PHYSICO-CHEMICAL STUDIES ON INORGANIC COATINGS

ABSTRACT

THESIS SUBMITTED FOR THE DEGREE OF Doctor of Philosophy IN CHEMISTRY

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ABSTRACT

The work described in this thesis is concerned with the high temperature oxidation and hot corrosion behaviour of nickel aluminide coating on mild steel and borosilicate coating on mild steel and Inconel 600 alloy.

CHAPTER I is the General Introduction. This chapter provides information regarding different types of inorganic coatings, their formation on metal substrates, and corrosion and oxidation behaviour of inorganic coatings. The coatings include phosphate, chromate, oxide, carbide, nitride, borate silicate etc. Literature survey up to the end of 1989 is given citing references of the important works carried out on different aspects of coatings.

CHAPTER II covers Experimental Section. It contains information about materials/chemicals, preparation and procedures used in applying coating on metals. Experimental details are provided for the oxidation and hot corrosion runs carried out on coated alloys. There is an account of the different techniques employed during oxidation/hot corrosion experiments, which include optical and scanning electron microscopy (SEM), X-ray diffraction analysis and energy dispersive X-ray analysis (EDAX).
CHAPTER III deals with the high temperature oxidation behaviour of nickel aluminide coatings on mild steel.

Nickel aluminide coatings have been prepared on mild steel by the diffusion of Ni/Al in different layers of Al/Al$_2$O$_3$ at high temperatures using an activator.

High temperature oxidation behaviour of nickel aluminide-coated mild steel has been studied at 750°C, 800°C and 850°C in air. The influence of rare earth oxide addition on the oxidation rates of nickel aluminide coating on mild steel has also been investigated.

The oxidation of nickel aluminide-coated steel proceeds by a diffusion controlled mechanism which is indicated by the parabolic nature of weight gain vs time plots at 750°C, 800°C and 850°C. The parabolic behaviour has also been noticed in presence of varying amounts of different rare earth oxides (RE$_2$O$_3$) such as Yb$_2$O$_3$, Tb$_2$O$_3$, Sm$_2$O$_3$, Y$_2$O$_3$, Ho$_2$O$_3$, Gd$_2$O$_3$, La$_2$O$_3$, Pr$_2$O$_3$, Nd$_2$O$_3$ or Er$_2$O$_3$. The addition of RE$_2$O$_3$ in relatively small amounts (upto 2 weight %) and at relatively low temperatures (upto 750°C) increases the oxidation rates slightly but at higher temperatures (800°C and 850°C) the oxidation rates of the nickel aluminide coating are lowered down markedly irrespective of rare earth oxide concentration.

It is difficult to present a simple relationship between the size of the rare earth and the oxidation rates of RE$_2$O$_3$-containing nickel aluminide coating on mild steel. However,
in general, the oxidation rate of the coated alloy decreases with increasing ionic size provided the irregular behaviour of the first few members of the lanthanide series is ignored. Similar behaviour was observed in case of simple aluminide coatings where the oxidation rate of the coated alloy decreases with increasing ionic radius of rare earth.

The micro-structure of nickel aluminide coating in general, comprises of 3 phases: NiAl$_2$(dark), Al$_2$O$_3$(light) and RE$_2$O$_3$(grey). During oxidation NiAl$_2$ gets converted into Al$_2$O$_3$ which constitutes inner scales, RE$_2$O$_3$ is largely concentrated at the alloy/scale interface although it is present as inclusion in the outer scales also. The oxidation proceeds by Fe$^{2+}$ diffusion resulting in the formation of copious FeO scales. The scales are usually compact and adherent with low porosity. The adherence seems to be improved by the presence of rare earth oxides. In nickel aluminide coated low or medium carbon steels, the decarburization during oxidation greatly affect the adherence of the scales and the beneficial effects of the addition of rare earth oxide are not so obvious. In cases where the oxide scales are not disturbed due to decarburization, the effect of rare earth oxide addition is more clearly pronounced and the oxidation rates are significantly lowered down. Wherever small pegs or ridges of rare earth oxides are formed at the alloy/scale interface they act as fastners between Al$_2$O$_3$ and alloy sub-
trate and are responsible for lowering down the oxidation rates of the alloys.

CHAPTER IV contains the results of a study concerning with high temperature corrosion of borosilicate coatings on mild steel. The study is comprised of three parts.

A. Oxidation behaviour of mild steel in presence of $\text{Na}_2\text{SO}_4$
B. Oxidation behaviour of borosilicate coating on mild steel
C. Oxidation behaviour of borosilicate coated mild steel in presence of $\text{Na}_2\text{SO}_4$

A. Oxidation behaviour of mild steel in presence of $\text{Na}_2\text{SO}_4$

The hot corrosion behaviour of mild steel in presence of a thin film of $\text{Na}_2\text{SO}_4$ (2 to 10 mg/cm$^2$) has been studied in the temperature range of $700^\circ$ to $900^\circ$C in a limited supply of air. The hot corrosion studies involve weight gain versus time and weight gain versus amount of $\text{Na}_2\text{SO}_4$ deposited measurements. At $700^\circ$C, the corrosion rates seem to be independent of the amount of $\text{Na}_2\text{SO}_4$ deposited. After initial oxide formation, $\text{Na}_2\text{SO}_4$ seems to act as a barrier layer and practically there is little change in oxidation rate (or weight gain) with increasing salt deposition. Therefore, it is not surprising to find out that the oxidation rates of $\text{Na}_2\text{SO}_4$-coated mild steel are lower than the mild steel itself at $700^\circ$C. At $700^\circ$C, no or very little hot corrosion attack is observed. At $800^\circ$C, the hot corrosion attack is significant as indicated by weight
gain vs time measurements and microstructure studies. The alloy is deleteriously attacked at 900°C.

At 800° and 900°C, Na₂SO₄(↓) attacks the multioxide scales already present on the steel. A salt fluxing reaction takes place resulting in the formation of NaFeO₂ and/or Na₂FeO₂ consumption of oxygen at the salt/scale results in an increasing S-activity and in consequence, sulfide is formed in the outer scales. Na₂SO₄(↓) also penetrates into the alloy and a limited sulfidation occurs in the regions of the vicinity of alloy/scale interface.

B. Oxidation behaviour of borosilicate coating on mild steel

The oxidation behaviour of borosilicate coating on mild steel was studied at 700°, 800° and 900°C in a stream of air. Furthermore, the influence of the addition of rare earth oxides: La₂O₃, Sm₂O₃, Gd₂O₃, Y₂O₃, Yb₂O₃, Ce₂O₃, Nd₂O₃, Er₂O₃, Pr₂O₃, Tb₂O₃ or Ho₂O₃ on the oxidation rates of borosilicate coated mild steel was also studied.

The borosilicate coating on mild steel was prepared by slurry method using powdered mixture of SiC₂, B₂O₃ and Al₂O₃ in the ratio of 1:2:3 (by weight), respectively. The corresponding rare earth oxide (RE) containing borosilicate coating was prepared similarly using RE₂O₃ as an additional constituents.

The oxidation of borosilicate coating on mild steel in air at 700° and 800°C proceeds by a diffusion controlled
mechanism as indicated by the parabolic nature of weight gain vs time plots. However at 900°C, there is deviation from the parabolic behaviour after exposure time ranging from 6 to 10 hrs as evident from the breaks in weight gain vs time plots.

Considering the effect of rare earth oxide addition on the oxidation rate of borosilicate alloy, at 700°C, the presence of rare earth oxide addition in fact increases the oxidation rate of borosilicate-coated alloy. However, at higher temperatures (800° and 900°C), the addition of RE₂O₃ lowers the oxidation rate of borosilicates-coated alloy considerably.

At 800° and 900°C, there is a progressive increase in oxidation rate with increasing ionic size of rare earth reaching a maximum in middle of the lanthanide series (Gd³⁺) and then the rate progressively decreases having a minimum around Nd³⁺, the difference between oxidation rates is though nominal.

The X-ray diffraction analysis of the borosilicate coating on mild steel indicates the presence of 3 phases: Al₂O₃, iron borosilicate FeB₂SiO₄ and SiO₂. The microstructure shows the presence of Al₂O₃ as polygonal grains and SiO₂ as inclusions in a dark or light grey matrix of iron borosilicate. The addition of RE₂O₃ results in the introduction of a new phase, thus RE₂O₃ is present in the microstructure.
as dispersoids in the borosilicate matrix and some of the RE₂O₃ is concentrated at the alloy/coating interface along with FeO. During disruption of the coating either due to decarburization (evolution of CO/CO₂) or thermal effects Fe₂O₃ is formed by anion diffusion and present as a thick layer.

The addition of rare earth oxide improves the adherence of protective oxide scales and thus lowers the oxidation rates of borosilicate coated alloys. However, separation between metal and scales is frequently observed due to decarburization during oxidation inspite of the compactness of the scales and the coating.

C. Behaviour of borosilicate coated mild steel in presence of Na₂SO₄

Hot corrosion studies have been carried out on borosilicate coated mild steel in presence of Na₂SO₄ at 700°C, 800°C and 900°C in a limited supply of air. Besides hot corrosion kinetics the morphology of the corroded alloy was investigated using optical and scanning microscopy and X-ray diffraction analysis.

The weight gain versus amount of Na₂SO₄ deposited plots indicate that the specimen exposed for relatively short periods (upto 6 hrs) exhibit a steep increase in weight gain with increasing Na₂SO₄ deposition. However, for borosilicate
coated specimen exposed for relatively longer periods (12 to 24 hrs), after an initial weight gain at low Na$_2$SO$_4$ concentrations, there is little or no change in weight gain values on further increasing the amount of Na$_2$SO$_4$ deposited. This behaviour is observed at all the three temperatures viz. 700$^\circ$, 800$^\circ$ and 900$^\circ$C but is more pronounced at 700$^\circ$ and 800$^\circ$C.

Weight gain vs time plots for the oxidation of Na$_2$SO$_4$ coated borosilicate coating on mild steel show that the behaviour is parabolic at 700$^\circ$C during the entire 24 hrs oxidation run but at 800$^\circ$C, the parabolic behaviour is exhibited upto 12 hrs followed by faster oxidation rate. At 900$^\circ$C, the behaviour is approximately linear. The net weight gains after 24 hrs exposure are independent of the amount of Na$_2$SO$_4$ deposition but strongly dependent of temperature.

The attack of Na$_2$SO$_4$ on borosilicate coated steel is not significant at 700$^\circ$C but quite appreciable at 800$^\circ$C. Na$_2$SO$_4$ appears to be very aggressive at 900$^\circ$C, the borosilicate coating is virtually disintegrated and subsequently salt attacks the alloy by a combination of fluxing and sulfidation reactions.

CHAPTER V covers the studies concerning with hot corrosion behaviour and high temperature oxidation of borosilicate coated Inconel 600 alloy.

The hot corrosion behaviour of Inconel 600 alloy has been studied in presence of Na$_2$SO$_4$ at 800$^\circ$, 900$^\circ$ and 1000$^\circ$C.
in a limited supply of air.

Weight gain versus amount of Na₂SO₄ plots show an increase in corrosion rate with increasing Na₂SO₄ at 800°, 900° and 1000°C up to a certain concentration of Na₂SO₄. On exceeding this concentration, the corrosion rate starts decreasing. It appears that Na₂SO₄(↓) reacts with the metal undergoing fluxing and sulfidation reactions and when the reaction is completed, the exceeded amount of Na₂SO₄ act as a protective layer resulting in no or very little change in weight. The weight losses occurred during corrosion of Inconel 600 are attributed to the loss of some reaction products due to volatilization of Na₂CrO₄/Na₂Cr₂O₄ and/or evolution of SO₂ and O₂ at 900°C and above.

High temperature oxidation studies on borosilicate coated Inconel 600 alloy have been carried out at 800°, 900° and 1000°C for 24 hrs in air. In general, the oxidation proceeds by a parabolic rate law at all the 3 temperatures as indicated by the linear nature of weight gain vs time plots. However, breaks are noted in the plots at 900° and 1000°C after 5 hrs and 8 hrs exposures respectively. In general, the presence of borosilicate coating, on Ni-base Inconel 600 alloy which is a corrosion and heat resistant alloy, lowers the oxidation rate of the substrate alloy. The effect is much more pronounced at 900° and 1000°C where the coated alloy has oxidation rates about one order of magnitude lower.
than the uncoated alloy. It appears that iron borosilicate 
$\text{Fe}_2\text{SiO}_4$ along with $\text{Al}_2\text{O}_3$ act as a barrier layer against 
oxidation.

