercial grade (2%CH_4-H_2) gas mixture was used to simulate a carburizing environment with a trace amount of oxygen to be 100 ppm. Finally, in order to study the behavior of these alloys in an intermediate environment between the previous extreme cases, the commercial 2%CH_4-H_2 gas mixture was allowed to pass in a water bubbler kept at 70°C to allow the gas bubbles to carry some steam. Admitting this 2%CH_4-H_2-steam mixture will simulate a carburizing environment with an excess amount of oxygen, which will tend to oxidize the two samples.

In the experimental work of this investigation 3 samples of each alloy were exposed in each test run. These runs consist of exposing samples to different durations, and new set of samples were used for each duration. Then, by measuring the weight gain of each sample and taking the average weight gain for each set of samples, characterization of the behavior of each alloy at specific environment is possible. Since the thermogravemetric behavior of each alloy is described by taking the average of the exposed samples' set in each test run, a statistical analysis is required to accurately determine the exact difference between the final behaviors of the two alloys. Testing the equality of the average weight gain of the two alloys at each duration is crucial with some significance level.

Statistical analysis was carried out in this study to test the means of each group of data point to check the variability of the two alloys in their behavior. Some assumptions have been made in order to test the means of each data points at specific durations. It is assumed that the central limit theorem applies and the data can be normally distributed. Since the variances of all data are unknown (no previous observations), one should check the equality of the variances for each alloy at every data point before checking for the means equalities. Then after testing the equality of the variances, the corresponding test of hypotheses is carried out to check the means. The following example will illustrate the procedure of testing variances and means. Consider the case of carburization data for the two alloys, used in this investigation, after exposing them to 200 hours. The collected weight gain data for each alloy is shown in the following table with the calculated averages and standard deviations.

Alloy	Sample 1	Sample 2	Sample 3	Average	Standard deviation
Haynes 214	15.3695	14.4775	15.9771	15.275	0.7543
Incoloy 803	10.6433	10.530	9.91755	10.3636	0.3905

Testing for variances equality:

Assuming that both populations are normally distributed:

Hypotheses $H_0 : \sigma_1^2 = \sigma_2^2$

$H_a : \sigma_1^2 \neq \sigma_2^2$

Rejection region $F_0 > F_{\alpha/2, \upsilon_1, \upsilon_2}$

Test statistic $F_0 = \frac{s_1^2}{s_2^2}$

Where:

α = significance level = 0.05

υ_1 = Degrees of freedom of set 1 = $n_1 - 1 = 2$

υ_2 = Degrees of freedom of set 2 = $n_2 - 1 = 2$

$$F_0 = \frac{0.7543^2}{0.3905^2} = 3.7322$$

$$F_{\alpha/2,\upsilon_1,\upsilon_2} = 39$$

Since $F_0 < F_{\alpha/2,\upsilon_1,\upsilon_2}$, which is outside the rejection region:

Null hypothesis is accepted and the two variances are taken to be equal.

$\sigma_1^2 = \sigma_2^2$

Testing for means equality:

Hypotheses $H_0 : \mu_1 = \mu_2$
$H_a : \mu_1 \neq \mu_2$

Rejection region $|t_0| > t_{\alpha/2,n_1+n_2-2}$

Test statistic $t_0 = \dfrac{\overline{X}_1 - \overline{X}_2}{s_p\sqrt{(1/n_1)+(1/n_2)}}$

Where: $\overline{X}_1 - \overline{X}_2$ = difference in the two means

$$s_p = \frac{(n_1 - 1)s_1^2 + (n_2 - 1)s_2^2}{n_1 + n_2 - 2}$$ = pooled estimate of the common variances

for the example considered earlier:

$s_p = 0.6006$

thus, $t_0 = 10.015$

and

$t_{\alpha/2, n_1+n_2-2} = 2.776$

Since $t_0 > t_{\alpha/2, n_1+n_2-2}$, inside the rejection region:

Null hypothesis is rejected and the two means are taken to be **different**.

5.2 OXIDATION IN AIR

From the statistical analysis, conducted for the collected data upon exposing the two alloys into an oxidizing environment in air, the following results can be obtained at every test run:

Duration (hrs)	0.25	6	25	100	200	500
Null hypothesis	reject	reject	reject	reject	reject	reject
Equality of means	$\mu_1 \neq \mu_2$	$\mu_1 \neq \mu_2$	$\mu_1 \neq \mu_2$	$\mu_1 \neq \mu_2$	$\mu_1 \neq \mu_2$	$\mu_1 \neq \mu_2$

This indicates that with 95% confidence, the means of the weight gain data of the two alloys at every duration cannot said to be equal. This shows clearly that the weight gain of Haynes 214 is less than that of Incoloy 803. The formation of a protective Al_2O_3 layer on the surface of Haynes 214 was responsible for the improved oxidation resistance by gaining less weight. Also, this analysis supports the weight gain data in that the Al_2O_3 layer formed at the gas/metal interface on Haynes 214 was more protective than Cr_2O_3 layer formed externally on Incoloy 803.