The hot corrosion behaviour of borosilicate coated 
Inconel 600 in presence of $\text{Na}_2\text{SO}_4$ has been studies at $800^\circ$, 
$900^\circ$ and $1000^\circ\text{C}$ in flowing air.

Following generalization can be inferred from the 
weight gain vs time and weight gain vs amount of $\text{Na}_2\text{SO}_4$ de­
sited plots:

(i) At a particular temperature and exposure time, the 
weight gain increases with increasing amount of salt 
coating till a maximum is reached. This is followed 
by the lowering in weight gain values with further 
increase in the amount of $\text{Na}_2\text{SO}_4$ deposition on metal 
coupons. 1-2 mg/cm$^2$ is the usual amount of the salt 
to achieve a maximum weight gain.

(ii) At a particular $\text{Na}_2\text{SO}_4$ concentration and temperature, 
maximum weight gain value is observed usually at an 
exposure time of about 12 hrs (at $900^\circ$ or $1000^\circ\text{C}$) and 
6 hrs ($800^\circ\text{C}$).

(iii) With a few exceptions, the corrosion rate (or weight 
gain values) increases with increasing temperature, 
the rate at $1000^\circ\text{C}$ being the highest.

It appears that there is little or no attack at $800^\circ\text{C}$. 
However at $900^\circ$ and $1000^\circ\text{C}$, the $\text{Na}_2\text{SO}_4$ induced hot corrosion
attack is deleterious and the borosilicate coating is disintegrated. The hot corrosion attack is also quite severe at the alloy interface. The corrosion products as identified by X-ray diffraction analysis include sulfides \((\text{Fe,Cr})_2S_3\), \(\text{NiS}\), \(\text{FeS}\) and mixed oxides such as \(\text{NaFeO}_2\), \(\text{FeCrO}_4\), \(\text{Na}_2\text{CrO}_4\), \(\text{NaNiO}_2\) etc. The nature of the corrosion products and the microstructural studies point out a sulfidation and salt fluxing mechanisms operating during hot corrosion attack on borosilicate coated Inconel 600 alloy.
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1990
Dedicated
To
My Parents
CERTIFICATE

This is to certify that the Ph.D thesis entitled "PHYSICO-CHEMICAL STUDIES ON INORGANIC COATINGS" which has been submitted by Mr. Rais Ahmad contains an original piece of research. The work has been carried out under my supervision and it has not be submitted elsewhere for the award of a degree or diploma.

MOHAMMAD AJMAL

( MOHAMMAD AJMAL )
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CHAPTER - I 1-37

INTRODUCTION 1

OXIDATION OF METALS AND ALLOYS 1

1.1 Oxidation of Iron 1

1.1.1 Oxidation of Iron base alloys 2

1.2 Hot Corrosion and its Importance 4

1.3 Importance of Coating 7

1.4 Organic Coatings 10

TYPES OF COATING

1.4.1 Stoved Phenolic Coatings 11

1.4.2 Epoxy/Phenolic Coatings 11

1.4.3 Polyester/Glass Flake Coatings 12

1.4.4 Powder Coatings 12

1.4.5 PVC Plastisol Coatings 12

1.5 Inorganic Coatings 12

1.5.1 Aluminide Coatings 13

1.5.2 Phosphate Coatings 16

1.5.3 Silicate Coatings 17

1.5.4 Borate Coatings 18

1.5.5 Carbide Coatings 19

1.5.6 Boride Coatings 20

1.5.7 Silicide Coatings 20

1.5.8 Nitride Coatings 22

1.6 Method of Coating Technology and their application 23
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.6.1</td>
<td>Pack Cementation</td>
<td>24</td>
</tr>
<tr>
<td>1.6.2</td>
<td>Gas Phase-Chemical Vapour Deposition</td>
<td>25</td>
</tr>
<tr>
<td>1.6.3</td>
<td>Slurry Coatings</td>
<td>25</td>
</tr>
<tr>
<td>1.6.4</td>
<td>Electroplating plus Pack Cementation</td>
<td>26</td>
</tr>
<tr>
<td>1.6.5</td>
<td>Fused Salt Electrolysis</td>
<td>26</td>
</tr>
<tr>
<td>1.6.6</td>
<td>Electrophoresis</td>
<td>27</td>
</tr>
<tr>
<td>1.6.7</td>
<td>Electro Beam Evaporation</td>
<td>27</td>
</tr>
<tr>
<td>1.6.8</td>
<td>Ion implanting process</td>
<td>27</td>
</tr>
<tr>
<td>1.6.9</td>
<td>Flame spray process</td>
<td>29</td>
</tr>
<tr>
<td>1.7</td>
<td>Ceramics and Glass type coating</td>
<td>30</td>
</tr>
<tr>
<td>1.8</td>
<td>High temperature Application of Inorganic Coating</td>
<td>34</td>
</tr>
<tr>
<td>1.9</td>
<td>Statement of the Problem</td>
<td>38</td>
</tr>
</tbody>
</table>

CHAPTER - II

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0</td>
<td>Materials and Method</td>
<td>40</td>
</tr>
<tr>
<td>2.1</td>
<td>Materials</td>
<td>40</td>
</tr>
<tr>
<td>2.2</td>
<td>Specimen preparation</td>
<td>40</td>
</tr>
<tr>
<td>2.3</td>
<td>Chemicals used</td>
<td>40</td>
</tr>
<tr>
<td>2.4</td>
<td>Apparatus used</td>
<td>40</td>
</tr>
<tr>
<td>2.5</td>
<td>Coatings preparation</td>
<td>41</td>
</tr>
<tr>
<td>2.5:A</td>
<td>Nickel Aluminide coating</td>
<td>41</td>
</tr>
<tr>
<td>2.5:B</td>
<td>Boro-Silicate coating</td>
<td>42</td>
</tr>
<tr>
<td>2.5:C</td>
<td>Sodium sulphate (Na₂SO₄) coating</td>
<td>42</td>
</tr>
<tr>
<td>2.6</td>
<td>Oxidation Kinetics</td>
<td>43</td>
</tr>
</tbody>
</table>
2.7 Hot Corrosion Studies 43
2.8 Metallographic Studies 44
2.9 Scanning Electron Microscopy (SEM) 44
2.10 Energy Dispersive X-ray Analysis (EDAX) 45
2.11 X-ray Diffraction Analysis 45

CHAPTER - III 46-55

3.1 HIGH TEMPERATURE OXIDATION BEHAVIOUR OF NICKEL ALUMINIDE COATINGS ON MILD STEEL 46
3.2 Results 47
3.2.1 Oxidation Kinetics 47
3.2.2 Metallographic Studies 48
3.3 Discussion 54
3.4 Conclusion 55

CHAPTER - IV 61-79

A. OXIDATION BEHAVIOUR OF MILD STEEL IN PRESENCE OF Na$_2$SO$_4$ 61
4.1 Results 61
4.1.1 Hot Corrosion studies 61
4.1.2 Oxidation studies 61
4.1.3 Microstructural studies 62
4.1.4 Discussion 63

B. OXIDATION OF BOROSILICATE COATING ON MILD STEEL 66
4.2.1a Oxidation kinetics 66
4.2.1b X-ray Diffraction Analysis 66
4.2.1c Microstructural studies 66
4.2.2 Experimental
4.2.2a Materials
4.2.2b Preparation of Borosilicate Coating
4.2.3 Results
4.2.4 Oxidation Kinetics
4.2.5 Microstructural studies
4.2.6 Discussion

C. BEHAVIOUR OF Borosilicate Coated Mild Steel
   in Presence of Na₂SO₄
4.3 Results
4.3.1 Hot Corrosion studies
4.3.2 Oxidation studies
4.3.3 Morphological studies
4.3.4 Discussion

CHAPTER - V
A. HIGH TEMPERATURE OXIDATION BEHAVIOUR OF
   Inconel 600 Alloy in Presence of Na₂SO₄
5.1 Results
5.1.1 Hot Corrosion studies
5.1.2 Microstructural studies
5.1.3 Discussion

B. HIGH TEMPERATURE OXIDATION BEHAVIOUR OF
   Borosilicate Coated Inconel 600 Alloy
5.2 Results
5.2.1 Microstructural studies
<table>
<thead>
<tr>
<th>Section</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.2.2</td>
<td>Discussion</td>
<td>86</td>
</tr>
<tr>
<td>C.</td>
<td>HIGH TEMPERATURE OXIDATION BEHAVIOUR OF BOROSILICATE COATED INCONEL 600 ALLOY IN PRESENCE OF Na$_2$SO$_4$</td>
<td>89</td>
</tr>
<tr>
<td>5.3</td>
<td>Results</td>
<td>90</td>
</tr>
<tr>
<td>5.3.1</td>
<td>Oxidation kinetics</td>
<td>90</td>
</tr>
<tr>
<td>5.3.2</td>
<td>Microstructural studies</td>
<td>91</td>
</tr>
<tr>
<td>5.3.3</td>
<td>Discussion</td>
<td>91</td>
</tr>
</tbody>
</table>

CHAPTER - VI

Conclusions  93
References    96
LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1</td>
<td>Parabolic rate constant $K_p$ ($g m^{2} cm^{-4} s^{-1}$) of pure nickel aluminide coating and Ni-Al coating containing 2 wt. % of $RE_2O_3$ on mild steel oxidized in the temperature range 750°, 800°, and 850°C ($x 10^{-8} g m^{2} cm^{-4} s^{-1}$).</td>
<td>56</td>
</tr>
<tr>
<td>3.2</td>
<td>Parabolic rate constant $K_p$ ($g m^{2} cm^{-4} s^{-1}$) of pure nickel aluminide coating and Ni-Al coating containing 1 wt. % of $RE_2O_3$ on mild steel oxidized in the temperature range 750°, 800°, and 850°C ($x 10^{-8} g m^{2} cm^{-4} s^{-1}$).</td>
<td>57</td>
</tr>
<tr>
<td>3.3</td>
<td>Parabolic rate constant $K_p$ ($g m^{2} cm^{-4} s^{-1}$) of pure nickel aluminide coating and Ni-Al coating containing 4.7 wt. % of $RE_2O_3$ on mild steel oxidized in the temperature range 750°, 800°, and 850°C ($x 10^{-8} g m^{2} cm^{-4} s^{-1}$).</td>
<td>58</td>
</tr>
<tr>
<td>3.4</td>
<td>Activation energies for the oxidation of nickel aluminide coating and Ni-Al coating containing 2 wt. % of $RE_2O_3$ of mild steel.</td>
<td>59</td>
</tr>
<tr>
<td>3.5</td>
<td>Activation energies for the oxidation of nickel aluminide coating containing 4.7 wt. % of $RE_2O_3$ on mild steel.</td>
<td>60</td>
</tr>
<tr>
<td>3.6</td>
<td>Activation energies for the oxidation of nickel aluminide coating containing 1 wt. % of $RE_2O_3$ on mild steel.</td>
<td>60</td>
</tr>
<tr>
<td>Table</td>
<td>Page</td>
<td></td>
</tr>
<tr>
<td>-------</td>
<td>------</td>
<td></td>
</tr>
<tr>
<td>4.2.7 Parabolic rate constant, $K_p$ for the oxidation of borosilicate coated-mild steel in presence of different rare earth oxides (14 weight %).</td>
<td>76</td>
<td></td>
</tr>
<tr>
<td>5.2 Parabolic rate constant $K_p$ ($\text{g m}^{-2}\text{cm}^{-4}\text{s}^{-1}$) of plain and borosilicate coated Inconel-600 alloy oxidized in the temperature range $800^\circ, 900^\circ$ and $1000^\circ\text{C}$ ($X \times 10^{-10} \text{g m}^{-2}\text{cm}^{-4}\text{s}^{-1}$).</td>
<td>88</td>
<td></td>
</tr>
</tbody>
</table>
Chapter 1
CHAPTER - 1

INTRODUCTION

OXIDATION OF METALS AND ALLOYS

1.1 Oxidation of Iron

When iron is exposed to oxygen at temperatures higher than 560°C, a relatively complex reaction system is involved due to the formation of multilayered scales comprising of wustite (FeO), magnetite (Fe₃O₄) and haematite (Fe₂O₃). The Fe-O diagram (Fig. 1.1.A) shows that at temperatures above 560°C, iron forms three oxides, the lowest valency oxide, FeO (wustite), has a NaCl type cubic structure and is metal deficient of the order of 5-12% of iron vacancies. Being cation conducting it grows entirely by the diffusion of iron and appears as innermost layer. The second oxide, Fe₃O₄ (magnetite), has a spinel type structure and is an oxygen excess compound. It grows largely by oxide ion diffusion with an appreciable contribution from iron ion diffusion (12%). The highest valency oxide, Fe₂O₃ (haematite), which forms outermost layer of the multilayer scales has rhombohedral crystal structure. It is slightly oxygen deficient, metal excess and largely grows by oxide ion diffusion. The relative percentages of FeO, Fe₃O₄ and Fe₂O₃ in the scales vary with temperature (Fig. 1.1.B), duration of oxidation and nature of oxidizing.
gas. However, above 600°C, FeO is the predominant species and since FeO has more defective structure than either of the two oxides, iron oxidizes much more rapidly above this temperature. Since the three oxides are formed simultaneously upon the iron surface and the ratio of the thickness of three layers is reported to be dependent of time and temperature, the mechanism of oxidation is not simple and requires several mechanistic approaches at various stages of oxidation. Below 560°C, FeO is unstable and if any is formed above this temperature it decomposes at room temperature into Fe$_3$O$_4$ plus Fe.

1.1.1 Oxidation of Iron-Base Alloy

Failure of pure iron to form sufficiently protective oxide layer suitable for practical application at temperatures above 500°C, demands the presence of an alloying element which has a higher oxygen affinity than iron and where oxide grows at a low rate. Generally, Cr or in some cases Al or Si serves this purpose, and when present in sufficient concentrations, protective scales of Cr$_2$O$_3$, Al$_2$O$_3$ or SiO$_2$ are formed exclusively.

At low alloying concentrations, the oxide scales are still similar to those on pure iron, with the alloying element remaining in solution in wustite and other oxides. The defect concentration may be modified, usually increased, resulting in change in oxidation rate. At higher concentra-
Fig. 1.1.A Iron Oxygen Phase diagram

Fig. 1.1.B Relative thickness of Fe₂O₃ and Fe₃O₄ in the scaling of iron in air.
tions, the composition range of FeO becomes restricted and eventually disappears as a single phase. Compound oxides of general formula $\text{Fe(FeM)O}_4$ with spinel structure are formed. Here M is the alloying element. Often these spinels can exist over a range of composition and usually their appearance in the scale results in a decrease in the overall oxidation rate. At higher concentration still a complete selective oxidation may occur with a maximum reduction in the overall oxidation rate.

Rahmel proposed a reaction mechanism for the oxidation of dilute binary iron alloys with alloying additions which are less noble than iron, e.g., V, Cr, Si and Mo. Initially these alloys oxidize like pure iron resulting in the formation of iron oxides. Subsequently oxygen dissolves in the alloy phase causing internal oxidation, and because of the preferential oxidation of iron, the alloying addition is enriched at the metal/oxide interface. As the oxide of alloying addition is formed, this reacts with FeO to form $\text{Fe(FeM)O}_4$, giving two phase inner layer.

1.2 Hot Corrosion and its Importance

The accelerated corrosion process in which metallic alloys and ceramics become degraded at elevated temperatures (500°C and above) under the combined action of a gas and a deposit is termed as hot corrosion. The excellent high temperature oxidation resistance of heat resistant Fe, Ni or Co-
base alloys is seriously affected when adhered $\text{Cr}_2\text{O}_3$ or $\text{Al}_2\text{O}_3$ protective scales are attacked by an electrolytic deposit. According to current usage in the literature, the phenomenon of hot corrosion is the accelerated oxidation in a high temperature gaseous environment of a material whose surface is coated by a thin fused salt film. It is very often encountered in the combustion environments. However, if the metal/alloy is in contact with a fused or molten electrolytic deposit in the presence or absence of an oxidizing environment, accelerated oxidation is often observed and the kinetic is no more parabolic. This type of accelerated oxidation or corrosion is also called hot corrosion.

Historically, hot corrosion was initially encountered in industrial gas turbines in the late 40's. Hot corrosion of boiler tubes made of low carbon steel was reported\textsuperscript{4} as early as 1945 leading to their failure. However, turbine manufacturers and users became aware of hot corrosion in the late 1960s, when serious corrosive attack occurred for helicopters and rescue planes in service over and near sea water during Vietnam conflict. The serious nature of hot corrosion received considerable attention during the last three decades when reports of attack on alloys used for land based gas turbines, and for aircraft and ship turbine engines were scientifically investigated\textsuperscript{5}.

A survey carried out by Rapp, Devan, Douglass, Nordine.
Pettit and Whittle, illustrates that most of the high temperature energy systems experience hot corrosion problem. The hot corrosion of blades and first stage guide vanes of gas turbines exposed to marine and industrial atmospheres has received considerable attention in the recent past. It is frequently encountered in marine or land-based gas turbines, thermal power generating units, incinerators, petroleum refineries, coal gasifiers and liquifiers, chemical plants, nuclear power reactors, carbonate and sulfide batteries, etc. Extensive corrosion of metals occurs in gas turbines that operate in marine or other salt contaminated environments. In the operation of gas turbines near and over the ocean, a fused Na$_2$SO$_4$-NaCl film from an ingested sea salt aerosol may coat the hardware and lead to the accelerated oxidation of turbine alloys.

Hot corrosion is associated with the formation of a corrosive and molten electrolytic deposit on the surface of the hot component. These deposits include a wide variety of fused salts, which include alkali and alkaline earth surfaces, chlorides, carbonates and vanadates or the salts which lower the liquidus temperatures. Amongst them Na$_2$SO$_4$ has received greatest attention due to its involvement in majority of the engineering systems which may be subjected to this type of attack. Na$_2$SO$_4$ may in some cases, be formed from a reaction between NaCl from ingested sea water aerosols in the air and SO$_2$ or SO$_3$ present either in the combustion gases or in the
combustion products of the fuel. The reaction can be represented as follows:\(^8\):

\[
2\text{NaCl} + \{\text{SO}_2\} + \{\frac{1}{2} \text{O}_2\} \rightarrow \text{Na}_2\text{SO}_4 + \text{Cl}_2
\]

Equilibrium calculations show that above reaction should go almost completely to the right. Likewise, water vapours could supply the oxygen with the formation of HCl vapour. On the other hand, sea water contains a significant amount of \(\text{Na}_2\text{SO}_4\) and thus the simple vaporization of the aerosol may provide the necessary \(\text{Na}_2\text{SO}_4\). Generally, NaCl is not found in the deposit. But recent papers\(^9-12\) have reported the existence of small amounts of NaCl in the deposits which caused severe attack. Other constituents of the deposits include calcium and magnesium sulfates (a one to one mixture of \(\text{Na}_2\text{SO}_4\) and \(\text{MgSO}_4\) with four moles of hydrated water has the melting point of 621°C, compared to 884°C for anhydrous \(\text{Na}_2\text{SO}_4\)), oxides and sulfates of Ni, Co and Fe and vanadates. When carbon is found in the deposits on blades from service, it enhances greatly the hot corrosion attack, as does the presence of a reducing gas such as \(\text{CH}_4\)\(^13\). Even though hot corrosion is an important form of materials degradation that has been studied rather extensively, there is no agreement on which of those its characteristics are the most important.

1.3 Importance of Coatings

A large number of coating materials have been used to
protect metals and alloys from corrosion at high temperature. The development of coating materials has been a subject of extensive research for at least three decades. The main objective behind coating development is to achieve certain properties which are a combination of characteristics of metals and alloys. The premature failure of the metal or alloy due to corrosion could be controlled with the help of coatings. The coatings on high temperature materials such as superalloys have wide applicability ranging from nuclear reactors to gas turbines and to the components used in power generating units. For example, the aerofoil section of a gas turbine requires protection against the hot gas environment in which it has to operate. There may be a high velocity oxidizing gas stream, impurities may be present in the fuel, temperature may be nonuniform or there may be a fuel ash deposit. The effect of these complex environmental aspects can be restricted through the careful selection of coatings which can withstand the severe operating conditions in which the materials have to function. The selection of coating materials depends on the nature of the components and its behaviour under operating conditions. The protective properties of coatings are dependent on two extremely important factors:

(i) The mechanical and chemical properties of the film itself.

(ii) Adhesion, the bond between the film and the surface it covers.
The first factor is independent of the surface to be covered and is entirely dependent on the properties of the constituents of the film. The second factor plays an important role in coating technology. It is determined by the physical and chemical properties of the surface of the coating and the substrate.

According to the properties of the coatings and the nature of the metals or alloys on which these coatings are applied, coatings are classified into metallic and non-metallic. Metallic coatings are comprised of films of metals or alloys deposited on the substrate by spraying or diffusion or electrolysis. Non-metallic coating is defined as the thin coating of nonmetallic substances on metals which protect the substrate from the action of surrounding medium and should also have a decorative effect. Coatings can be classified into two groups:

1. Organic
2. Inorganic

Organic coatings contain an organic compound of high molecular weight such as dye, rubber, plastic or a combination of two or more such materials and a carrier which is usually a mineral oil. Inorganic coatings include compounds of metals or non-metals such as phosphates, chromates or oxides formed in situ on the surface of metals or coatings based on silicate or borate enamels which contain simple silicate or simple borate
or complex borosilicate or aluminosilicates. The hard refractory materials such as carbides, silicides, borides, nitrides etc. are used for specialized applications in aerospace industry.

1.4 Organic Coatings

Organic coatings are mainly applied to mild steel structures and equipments. To a lesser extent, they are also used on aluminium and zinc sprayed and galvanized steel. Perhaps the most important application of organic coatings is in processing plants used in chemical industries. The use of organic coatings has increased considerably in recent years because of the production of many new synthetic resins on a commercial scale. This has resulted not only in more corrosion resistant paints but also in a wide range of plastics that can be economically applied as relatively thick linings by dipping or spraying. For equipments such as pumps, open topped tanks etc., the exteriors of which are likely to be splashed by corrosive process liquors, paints with a higher standard of chemical resistance are required. Thixotropic bitumen or coal tar pitch paints that will give a thickness upto 250 μm per coat are the oldest of the chemical resistant paints. They will withstand both dilute inorganic acids and alkalis. High build chlorinated rubber paints which will give a thickness of 100 μm per coat are commonly used for process plant equipment. Because of their
good resistance to alkalis, chlorinated rubber paints are very suitable for their use on concrete. Epoxy resin paints produce a hard and abrasion resistant coating and are resistant to fats, oils and many organic solvents. Polyurethane paints are 2-pack paints consisting of polyester resin cured with an isocyanate. They have excellent resistance to water immersion.

All these coatings described above require special equipment for application i.e. ovens for high temperature curing, tanks for dipping or special guns for spraying.

Types of Coating:

1.4.1 Stoved Phenolics Coatings

The acid resistance of these coatings is outstanding except to strongly oxidizing acids such as concentrated sulphuric and nitric. They are also resistant to a wide range of organic solvents. In dry conditions they can be used up to 200°C and in wet conditions upto 100°C. They are brittle coatings and have a thickness upto 25 μm.

1.4.2 Epoxy/Phenolic Coatings

They are slightly inferior to phenolic coatings in respect of acid resistance but much better in resistance to alkaline solutions. They are less brittle than the phenolic coatings.
1.4.3 Polyester/Glass Flake Coatings

They produce much thicker and tougher coatings than phenolics and so are less likely to suffer damage in service. The corrosion resistance of these coatings depends on the polyester used. They are applied for renovation of steel tanks used for oil storage in which the bottoms have corroded.

1.4.4 Powder Coatings

Most plastics are available as powders and can be applied as coatings by fluidized or spraying techniques. Those that have proved most useful for chemical plant protection are polyethylene, polypropylene, nylon 11 and epoxy.

1.4.5 PVC Plastisol Coatings

These are applied by preheating the object to be coated and then dipping into a tank of liquid plasticized PVC emulsion. This is followed by curing in an air oven at a temperature of about 200°C. Very large items can be dealt with in this way. The thickness of the coating depends on the thickness of the metal and the extent of the preheating but the usual range is 3 to 6 mm. The coating is tough and abrasion resistant. These coatings are very resistant to acids and alkalis. They are generally applied on floor gratings, ducting and pipe.

1.5 Inorganic Coatings

Amongst the various types of inorganic coatings used
for corrosion resistance, phosphate, oxide, silicate, chromate and borate coatings are applied in less severe corrosive environments and at moderate temperatures whereas aluminide, boride, silicide, carbide and nitride coatings are found to be suitable for more severe corrosive environments and at elevated temperatures.

1.5.1 Aluminide Coatings

These are the most widely used coatings and are suitable under high temperature oxidation environments. These coatings are based on aluminide compounds. They have been used on Ni- and Co-based superalloys where nickel and cobalt aluminides are formed, respectively. They are most effective in less severe environments and at moderate temperatures.