5.3 CARBURIZATION WITH TRACE AMOUNT OF OXYGEN

Statistical analysis was carried out for data collected after exposure the two alloys to 2%CH_4-H_2 commercial grade gas mixture with 100ppm of oxygen impurity. Results of such analysis are summarized in the following table:

Duration (hrs)	6	51	100	200	500
Null hypothesis	accept	accept	accept	reject	reject
Equality of means	$\mu_1 = \mu_2$	$\mu_1 = \mu_2$	$\mu_1 = \mu_2$	$\mu_1 \neq \mu_2$	$\mu_1 \neq \mu_2$

It is shown from the weight gain data analysis that up to an exposure for 100 hours and under 95% confidence the difference in mean values for the two alloys is negligible. In other words, the mean values for weight gain results up to 100 hours cannot said to be different. This means that the weight gain for both alloys is almost the same due to the absence of protective layer that will slowdown the rate of reaction, because once a protective layer is formed, diffusion of gas species through the oxide layer will be very difficult. Also, the reactions on both alloys are happening at the same rate, since the weight gain for both alloys, from statistical point of view, cannot said to be different.

After, exposure to 200 and 500 hours deviation in the mean results is noticed between the two alloys. The formation of a protective Cr_2O_3 layer is responsible for the reduced weight gain. In such environments and from the obtained data, the formation of Cr_2O_3 protective layer is assured after steady state condition is met. This is supported as well by the microstructural characterization (Figure (21)). On the other hand, Haynes 214 was unable to form protective oxide layer of any kind, instead of that, internal oxidation of Al continues to increase the weight gain of the alloy.

5.4 CARBURIZATION IN METHANE-HYDROGEN-STEAM ENVIRONMENT

In this environment, the behavior of the two alloys (used throughout this investigation) is greatly similar to the oxidation in air case. This is mainly due to the presence of steam carried into the system by CH_4-H_2 gas mixture. Statistical analysis (shown in the following table) for this situation shows that the mean values for weight gain data for both alloys are different.

Duration (hrs)	6	50	100	200	500
Null hypothesis	reject	reject	reject	reject	reject
Equality of means	$\mu_1 \neq \mu_2$	$\mu_1 \neq \mu_2$	$\mu_1 \neq \mu_2$	$\mu_1 \neq \mu_2$	$\mu_1 \neq \mu_2$

A remarkable improvement in weight gain data for both alloys upon exposing them to carburizing environment with steam. The amount of steam present into the environment was enough to enhance the formation of protective Al_2O_3 in the case of Haynes 214 and Cr_2O_3 layer in Incoloy 803. The weight gain for both alloys drop significantly because of the protectiveness provided by the external oxide layers formed at the gas/metal interface for both alloys. The formation of protective oxide layers can be seen form Figures (4.6 and 4.10) where the elemental distribution of cross sectional view is shown.

CHAPTER 6

CONCLUSIONS

The high temperature corrosion behavior of commercial alloys Haynes 214 and Incoloy 803 exposed to three different environments varying in their oxygen content at a temperature of 800°C has been considered throughout this investigation. Results obtained allow the following conclusions to be drawn:

1. In highly oxidizing environments Haynes 214 shows better oxidation behavior than Incoloy 803, due to its ability to form continuous protective Al_2O_3 layer compared to the faster growing Cr_2O_3 layer formed on the surface of Incoloy 803.
2. Under low oxygen partial pressure Haynes 214 is incapable of forming continuous and external Al_2O_3 layer, rather Al oxidizes internally in the form of dispersion, which is responsible for the increase in weight gain.
3. In the low oxygen partial pressure atmosphere Incoloy 803 remains capable of forming external, continuous and protective Cr_2O_3 layer which is responsible for the reduced weight gain in comparison to the Haynes 214.
4. The differences in behavior appear to be distinguishable within the steady state stage.

5. Further work is required to elucidate the parameters involved during transition from internal to external oxidation of Al.
6. For heat resistance alloys, if the environment contains high oxygen content then the alloy to be chosen should contain high Al content. However, if the environment contains low oxygen content then alloy with low Al concentration is preferred.

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