In more severe or highly corrosive environments, diffusion coatings based on the addition of noble metals to aluminide are used. Noble metal enriched aluminide coatings have been used to protect superalloy components in the hot section of FT$_4$ engines installed on oil rig in the north sea in 1980. These components operate in a highly sulfidating environment. Lavendel and Henry$^{15}$ have prepared corrosion resistant aluminide coatings on Fe- and Ni-base alloys. The fused slurry of nickel-containing coatings having 55-58 % Al and 5-10 % Si was deposited on mild steel and inconel-600 substrates. Phase composition and distribution in the coating were controlled by adjustment of the reciprocal activities of Al and Ni in the
reactive liquid generated during fusion. Slurries with balanced Al-Ni concentration produce single phase coatings. The coating forms a thin adherent protective scale on Inconel-600 within the first 125 hrs. of cyclic exposure at 1100°C. The coating is degraded either by the loss of Al or enrichment in Ni or Fe by interdiffusion with the substrate. The 7-NiAl a transformation product of 3-NiAl retains enough Si in solution to maintain unchanged oxidation kinetic. The coating is better than the common aluminide coating and is good for use in gas turbines.

Aluminide coatings are known to protect steels from oxidation and corrosion in hydrocarbon and sulfur bearing atmospheres besides increasing the oxidation resistance e.g. refinery processing. Aluminide coated steel tubes are finding increasing use as reactor internals, heat exchangers etc. These coatings also find wide applications in both coal gasification and liquifaction technologies. The aluminized steel performs better than stainless steel.

The influence of chromo-aluminide coatings on the creep and stress rupture properties of a wrought Udimet-520 nickel-base superalloy used in gas turbine blade applications has been reported. Creep and stress rupture tests were conducted at 802°C on coated and uncoated wrought bars in the fully heat treated conditions. The tests showed that the application of the chromoaluminide coatings caused a marked deterioration
in rupture strength and ductility. The mechanical behaviour in the coated creep resistant alloy was correlated with the microstructures. The formation of nickel aluminides by the thermal explosion mode of gasless combustion synthesis was investigated\textsuperscript{17} for Ni-Al powders ranging in composition from 5 to 30\% of Al. Compound formation was found to take place sequentially starting with the most aluminium-rich and ending with AlNi\textsubscript{3} as the predominant compound in the product. Compound formed through both solid and liquid state reactions, with the relative contribution of each depending on the rate of heating of the powders to the reaction temperature. Aluminium (Al-N) thin films used as protective overcoats for terbium-iron mageneto-optical media\textsuperscript{18}. Protective performance of the aluminium nitride overcoats was evaluated by electrochemical polarization, immersion tests and environmental exposure studies. The corrosion currents for Al-N coated Tb-Fe films were significantly lower than those of unprotected Tb-Fe films indicating that Al-N protected films have lower corrosion rates. Further, Al-N coatings were found to exhibit better corrosion resistance than silicon dioxide (SiO\textsubscript{2}) overcoated Tb-Fe films.

This coating can be formed by a number of techniques such as hot dipping, flame spraying and pack cementation. Among these processes, pack cementation is ideally suited for the coating. There have been a few investigations on the
structure and phase composition of aluminide diffusion layers on both plain carbon and stainless steels\textsuperscript{20,21}. The nature and growth kinetics of the coating are influenced by temperature, time and type of activator (halide salt)\textsuperscript{22}. Pack aluminizing of steel in unalloyed Al pack yields non uniform, brittle FeAl\textsubscript{3} and Fe\textsubscript{2}Al\textsubscript{5} coatings. Smooth, adherent and uniform FeAl coating could be obtained using a ferro aluminium pack with NH\textsubscript{4}F.HF activator. The coating layer grows parabolically with time.

1.5.2 Phosphate Coatings

Amongst the inorganic coatings used, phosphate coatings are the most extensively used and a large number of references are available concerning with their preparation, properties and uses. These coatings are prepared by treating metals and alloys with phosphoric acid or solutions of primary phosphates of Mn, Fe, Zn, Al or Cd. The basic properties of phosphate coatings depend on the surface preparation, the solution composition and operating conditions. Although these coatings are unstable in acid and alkalies, their most valuable property is to absorb oil. They greatly improve the adhesion of paints on metals and retard the process of corrosion under the paint film even in those regions where the paint has been damaged. Boron phosphate coating\textsuperscript{23,24} prepared by mixing equimolar amounts of P\textsubscript{2}O\textsubscript{5} and B\textsubscript{2}O\textsubscript{3} at 600–650°C are the recent and important phosphate coatings. Conversion coatings\textsuperscript{25} for Al
have been prepared by using Zn, Cr and Ni phosphates. In these coatings the crystalline and amorphous phosphates are present in the form of $54Zn_3(PO_4)_2$, $11AlPO_4$, $Ni(PO_4)_2$, $114H_2O$ and $Cr(OH)_2$. $HCrO_4$. $Al(OH)_3.2H_2O$ respectively. These coatings are suitable for the construction of containers and applications in aerospace industry. A white crystalline inorganic coating has recently been described by the reaction of $AlCl_3$ and $H_3PO_4$ in presence of $C_2H_5OH$ and HCl.

A chemical method for protecting carbon steel surfaces by forming pyrrhotite/pyrite coatings has been developed. The protective nature of the coatings has been studied by weight loss kinetics, scanning electron microscopy and electrochemical measurements. Mechanically stable, heat resistant and high speed gas flow resistant phosphate coatings have recently been prepared by the addition of $Al_2O_3$ 15-20 %, $B_2O_3$ 1-4 %, CaO 1-3 % and BaO 1.5-3.5 % to a composition containing $SiO_2$ 10-30 %, $Al(OH)_3$ 5-15 % and an Al phosphate binder.

1.5.3 Silicate Coatings

The basic constituent of silicate coatings is an alkali or alkaline earth silicate. These coatings are suitable for aluminium or steel and provide excellent high temperature corrosion resistance in air, $H_2S$ and cathodic protection of under ground metal structures. An addition in silicate coatings is the introduction of complex silicates of glass composition. These coatings protect iron against oxidation.
at varying degrees. The exception is sodium borosilicate glass coatings which rapidly becomes saturated with iron oxides thereby loosing its protective properties. Recently some Si-based ceramic coatings\textsuperscript{29-31} have been developed for heat resistant Ni, Co and Fe-base alloys. The substrate matrix contains embedded particles which are capable of forming protective oxides. The coating is found suitable for gas turbines. These are also used as sacrificial coatings\textsuperscript{32} to prevent the severe corrosion caused by the stray current, differences in stress through structure and the differences in soil conditions.

1.5.4 Borate Coatings

Only a limited amount of work has been carried out on borate coatings. Coatings of orthoboric acid\textsuperscript{33-34} on high purity iron were found to decrease the oxidation rate in the temperature range 700 to 1100°C. When in contact with the heated iron surface, the \( \text{B}_2\text{O}_3 \) powder metals and dissolves any residual or reformed scale. It has been proposed that the oxygen dissolves in the melt and is transported to the melt/iron interface. At the interface, solution of iron and oxygen ions continues until a complex iron oxide-boron oxide complex is precipitated. The complex oxide is iron boroferrite \( 4\text{FeO.}\text{Fe}_2\text{O}_3.\text{B}_2\text{O}_3 \). The effect of boric acid upon the oxidation rate of Fe-2.1/4Cr-1Mo is to change the growth kinetics by influencing the micro structure of the growing oxide layers\textsuperscript{35}. Two effects are most apparent
from this initial low resolution study. First, the boron is segregated in the magnetite layer, which does not contain chromium and molybdenum. Secondly, the oxide layers develop blisters or bubbles, at the outer surface. These micro structural features are being further investigated, as is the mechanism of inhibition.

1.5.3 Carbide Coatings

These coatings are very important and are better than other inorganic coatings because they are hard, strong, durable and have better heat as well as oxidation resistance. Silicon carbide, boron carbide and the transition metal refractory carbides have been used as coating materials. The carbide coatings have a wide range of applications in nuclear reactors and other high temperature assemblies working in corrosive environments. The most convenient method to deposit carbide is thermally decomposing the halide vapours and diffusing carbon simultaneously. In another method the oxides of metals are mixed with graphite and Al powder and the product is heated in a crucible containing metal which has to be coated. Heat resistant chromium carbide coating on steel is obtained by using a mixture of low alkali borosilicate glass and chromium carbide powder. The coating is done in an atmosphere of argon. The rate determining step in the coating is the interaction of boro-silicate glass with oxide films on carbide grains. The carbide coating showed good adhesion and protection
against high temperature corrosion. Recently titanium carbide coatings have been obtained. They are applied to iron-base alloys used by navy to overcome marine corrosion.

1.5.6 **Boride Coatings**

Boride coatings are prepared by gas plating, e.g., \( \text{TiCl}_4 + 2\text{BCl}_3 + 5\text{H}_2 \rightarrow \text{TiB}_2 + 10\text{HCl} \). The coating formed at temperature higher than 600°C and deposition takes place at 780-950°C with a coating thickness of > 3 μ. Recently, Moskowitz et al. have obtained boride coatings by spray and fuse self fluxing process. Powdered Ni or Co-base alloys containing chromium were mixed with elemental boron sprayed on the substrate surface and fused, self fluxing alloy powder was precipitated from a viscous melt of the alloy and forms a hard coating of chromium boride or chromium carbide.

1.5.7 **Silicide Coatings**

Silicide coatings are heat resistant and protect Nb, W, Ta, Mo and other refractory materials from high temperature oxidation. Silicon is deposited on metal surface by passing mixture of \( \text{H}_2 \) and silicon halides over the metal surface. A silicide coating has been prepared from a Hame spray powder mixture. It contains agglomerates of a metal silicide mixed with a coating metal powder. The metal silicide is selected from the group consisting of disilicides of
Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Mn, Co, B and Mg. Metal silicides have a good corrosion resistance at high temperature, and may therefore be used as protective coatings. The oxidation behaviour of zirconium silicide coating was studied in an atmosphere of oxygen or water vapour. The coatings were prepared by depositing silicon from monosilane on heated zirconium samples. The oxidation of these coatings follows the general rate law \((\Delta m)^n = Kt\). The kinetic results can be explained by the existence of two different silicide layers. The experiments have shown good corrosion resistance of this coating compared with that of pure zirconium.

A novel method of producing high melting point complex, oxide coatings was sought, which was both rapid and reproducible. The technique was required for the production of thin \(\text{Mg}_2\text{SiO}_4\) layers on silicon wafers for diffusion couple experiments. Recent experiments using 500 W Nd-YAG laser revealed that sufficient surface heating can be provided by laser excitation to cause a \(\sim 5 \mu m\) layer of TiC, TiN or Al\(_2\)O\(_3\) to be completely evaporated, by one laser pass, under optimal conditions. The influence of molten-vanadium-rich deposits upon silicon coated Ni/20Cr alloy has been examined at 900°C under oxygen using 20-80 % mixtures of \(V_2O_5\) and \(Na_2SO_4\) as corrodatant. Coatings applied by Pack, vapour deposition plasma spraying and ion-plating were all effective. Ion implanted coatings were found to be most reliable with good
adhesion, uniform composition and even thickness. It was also found that barrier type layers involving both Si and Cr containing species are associated with the improved behaviour. Ion implanting of Si affords a more reliable form of coating.

1.5.8 Nitride Coatings

Only a limited amount of work has been carried out on the nitride coatings. They have very good adhesion and high temperature corrosion resistance properties. NH₃ is used as nitriding agent. It is mixed with vapours of metal halide and passed over the substrate to give nitride coating. For example, titanium nitride coating is prepared by the reaction of TiCl₄ and NH₃ in the temperature range of 900-1200°C in a nitride coated steel or in a quartz reaction vessel. The coating of boron nitride on Cu, Ni, W and Mo metals and steels have been deposited by a simple method. The nitride films of 0.35 μm thickness were deposited by using high frequency heating in N₂ at 450°C and 0.03 torr. I.R. spectroscopy and X-ray diffraction techniques were used to characterize the film compatibility temperature, which follows the order: Ni > Steel > Mo > Co > W. The BN coating has a better adhesion than SiO₂ and Al₂O₃ coatings.

Aluminium nitride thin films were used as protective overcoats for terbium-iron magneto-optical media. Protective
performance of the aluminium nitride overcoats was evaluated by electrochemical polarization, immersion tests and environmental exposure studies. Al-N coatings were found to exhibit better corrosion resistance than silicon dioxide overcoated Tb-Fe films. The production of thin layers of TiN and AlN on the surface of various engineering components by a variety of techniques has received considerable attention in the past few years\textsuperscript{60-67}. This is due to some exceptional properties of TiN such as high hardness, good erosion and corrosion resistance, chemical stability and an attractive golden colour. TiN films prepared by three different techniques were compared. Sputter deposition and ion plating were the techniques used. Corrosion testing was carried out potentiodynamically in deaerated 1N H\textsubscript{2}SO\textsubscript{4} aqueous solution at 25°C. Test results indicate that dense ion plated TiN films have a passive corrosion current density as much as five orders of magnitude less than other coatings.

1.6 Method of Coating Technology and Their Application

A number of processes are available for depositing protective coatings on the surface of the substrate. These methods range from paint, dip, electroplating, chemical vapour deposition to the recently developed physical vapour deposition methods. The methods can be used to produce multilayer complex coatings.
1.6.1 Pack Cementation

It is widely used for depositing aluminide and chromised coatings. In this method, the components are embedded in a retort which contains a powder pack. This powder pack consists of metal(s) required to be deposited (Al, Cr, Si etc.), a halide energiser (Cl⁻, Br⁻, I⁻) and in some cases an inert diluent. The retort is heated in the temperature range of 750°C-1050°C for more than one hour under inert or reducing conditions. For example, in case of aluminising the super alloy components, the latter are immersed in a mixture of finely divided powders of alumina / aluminium/aluminium alloy containing compounds of Ni, Cr, Bi, Si etc. A small amount of halide is then added in order to provide easy passage for vapour phase transport of aluminium from the pack mixture to the surface of the substrate to be protected. The most important step is the formation of aluminium monohalide gas which is transported to the Ni or Co-base super alloy component. This leaves a deposition of aluminium on the metal surface. At high temperature aluminium reacts with substrate to form nickel or cobalt aluminide. Deposition of coating depends on the time of exposure, temperature range and constitution of the pack. Picholr⁶⁸ has shown that the morphology and composition of aluminide coatings and the corrosion behaviour depends on the condition whether nickel or cobalt diffuse outwards to react with aluminium or vice versa. The protection afforded
by these coatings is based on their ability to form and replenish protective scales of alumina.

1.6.2 **Gas Phase—Chemical Vapour Deposition (CVD)**

CVD method is a slight modification of pack cementation. In this method the coating metal is vaporized by heating electrically and the vapour is deposited on the parts to be coated. Both metals and semi conductors can be deposited by CVD. CVD is divided into four groups:

1. Thermal deposition e.g. Al-tri isobutyl to produce Al. The coating of Ru, Pd, Au, Bi, Sb and Zr can also be thermally deposited.

2. Reduction of a halide by $\text{H}_2$ results in depositions of Os, Rh, W, V and Nb.

3. Reaction of a halide to give a refractory compound of a metal like carbide, nitride or oxide of titanium.

4. Disproportionation reaction: For example, $\text{AlCl}_3$ gives Al and $\text{AlCl}_3$. In CVD, bonding between the coating materials and substrate takes place by interdiffusion process. CVD can form wear resistant layers and high temperature coatings.

1.6.3 **Slurry Coatings**

In this method the coating powder mixture is sprayed on the component surface at low temperature and then the
component is heated to higher temperature to obtain the desired coating by interdiffusion. In some cases halide carriers are employed in the heating chamber to provide vapour transport of the coating elements to the surface of the component. Slurry technique has been successfully used for the preparation of inorganic coatings on austenitic and mild steel. Inorganic coatings include phosphate, borate, silicate, chromate, oxide and carbide. The inorganic coating materials were mixed with citric acid, TiO₂, MnO₂, boric acid etc. to promote surface adhesion. The slurries were prepared by mixing the materials with water, alkali or acid solutions. Precious metal aluminide coatings and silicon modified slurry coatings for super alloys have been developed recently.

1.6.4 Electroplating plus Pack Cementation

TEW are accredited with the first development of a Pt modified aluminide coating designated LDC₂. The method involves the electrodeposition of a thin layer (upto 10 µm) of Pt followed by a pack aluminising treatment during which the Al and Pt interdiffuse with each other and with the substrate alloy.

1.6.5 Fused Salt Electrolysis

This is a high temperature process in which Al is deposited from a molten salt bath to a nickel based alloy cathode and then diffuses inward to form a nickel aluminide
coating. Fused salt electrolysis is a very expensive method so it is not widely used.

1.6.6 Electrophoresis

This is a coating process in which finely divided particles of coating materials are suspended in a liquid dielectric medium and migrate under the influence of an electrostatic field and deposit on an electrode. The migration occurs because the particles are positively and negatively charged depending on the composition of the system. There are many advantages of this method. It is applicable for a variety of materials (both metallic and ceramic). It has a very high rate of deposition and a good control of thickness. The major disadvantage is that some coatings are easily damaged on handling so a separate heat treatment is required for sintering and densification.

1.6.7 Electron Beam Evaporation

Metallic coatings are deposited on the substrate by thermal evaporation of a metal source followed by condensation of the vapour on the component. Beat or filamentary source and electron beam evaporation are the basic methods used for evaporation.

1.6.8 Ion Implanting Process

Ion plating or ion vapour deposition has become a widely accepted process for the application of dense, uniform and very
adherent aluminium coatings for corrosion protection. This process has replaced cadmium electroplating. This is because cadmium has many drawbacks. The material that has replaced cadmium is aluminium. Al coatings provide good corrosion protection for high strength steels at high temperatures without causing embrittlement, there is a considerable reduction in the evaporation loss rate under hard vacuum (space) conditions. Environmental corrosion tests of Al coated steel fasteners installed on a C-130 air craft have been reported to show better performance\textsuperscript{74-76}. The ion-implanting is also known to modify greatly the rate of gas-metal reactions. These reactions were performed in oxidizing conditions. The scale thickness was found to be more than that of initially implanted layers. Iron and titanium were used as test materials\textsuperscript{77-83}. The metals oxidized by outward cation diffusion face a complete blocking of the oxidation of metals and the implanted species is more easily oxidized than the host metal. But, in case of Ti, no blocking effect was observed during oxidation and it was concluded that ion implantation is not a suitable technique for protecting Ti against long term oxidation at temperatures above 700°C.

In the simple sputtering process, inert ions (usually argon), form a plasma (glow) discharge in a low pressure chamber, are accelerated under a high voltage to a surface of target (cathode) made up of the alloy to be coated, where
the binding energy is lowest, momentum interchange in the surface atomic layers of the target causes sputtering of atoms. Some of these atoms may be ionized and are deposited on the substrate to be coated. Recently Benett et al. used ion-implantation technique in studying the high temperature oxidation studies. They produced ion implanted coating of Y, Ce, Si, Al, Li, Ti and Cs on Ti, Zr, Cr, Fe, Ni and Cu metals and their alloys. The oxidation studies indicate beneficial effects of Ce, Y and Si ion implanted coatings on Fe-Cr alloy in the temperature range of 700-1000°C for the period varying from 780 to 5000 h. The scales formed on the ion implanted metals are protective in nature whereas the scales formed on the uncoated metals are porous in nature though the coated and uncoated alloys exhibited similar oxidation behaviour.

1.6.9 Flame Spray Process

In this process, the metal wire or powder is fed through a melting flame so the metal as finely divided liquid particulates is blown onto the surface of the substrate bring a protective layer. Union carbide has developed a new flame spraying process known as “Detonation Gun” which is an improved form of the original flame spray process. Detonation gun resembles a large calibre machine gun. Measured quantities of oxygen acetylene and particles of coating material are detonated in the firing chamber. This creates a hot
high speed gas steam which heats the particles to a plastic state and accelerates them at a supersonic velocity from the gun barrel. The near molten particles impinge on the surface of the work piece and produce a tenacious mechanical bond. The temperature above 3200°C is reached inside the gun but the work piece temperature remains comparatively low to minimize distortion and retain the metallurgical properties of the base material. This process is not used for depositing oxidation and corrosion resistant coatings to turbine rotor blades because the coatings formed do not provide good thickness, porosity and adhesion.

1.7 Ceramics and Glass Type Coatings

Ceramic thermal barrier coatings have been used for 10 to 15 years for extending the oxidation and thermal fatigue durability of sheet metal components in aircraft gas turbine engines. Ceramic coatings in practical use are applied by plasma spraying. Model experiments at NASA laboratories emphasized the potential of such coatings for increasing longevity or decreasing cooling air requirements by their capability of forming insulating layers on hot-section airfoils in all types of gas turbine engines. Recently developed series of thin ceramic coatings have been produced by sol-gel technology and and vapour deposition procedures. Work within the UKAEA on the production, characterisation and evaluation of these coatings is described as they could find a wider
applications in industries.

Sol-gel silica and ceria coatings have been evaluated for the fuel cladding applications. These were applied to the 20/25/Nb stainless steel in the standard metallurgical condition (i.e. after hydrogen annealing at 930°C for 50 min.) either directly or after preoxidation of the steel in carbon dioxide for 2 hr at 800°C. The thickness of the precoating oxide film was 1 µm, while those of the ceria and silica coatings ranged between 0.3-0.8 µm and 1-4 µm, respectively. All the sol-gel ceria coatings, irrespective of the initial steel substrate to which they were applied, improved oxide adherence. Two new series of thin ceramic coatings have been developed, produced respectively by sol-gel and vapour deposition (PAVD and CVD) procedures. These coatings have improved significantly the oxidation behaviour of the 20/25/Nb stainless steel during 15000 hrs exposure to carbon dioxide at 825°C. The vapour deposited silica coatings were found effective for considerable periods at temperatures upto 1000°C. In general, the protection afforded by the coatings was not diminished either by thermal strain induced by daily thermal cycling or mechanical strain from a continuously applied load. Both series of coatings have been scaled up for specific nuclear application and quality assurance inspection techniques have been developed. The stabilized ZrO₂ coating seems to have unique properties as thermal barrier coating compared to Ca₂SiO₄, Al₂O₃ + TiO₂, etc. The corrosion resistance of this coating
in engines running on residual fuel is poor. MgO-stabilized ZrO$_2$ seems to have better corrosion resistance than ZrO$_2$ stabilized with Y$_2$O$_3$ or CaO. This depends to a certain degree on powder quality. The degree of stabilisation plays a major role regarding the reaction between the stabilising element and species in combustion gas or the liquid salt layer. Critical properties for ceramic coatings are corrosion and thermal shock fatigue, wear and fracture toughness. These properties depend on the microstructure and thereby on the spray parameters, pretreatment and heat treatment. Misawa$^{90}$ have reported two ZnO-B$_2$O$_3$-SiO$_2$ glasses, glass A (ZnO : 65.4, B$_2$O$_3$ : 24.5, SiO$_2$ : 10.1 weight percent) and glass B (ZnO : 63, B$_2$O$_3$ : 29, SiO$_2$ : 8 weight percent), which were prepared for the purpose of passivating high voltage silicon devices. Their physical and electrical properties were compared using DTA characteristics, SEM observations, X-ray diffraction patterns, thermal expansion coefficients and surface charge densities, as a function of firing temperature. Reverse characteristics of semiconductor devices passivated with these glasses were also investigated. The development of porous glassy silica from phase separation and leaching of sodium-borosilicate glasses, has been reviewed by Res et al. Na$_2$O-B$_2$O$_3$-SiO$_2$ glasses can be heat treated and separated into two phases, one almost pure SiO$_2$ which is insoluble in water and the other a Na$_2$O-B$_2$O$_3$ rich phase which is water-soluble. The latter may be leached out leaving a porous silica glass
skeleton with interconnected pores. Substitution of SiO$_2$ in the ternary sodium borosilicate system with Al$_2$O$_3$ plus Ta$_2$O$_5$ was found to produce glass which decomposed into microphases and/or crystallized phases after heat treatment$^{91}$. A study has been made of four Al$_2$O$_3$-Al composite materials fabricated by the direct oxidation of molten aluminium alloys$^{92}$. Their microstructures are described and measurements of density, coefficient of thermal expansion, thermal conductivity, hardness, fracture toughness, and thermal shock resistance are reported.

The addition of both SiO$_2$ and Y$_2$O$_3$ to AlN led to decrease of 27 R polytype in specimens sintered above 1600°C and also to an increase of thermal diffusivity of AlN ceramics$^{93}$. Furthermore, SiO$_2$ and Y$_2$O$_3$ added AlN ceramics were fully densified by liquid phase sintering, and resulted in higher thermal diffusivity. The formation temperature of the liquid phase was lowered more by the addition of both SiO$_2$ and Y$_2$O$_3$ than only Y$_2$O$_3$ to AlN ceramics. Hot pressed Si$_3$N$_4$, sintered Si$_3$N$_4$ and three kinds of sialon with different compositions were oxidized in dry air and wet nitrogen gas atmospheres at 1100 to 1350°C and 1.5 to 20 KPa water vapour pressure$^{94}$. All samples were oxidized by both dry air and water vapours at high temperature, and formed oxide films consisting of SiO$_2$, Y$_2$Si$_2$O$_7$ and Y$_4$Al$_2$O$_7$. The oxidation rate was in the order sialon > sintered Si$_3$N$_4$ > Hot-pressed Si$_3$N$_4$. The oxidation
rate of sialon increased with increasing $Y_2O_3$ content and oxidation kinetics obeyed the usual parabolic law. The oxidation rates in dry air and wet nitrogen were almost the same. The rate in wet nitrogen was found unaffected by water vapour pressure above 1.5 KPa. The activation energy was about 800 KJ mol$^{-1}$.

The above mentioned contentions amply demonstrate that the ceramic coating gives very good heat protection of the metal parts provided that the thermal conductivity of the coating can be maintained under engine operating conditions. This may have an advantageous effect on the ignition delay because of the higher temperature level of the gases prior to ignition. A ceramic layer will prevent heat transfer from the hot working medium to the coolant and surroundings. It will contribute to a reduction of the temperature and heat load of the metallic base and will provide corrosion protection.

1.8 High Temperature Applications of Inorganic Coatings

The first application of such coatings was in aircraft engines. This was followed by increased use of coatings in ground based marine engines in early seventies. In many applications, turbine air stream environments are such that the useful life of airfoils is limited by coating failure. This has prompted substantially increased levels of development efforts to provide more durable coatings. The coatings widely used for the protection of super alloy gas turbine airfoils
were based on surface enrichment of nickel based alloys with aluminium as described first by Goward et al.\textsuperscript{95,96} followed by others\textsuperscript{97-100}. The coatings are usually applied by pack cementation process which is more accurately described as chemical vapour deposition. This activity determines the nickel-aluminium intermetallic phase, Ni\textsubscript{2}Al\textsubscript{3} or NiAl, formed on the alloy surface by reaction with aluminium species in the gas phase. These aluminide coatings provide only limited protection in modern applications involving very high temperature (1093°C) or severe hot corrosion environments.

Gas turbine engines are used in a wide variety of applications. Diffusion coatings\textsuperscript{101,102} based on surface enrichment with chromium, have received some attention and found limited applications for protection of utility gas turbine airfoils in Europe and Japan. Temperature capabilities of such coatings are ultimately limited by the volatility of CrO\textsubscript{3}, formed by reaction of Cr\textsubscript{2}O\textsubscript{3} protective scales with oxygen. Beneficial high temperature (871-1204°C) oxidation properties of diffusion and overlay coatings containing aluminium are based on the formation of alumina under oxidising conditions. The practical durability of aluminium containing coatings is dependent on the adherence of the protective oxide. Oxygen active elements such as Yttrium are added to overlay coatings\textsuperscript{103-105} to promote oxide adherence, these coatings are nominally independent of substrate alloy composition.
Innumerable studies have indicated that the presence of chromium imparts resistance to hot corrosion degradation of alloys and coatings induced by the presence of salt layers reasonably modeled by sodium sulphate (Na$_2$SO$_4$). Increasing the chromium content of CoCrAlY tends to decrease the corrosion rate. Studies by Rapp et al.\textsuperscript{106} and Elliott et al.\textsuperscript{107} on the solubility of oxides such as Al$_2$O$_3$ and Cr$_2$O$_3$ in Na$_2$SO$_4$ as a function of P$_{SO_3}$ indicate different behaviour between these oxides. This might tend to indicate that chromium in coating, forming protective Cr$_2$O$_3$, could be more resistant to hot corrosion at certain acidity levels. The most advanced of the MCr Aly series of coatings is typified by a particular nominal composition (in wt. %) of 18% chromium, 23% cobalt, 12% aluminium, 0.5% Yttrium, balance nickel\textsuperscript{108}. The composition is referred to in the industry as NiCoCrAly. As applied by electron beam vapour deposition (EB) on a production scale, it has proved to be useful for the protection of aircraft engine blade airfoils fabricated by directional solidification (DS) of superalloys.

To provide compensation for this lesser oxide adherence of NiCoCrAly coatings on the new alloy, a series of more complex coating compositions, containing silicon, tantalum and hafnium, was formulated for experimental evaluation. The oxidation resistance was determined by cyclic burner rig tests. The requirements for a thermal barrier coating (TBC) are low thermal conductivity, resistance to corrosive and erosive
environments, high coefficient of thermal expansion (i.e. compatible with metals) and thermal shock resistance. A stabilized ZrO₂ coating\textsuperscript{103} seems to have unique properties as a thermal insulator.
19 STATEMENT OF THE PROBLEM

The work described in this thesis deals with the high temperature corrosion behaviour of inorganic coatings. The work carried out during this investigation is distributed into the following chapters.

Chapter I is General Introduction. In this chapter, a literature survey of the various studies on coating in general and inorganic coating in particular has been carried out. Preparation of the coatings, procedures, characterization and their high temperature corrosion behaviour are some of the topics which are dealt in this chapter. Emphasis has been laid upon the work carried out during the last 2 decades.

Chapter II This chapter describes experimental part of the research work. It includes materials, procedures such as preparation, characterization of the coatings, measurement of high temperature kinetics, metallography, etc. and the specification of the physico-chemical techniques.

Chapter III This chapter includes the preparation of nickel aluminide coatings on mild steel in presence of different rare earth oxides. The high temperature oxidation behaviour of nickel aluminide coating under various conditions has been described.

Chapter IV This chapter deals with the high temperature
oxidation and hot corrosion behaviour of borosilicate coatings on mild steels. The preparation of borosilicate coating in presence of different rare earth oxides has been described. The high temperature oxidation studies have been carried out at different temperatures and hot corrosion studies have been conducted at various Na₂SO₄ concentrations and temperatures. The performance of the borosilicate coating has been established on the basis of the results of high temperature corrosion studies.

**Chapter V** This chapter includes the results from high temperature oxidation and hot corrosion studies on borosilicate coated Inconel 600 alloy. The overall high temperature performance of this coating under different conditions have been evaluated.

**Chapter VI** This chapter includes the summary of the work done on the high temperature oxidation and the hot corrosion behaviour of the inorganic coatings on iron base alloys and the conclusions drawn.
Chapter II
CHAPTER - II

EXPERIMENTAL

2. Materials and Methods

2.1 Materials

Specimens of 18 x 9 x 1 mm or 12 x 14 x 0.8 mm size were cut from the sheet of mild steel (C : 0.30, Si, 0.15, S : 0.03, Fe-balance) and Inconel-600 (Ni : 76.9, C : 0.06, Mn : 0.20, Fe : 6.66, S : 0.007, Si : 0.38, Cu : 0.16, Cr : 15.58). The specimens were used as a substrate materials for coating purposes.

2.2 Specimen preparation

The specimens were abraded sequentially with 180, 320 and 600 grit SiC papers, using a motor driven disc polisher. The specimens were washed with water and alcohol and dried finally degreased with CCl₄.

2.3 Chemicals Used

NiO, Al₂O₃, NiCl₂, B₂O₃, SiO₂, NH₄Cl and Al powder were all reagent grade BDH products. Rare earth oxides : La₂O₃, Sm₂O₃, Gd₂O₃, Pr₂O₃, Nd₂O₃, Tb₂O₃, Y₂O₃, Yb₂O₃, Er₂O₃, Ce₂O₃ and Ho₂O₃ were spectroscopically pure chemicals (John Mathey Products.

2.4 Apparatus Used

A laboratory fabricated helical thermal balance and
a Sartorius Electronic Microbalance Model 4410-MP8 with a sensitivity of 1 µg attached with a pen ink recorder were used for oxidation kinetic measurements (Fig. 2.1). The specimen was suspended to the right pan of the balance through a quartz fibre, with a platinum loop at the end. After the balance has been poised the hot furnace (set at the desired temperature) was raised around the sample and the oxidation commenced.

2.5 Coatings Preparation

2.5:A Nickel Aluminide coating

Two coating mixtures were prepared: one by mixing powdered NiO and Al₂O₃ in the molar ratio of 1:1 and the other by mixing powdered NiCl₂, NiO, Al₂O₃ and Al in the ratio of 0.5 : 2.5 : 1.5 : 0.5 (parts by weight). The nickel aluminide coating is prepared by pack cementation process. The powders were applied on the mild steel specimens in a silica boat and heated in a muffle furnace at 800°C for 1/2 hour in the presence of N₂(g) and finally cooled in the furnace. A thin dark coating (thickness 71 µm) was formed on the mild steel specimen which had an excellent adhesion.

Rare earth oxide-containing nickel aluminide coatings were prepared by using varying amounts of rare earth oxides: NiCl₂ : NiO : Al₂O₃ : Al : RE₂O₃ as 0.5 : 2.5 : 1.5 : 0.5 : 1.0 RE₂O₃ is varied between 1 to 4.7 by weight percent. The rare earth oxides used in nickel aluminide coating were Sm₂O₃,
Gd$_2$O$_3$, La$_2$O$_3$, Y$_2$O$_3$, Yb$_2$O$_3$, Pr$_2$O$_3$, Er$_2$O$_3$, Tm$_2$O$_3$, Tb$_2$O$_3$ and Ho$_2$O$_3$. The methods of application and heat treatment were similar to those used for nickel aluminide coating.

2.5:B Boro-Silicate coating

Coating mixture was prepared by mixing of the powdered Al$_2$O$_3$, B$_2$O$_3$ and SiO$_2$ in the ratio of 3:2:1 (by weight) respectively. The mixture was suspended in a 10% H$_3$PO$_4$ solution so as to give a slurry. The slurry was applied on the mild steel or Inconel-600 specimens with the help of a brush. The specimens were heated in a muffle furnace at 800°C for 75 minutes in air and finally cooled in the furnace itself. A dark coloured coating of thickness about 65 μm was formed on the alloy specimens. The coating had an excellent adherence.

Rare earth oxide-containing borosilicate coatings were prepared by using a slurry containing Al$_2$O$_3$: B$_2$O$_3$: SiO$_2$: RE$_2$O$_3$ in the ratio of 3:2:1 or 2 (by weight) or RE$_2$O$_3$ as 14 and 25 weight % in a 10% H$_3$PO$_4$ solution. The rare earth oxides used in borosilicate coating were: La$_2$O$_3$, Sm$_2$O$_3$, Gd$_2$O$_3$, Y$_2$O$_3$, Yb$_2$O$_3$, Ce$_2$O$_3$, Nd$_2$O$_3$, Er$_2$O$_3$, Pr$_2$O$_3$, Tb$_2$O$_3$ or Ho$_2$O$_3$. The method of application and heat treatment were similar to those used for borosilicate coating.

2.5:C Sodium Sulphate (Na$_2$SO$_4$) coating

Borosilicate-coated and uncoated specimens were uniformly coated with Na$_2$SO$_4$ in the following concentrations.
(≈ 4 µm thick) containing about 0.6 mg/cm$^2$ Na$_2$SO$_4$
(≈ 8 µm thick) containing about 1.2 mg/cm$^2$
(≈ 15 µm thick) containing about 2.8 mg/cm$^2$

The coating was done by spraying a nearly saturated solution of Na$_2$SO$_4$ on specimens preheated at about 300°C. The spraying was continued till a nearly uniform coating of the salt covering all the faces is obtained. The coated specimens were dried and weighed prior to hot corrosion studies.

2.6 Oxidation kinetics

The oxidation runs were carried out either on a laboratory fabricated helical thermal balance or a Sartorius Electronic Microbalance. The time for the oxidation run was 24 hours in the temperature range of 700°C to 1000°C.

2.7 Hot Corrosion Studies

Hot corrosion studies were carried out under atmospheric pressure in the presence of Na$_2$SO$_4$ at 700°C, 800°C, 900°C and 1000°C. The duration corrosion runs were usually of 1, 6, 12 and 24 h. The coated specimens were kept in silica boats, and the boats were transferred in a tubular furnace maintained at the desired temperature. The samples were oxidized in the flowing air. At the end of the run, the boats were taken out slowly from the furnace, cooled in a decicator and weighed.
2.8 **Metallographic Studies**

The mounted specimens were abraded with 180 and 600 grade SiC papers, respectively. The abraded specimens were then polished sequentially on a motor driven disc polisher using 40 μ, 8 μ and 6 μ diamond pastes. In order to avoid dissolution of water soluble inorganic compounds present in the scales, kerosene oil were used as a lapping liquid during the entire polishing operation. Polished specimens were washed with alcohol and acetone and finally cleaned with a sylvit cloth. The polish samples were examined under a Leitz photometallurgical microscope. The polished samples were then etched with 1 % Nital or 10 % acid ferric chloride solution for 2-3 minutes. In most cases, repeated alternate operations of polishing and etching gave satisfactory results. The polished and etched specimens were examined under Leitz photometallurgical microscope attached with a 35 mm camera. The regions of the microstructure giving relevant details were photographed.

2.9 **Scanning Electron Microscopy (SEM)**

Polished specimens were coated with gold film of ~500 Å thickness using a Edwards sputter coater and were examined under a JEOL JSM-35C Scanning Electron Microscope. The desired regions of the scales and the substrate were photographed at an appropriate magnification.
2.10 Energy Dispersive X-ray Analysis (EDAX)

Elemental distribution or elemental concentration profiles within the scale and the matrix of the corroded alloys were obtained by EDAX.

2.11 X-ray Diffraction Analysis

The presence of different constituents in the scales of the corroded alloys was identified by conventional X-ray diffraction analysis. The X-ray diffractograms were obtained by a X-ray diffractometer assembly, using Cu Kα/Co Kα/Fe Kα radiations with an appropriate filter.
Fig. 2.1 Schematic diagram of the apparatus used for oxidation kinetic measurement.
Chapter III
3.1 HIGH TEMPERATURE OXIDATION BEHAVIOUR OF NICKEL ALUMINIDE COATINGS ON MILD STEEL

Nickel aluminide type protective coatings are of relatively recent origin and have been actively investigated during the last 15 years. These coatings are extensively used in aeronautical industry where components made up of nickel-base super alloys are protected against oxidizing and corrosive environments. The oxidation behaviour of coated component seems to be strongly dependent on the aluminizing technique. There are various techniques for obtaining Ni-Al type aluminide protective coatings on Ni-base super-alloys destined for certain high temperature applications in aircraft gas turbines. Preferential diffusion of Ni or Al occurs in different layers which are formed during the heat cycles, this phenomenon is the basis of all the techniques.

Unlike aluminide and chromoaluminide coatings which have been used in steels, the nickel aluminide coatings are yet to be introduced for general industrial applications involving high temperature corrosive environments.

The details of specimen preparation and coating procedures have already been described in Chapter II.
3.2 **RESULT**

3.2.1 **Oxidation Kinetics**

Figures 3.1 to 3.12 show weight gain vs time plots for the oxidation of nickel aluminide coatings on mild steel in the presence of varying concentrations of different rare earth oxides at 750°, 800° and 850°C in air. The weight gain vs time plots are parabolic as indicated by the linear nature of weight gain² vs time plots, figures 3.13 to 3.24. Tables 3.1 to 3.3 list the values of parabolic rate constant, $K_p$, for the oxidation of Nickel aluminide coatings on mild steel in the presence of different coatings and rare earth oxides at 750°, 800° and 850°C. At 750°C and 800°C, the coated alloys containing 2% RE₂O₃ by weight generally show a little higher oxidation rates than the uncoated alloys. However, at 850°C, with the exception of Nd₂O₃ and Ho₂O₃, all the rare earth oxides containing coated alloys have slightly lower oxidation rates. With higher concentration of RE₂O₃ (~ 4.7 wt. %), the oxidation rates are usually lowered down. Figure 3.30 shows plots of parabolic rate constant, $K_p$ vs ionic radii of RE³⁺ at 700°, 850° and 800°C. A regular trend is not observed, however, at 750° and 800°C the first few members (upto Ho³⁺) show an increase in oxidation rates with increasing ionic radii followed by a decrease in oxidation rates although the rates by and large are similar. Figures 3.25 to 3.29 show Arrhenius plot for the oxidation of coated alloys in the presence of rare earths. In most of
the cases the law is followed. The values of activation energies for the oxidation of nickel aluminide coating in presence of different rare earth oxides are given in tables 3.4 to 3.6.

3.2.2 Metallographic Studies

Figure 1 shows an optical photomicrograph of the surface structure of nickel aluminide coating on mild steel. Presence of two phases NiAl₂ (dark) and Al₂O₃ (light) in a grey matrix of iron oxide is indicated. Fig. II shows a scanning electron micrograph of a cross section of the same coating, the dark circular grains of NiAl₂ are encompassed by light Al₂O₃. These grains are dispersed in a iron-rich matrix.

Figure III shows a photomicrograph of a cross section of nickel aluminide coating on mild steel oxidized at 750°C in air. Multilayer scales are formed which seem to be reasonable adhered to the alloy substrate. The inner scales contain Al₂O₃ and the outer scales containing NiO with inclusions of Fe₂O₃. The diffusion of Al in the alloy matrix is indicated by the presence of internal Al₂O₃ globules. At 800°C, the attack is relatively severe due to oxidation and the oxide scale are separated from the matrix, the innermost layers of scales contain Al₂O₃ followed by oxide layers of Fe₂O₃/Fe₃O₄ containing NiO inclusions (Fig. IVa and IVb). The attack is most severe at 850°C and the presence of nickel aluminide
coating on mild steel does not have beneficial effect. The inner scales which are relatively adherent contain Al₂O₃ followed by much thicker scales of iron oxides containing NiO in the outer layers (Fig. V).

Figures VI and VII show optical micrographs of the surface of nickel aluminide coatings containing 1 and 2 wt. % of Sm₂O₃, respectively. There are three distinct phases NiAl₂ (dark), Al₂O₃ (light) and Sm₂O₃ (steel grey). Al₂O₃ is invariably incorporated with NiAl₂ whereas Sm₂O₃ forms a distinctly separate phase. Scanning electron micrograph (Fig. VIII) of the cross section of the coating shows coarse grains of NiAl₂ (dark grey) along with fine grains of Sm₂O₃.

Figure IX shows a cross section of Ni-Al coating on mild steel containing 2 wt. % of Sm₂O₃ and oxidized at 750°C. The scales are quite adherent, the inner Al₂O₃ light grey scales are intact and linked with the outer Fe₂O₃ (white) by pegs provided by Sm₂O₃ and NiO. Fig. X shows a cross section of oxidized Ni-Al coating on mild steel at 800°C. The inner Al₂O₃ dark grey scales are linked with outer thick scales of FeO by pegs and ridges provided by RE₂O₃. The scales are compact though but cleaved or disrupted at some locations due to decarburization during oxidation. Figs. XI and XII show cross sections of nickel aluminide coatings on mild steel containing 2 and 4.7 % of Sm₂O₃, respectively and oxidized at 850°C in air. In 2 % RE₂O₃-containing alloy inner scales
contain \( \text{Al}_2\text{O}_3 \) in the form of stratified layers of \( \text{Al}_2\text{O}_3 \) and are separated from the middle scales containing FeO admixed with Sm\(_2\)O\(_3\), the outermost scales contain Fe\(_2\)O\(_3\) incorporated with NiO. In 4.7% of RE\(_2\)O\(_3\)-containing alloy, the Al\(_2\)O\(_3\) scales are more adherent, the FeO are incorporated with RE\(_2\)O\(_3\) and the outermost scales contain Fe\(_2\)O\(_3\) admixed with NiO. Both the alloys oxidize at a relatively fast rate, the presence of higher concentration of RE\(_2\)O\(_3\) in the other alloy has indeed reduced decarburization quite appreciably.

Figure XIII shows a surface photomicrograph of a nickel aluminide coating containing 4.7% of Y\(_2\)O\(_3\), three phases are distinct: NiAl\(_2\) (dark grey), Al\(_2\)O\(_3\) (white) and Y\(_2\)O\(_3\) (light grey), the distribution seems to be fairly uniform. A similar 3-phase structure has been exhibited by the Scanning Electron Micrograph of a cross section of 1% of Y\(_2\)O\(_3\) containing nickel aluminide of 1% of Y\(_2\)O\(_3\) (Fig. XIV).

Figure XVa shows a scanning electron micrograph of nickel aluminide coating containing 1% of Y\(_2\)O\(_3\) and oxidized at 750°C. The scales are adherent but cleavage is formed due to decarburization. Figure XVb shows scanning electron micrograph of a cross section of 1% of Y\(_2\)O\(_3\) containing nickel aluminide coating on mild steel oxidized at 800°C. The scales are quite compact and adherent, a cleavage at the alloy/scale interface is formed due to decarburization although this cleavage is filled by Al\(_2\)O\(_3\)/RE\(_2\)O\(_3\) at some places, the outer
scales containing Fe₂O₃ admixed with NiO are quite thick and uniform. Figure XVIb shows a micrograph of 4.7% Y₂O₃ containing nickel aluminide coating on mild steel oxidized at 850°C, the alloy oxidizes at a relatively fast rate. The porous scales are separated from the matrix due to decarburization. The inner scale present in the form of a band layer contain FeO·NiO.

Figure XVIa shows the surface structure of 1% of La₂O₃ containing nickel aluminide coating on mild steel, the 3-phase structure is consisted dark coloured NiAl₂, light coloured Al₂O₃ and light grey coloured La₂O₃. A nearly homogeneous structure is formed during coating on mild steel. Figure XVII shows a cross section of 1% La₂O₃ containing nickel aluminide coating lump type grains containing NiAl₂ (dark) and RE₂O₃ (light grey) are formed along with particles of Al₂O₃ scattered at random. Figure XVIII shows a photomicrograph of a cross section of La₂O₃-containing nickel aluminide coating oxidized at 750°C. The iron oxide scales are non-porous uniform and compact but are perhaps separated from the alloy substrate due to polishing artifacts. La₂O₃ is present at alloy/scale interface and some Al₂O₃ is present at the innermost scales. A similar structure has been shown in the same alloy oxidized at 800°C (Fig. XIX). Figures XXa and b show scanning electron micrograph of coating containing 2% and 4.7% of La₂O₃, respectively and oxidized at 800°C. The scales formed are uniform and adherent. The inner thin
scales contain $\text{Al}_2\text{O}_3$ followed by thick iron oxide scales. At the alloy interface, $\text{RE}_2\text{O}_3$ is present and seems to play an important role in adherence of the scales. At 850°C, the coated steels containing $\text{La}_2\text{O}_3$ show severe oxidation; massive scales are formed (Fig. XXI) the inner scales contain $\text{Al}_2\text{O}_3$ incorporated with $\text{RE}_2\text{O}_3$ followed by thicker scales weight gain versus time plots. The addition of rare earth oxides in relatively small amounts (upto 2 by wt. %) and at relatively low temperatures (upto 750°C) increases the oxidation rate slightly but at higher temperatures (about 800°C) the oxidation rates of the nickel aluminide coating lower down markedly irrespective of rare earth oxide concentration. It is difficult to present a simple relationship between the size of the rare earth and the oxidation of rates of $\text{RE}_2\text{O}_3$-containing nickel aluminide coating on mild steel however, in general the oxidation rate of the coated alloy decreases with increasing ionic size provided we do not consider the irregular behaviour of the first few members of the lanthanide series. Similar behaviour has been observed in the case of simple aluminide coating where the oxidation rate of the coated alloy decreases with increasing ionic radius. In aluminide coating the effect of rare earth addition on the oxidation rates of the steel is more prominent when it shows invariably the lowering in oxidation rates and is attributed to vacancy sinks provided by rare earth oxide particles thus preventing void formation at the alloy/scale interface.
The structure of nickel aluminide coating, in general, comprises of NiAl \(_2\) (dark), Al\(_2\)O\(_3\) (light) and RE\(_2\)O\(_3\) (grey). During oxidation, NiAl\(_2\) provides Al\(_2\)O\(_3\) forming inner scales. RE\(_2\)O\(_3\) is largely concentrated at the alloy/scale interface although it is also present as inclusion in the outer scales also. The oxidation invariably proceeds by Fe\(^{2+}\) diffusion of iron oxides. The presence of a rare earth oxide does not seem to have any effect on the performance of the steel.

The photomicrograph of the cross section of \(1\%\) of Gd\(_2\)O\(_3\) containing nickel aluminide coating on mild steel shows the presence of polygonal grains of Al\(_2\)O\(_3\) (light) along with dark grey NiAl globules (Fig. XXII). Figure XXIII and Figure XXIV show scanning electron micrograph of coating containing 2\% of Gd\(_2\)O\(_3\) and oxidized at 800\(^\circ\)C. The presence of RE\(_2\)O\(_3\) (dark grey) at the alloy/scale interface provided reasonable adherence. The inner thin scales are richer in Al\(_2\)O\(_3\) and NiO is incorporated in the outer oxide scales. Figures XXV to XXVII show surface photomicrograph of nickel aluminide coating containing Pr\(_2\)O\(_3\), Er\(_2\)O\(_3\) and Tb\(_2\)O\(_3\), respectively. The micrographs show the presence of a 3-phase structure, namely NiAl\(_2\) (dark), Al\(_2\)O\(_3\) (light) and RE\(_2\)O\(_3\) (dark grey). The NiAl\(_2\) grains are polygonal in which fine grains of RE\(_2\)O\(_3\) and Al\(_2\)O\(_3\) are incorporated.
3.3 **DISCUSSION**

The presence of a nickel aluminide coating on mild steel significantly lowers down the oxidation rates of the steel in the temperature range of 700°-850°C. The oxidation of nickel aluminide coatings on mild steel proceeds by a diffusion controlled mechanism as indicated by the parabolic nature of the resulting in the formation of copious oxide scales depending upon the temperature. The scales are usually compact and adherent with low porosity and the adherence seems to be improved by the presence of rare earth oxides. Present of small pegs or ridges of rare earth oxides at the alloy/scale interface are found in some cases these act as fasteners between $\text{Al}_2\text{O}_3$ and alloy substrate. In low or medium carbon steels such a situation would have warranted lower oxidation rates for the alloys but decarburization during oxidation results in the evaluation of CO/CO$_2$ which disrupts the otherwise protective scales. In cases where the morphology of oxide scales is not seriously disrupted due to decarburization, the effect of rare earth oxide addition is more clearly pronounced and the oxidation rates are significantly lowered down.
3.4 CONCLUSIONS

i) The oxidation rates of mild steel are markedly lowered in presence of a nickel aluminide coating.

ii) The presence of rare earth provides grain refinement of the structure.

iii) At relatively low temperatures and low concentrations of RE$_2$O$_3$, the presence of RE$_2$O$_3$ generally results in a slight increase in the oxidation rates.

iv) At high temperatures (above $800^\circ$C), the addition of RE$_2$O$_3$ considerably lowers the oxidation rates of nickel aluminide coated steels.

v) In considerable number of cases, there is evidence of the presence of small pegs or ridges at alumina scale/alloy interface which act as fastners between alloy and the scales.

vi) Decarburization during oxidation seems to upset the beneficial effects of rare earth oxide additions.
<table>
<thead>
<tr>
<th>S.No.</th>
<th>Coatings</th>
<th>Temperature Range</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>750°C</td>
</tr>
<tr>
<td>1.</td>
<td>Uncoated</td>
<td></td>
</tr>
<tr>
<td>2.</td>
<td>Ni-Al Pure</td>
<td>1.94</td>
</tr>
<tr>
<td>3.</td>
<td>Ni-Al+La₂O₃</td>
<td>2.19</td>
</tr>
<tr>
<td>4.</td>
<td>Ni-Al+Sm₂O₃</td>
<td>2.22</td>
</tr>
<tr>
<td>5.</td>
<td>Ni-Al+Y₂O₃</td>
<td>1.59</td>
</tr>
<tr>
<td>6.</td>
<td>Ni-Al+Gd₂O₃</td>
<td>1.94</td>
</tr>
<tr>
<td>7.</td>
<td>Ni-Al+Yb₂O₃</td>
<td>2.63</td>
</tr>
<tr>
<td>8.</td>
<td>Ni-Al+Nd₂O₃</td>
<td>2.30</td>
</tr>
<tr>
<td>9.</td>
<td>Ni-Al+Pr₂O₃</td>
<td>3.00</td>
</tr>
<tr>
<td>10.</td>
<td>Ni-Al+Tb₂O₃</td>
<td>3.19</td>
</tr>
<tr>
<td>11.</td>
<td>Ni-Al+Er₂O₃</td>
<td>3.50</td>
</tr>
<tr>
<td>12.</td>
<td>Ni-Al+Ho₂O₃</td>
<td>4.07</td>
</tr>
</tbody>
</table>
Table 3.2

Parabolic rate constant $K_p \left( \text{gm}^2 \text{ cm}^{-4} \text{ s}^{-1} \right)$ of pure nickel aluminide coating and Ni-Al coating containing 1 wt. % of $\text{RE}_2\text{O}_3$ on mild steel oxidized in the temperature range $750^\circ\text{C}$, $800^\circ\text{C}$ and $850^\circ\text{C}$.

( x $10^{-8}$ $\text{gm}^2 \text{ cm}^{-4} \text{ s}^{-1}$).

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Coatings</th>
<th>Temperature Range</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$750^\circ\text{C}$</td>
</tr>
<tr>
<td>1.</td>
<td>Ni-Al+$\text{La}_2\text{O}_3$</td>
<td>2.63</td>
</tr>
<tr>
<td>2.</td>
<td>Ni-Al+$\text{Sm}_2\text{O}_3$</td>
<td>1.76</td>
</tr>
<tr>
<td>3.</td>
<td>Ni-Al+$\text{Y}_2\text{O}_3$</td>
<td>1.34</td>
</tr>
</tbody>
</table>
Table 3.3

Parabolic rate constant Kp (gm² cm⁻⁴ s⁻¹) of pure nickel aluminide coating and Ni-Al coating containing 4.7 wt. % of RE₂O₃ on mild steel oxidized in the temperature range 750⁰, 800⁰ and 850⁰C (x 10⁻⁸ gm² cm⁻⁴ s⁻¹).

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Coatings</th>
<th>Temperature Range</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>750⁰C</td>
</tr>
<tr>
<td>1.</td>
<td>Ni-Al+La₂O₃</td>
<td>1.52</td>
</tr>
<tr>
<td>2.</td>
<td>Ni-Al+Sm₂O₃</td>
<td>0.72</td>
</tr>
<tr>
<td>3.</td>
<td>Ni-Al+Y₂O₃</td>
<td>0.46</td>
</tr>
</tbody>
</table>
Table 3.4

Activation energies for the oxidation of nickel aluminate coating and Ni-Al coating containing 2 wt. % of RE$_2$O$_3$ on mild steel.

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Coatings</th>
<th>Activation energies $\Delta QKCal$/mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Pure Ni-Al</td>
<td>$0.88 \times 10^4$</td>
</tr>
<tr>
<td>2.</td>
<td>Ni-Al+Yb$_2$O$_3$</td>
<td>$0.45 \times 10^4$</td>
</tr>
<tr>
<td>3.</td>
<td>Ni-Al+Tb$_2$O$_3$</td>
<td>$0.35 \times 10^4$</td>
</tr>
<tr>
<td>4.</td>
<td>Ni-Al+Sm$_2$O$_3$</td>
<td>$0.50 \times 10^4$</td>
</tr>
<tr>
<td>5.</td>
<td>Ni-Al+Y$_2$O$_3$</td>
<td>$0.88 \times 10^4$</td>
</tr>
<tr>
<td>6.</td>
<td>Ni-Al+Ho$_2$O$_3$</td>
<td>$0.77 \times 10^4$</td>
</tr>
<tr>
<td>7.</td>
<td>Ni-Al+Gd$_2$O$_3$</td>
<td>$0.77 \times 10^4$</td>
</tr>
<tr>
<td>8.</td>
<td>Ni-Al+La$_2$O$_3$</td>
<td>9263.15</td>
</tr>
<tr>
<td>9.</td>
<td>Ni-Al+Pr$_2$O$_3$</td>
<td>4842.10</td>
</tr>
<tr>
<td>10.</td>
<td>Ni-Al+Nd$_2$O$_3$</td>
<td>8000.00</td>
</tr>
<tr>
<td>11.</td>
<td>Ni-Al+Er$_2$O$_3$</td>
<td>0.50</td>
</tr>
</tbody>
</table>
### Table 3.5

Activation energies for the oxidation of nickel aluminate coating containing 4.7 wt. % of RE₂O₃ on mild steel.

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Coatings</th>
<th>Activation energies (kCal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Ni-Al+La₂O₃</td>
<td>4.8 x 10⁴</td>
</tr>
<tr>
<td>2.</td>
<td>Ni-Al+Sm₂O₃</td>
<td>0.5 x 10⁴</td>
</tr>
<tr>
<td>3.</td>
<td>Ni-Al+Y₂O₃</td>
<td>1.7 x 10⁴</td>
</tr>
</tbody>
</table>

### Table 3.6

Activation energies for the oxidation of nickel aluminate coating containing 1 wt. % of RE₂O₃ on mild steel.

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Coatings</th>
<th>Activation energies (kCal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Ni-Al+La₂O₃</td>
<td>1.22 x 10⁴</td>
</tr>
<tr>
<td>2.</td>
<td>Ni-Al+Sm₂O₃</td>
<td>0.69 x 10⁴</td>
</tr>
<tr>
<td>3.</td>
<td>Ni-Al+Y₂O₃</td>
<td>0.48 x 10⁴</td>
</tr>
</tbody>
</table>
FIG 3.1 Nickel Aluminide coating containing 2 wt % RE₂O₃ at 750°C

FIG 3.2 Nickel Aluminide coating containing 2 wt % RE₂O₃ at 750°C

FIG 3.3 Nickel Aluminide coating containing 2 wt % RE₂O₃ at 800°C

FIG 3.4 Nickel Aluminide coating containing 2 wt % RE₂O₃ at 800°C
FIG 3.5 Nickel Aluminide coating containing 2 wt % RE₂O₃ at 850°C

FIG 3.6 Nickel Aluminide coating containing 2 wt % RE₂O₃ at 850°C

FIG 3.7 Nickel Aluminide coating containing 1 wt % RE₂O₃ at 750°C

FIG 3.8 Nickel Aluminide coating containing 1 wt % RE₂O₃ at 800°C
FIG 3.9 Nickel Aluminide coating containing 1wt.% RE$_2$O$_3$ at 850°C.

FIG 3.10 Nickel Aluminide coating containing 4.7wt.% RE$_2$O$_3$ at 750°C.

FIG 3.11 Nickel Aluminide coating containing 4.7wt.% RE$_2$O$_3$ at 800°C.

FIG 3.12 Nickel Aluminide coating containing 4.7wt.% RE$_2$O$_3$ at 850°C.
FIG 3.13 Nickel Aluminide coating containing 2 wt % RE₂O₃ at 750°C

FIG 3.14 Nickel Aluminide coating containing 2 wt % RE₂O₃ at 750°C

FIG 3.15 Nickel Aluminide coating containing 2 wt % RE₂O₃ at 800°C

FIG 3.16 Nickel Aluminide coating containing 2 wt % RE₂O₃ at 800°C
**FIG 3.17** Nickel Aluminide coating containing 2 wt % RE₂O₃ at 850°C

**FIG 3.18** Nickel Aluminide coating containing 2 wt % RE₂O₃ at 850°C

**FIG 3.19** Nickel Aluminide coating containing 1 wt % RE₂O₃ at 750°C

**FIG 3.20** Nickel Aluminide coating containing 1 wt % RE₂O₃ at 800°C
FIG. 3.21 Nickel Aluminide coating containing 1 wt. % RE$_2$O$_3$ at 850°C.

FIG. 3.22 Nickel Aluminide coating containing 4.7 wt. % RE$_2$O$_3$ at 850°C.

FIG. 3.23 Nickel Aluminide coating containing 4.7 wt. % RE$_2$O$_3$ at 800°C.

FIG. 3.24 Nickel Aluminide coating containing 4.7 wt. % RE$_2$O$_3$ at 750°C.
Fig. 3.26 Arrhenium plots for the Oxidation of 2 wt.% RE₂O₃-containing Ni-aluminide coating.

Fig. 3.25 Arrhenium plots for the Oxidation of 2 wt.% RE₂O₃-containing Ni-aluminide coating.
**Figure 27** Arrhenius plots for the oxidation of 2 wt% RE₂O₃-containing Ni-aluminide coating.

**Figure 28** Arrhenius plots for the oxidation of 1 wt% RE₂O₃-containing Ni-aluminide coating.
FIG. 3.29 Arrheniun plots for the Oxidation of 4.7 wt. % RE₂O₃-containing Ni-aluminide coating.
Figure 3.30 Ionic radii vs $K_p$ plots at different temperatures for RE$_2$O$_3$ containing Ni-aluminide coating.
Fig. I  Optical photomicrograph of Ni-aluminide surface coating on mildsteel (625 X)

Fig. II  SEM picture of Ni-aluminide surface coating on mildsteel (1000 X)
Fig. III Optical photomicrograph of Ni-aluminide coating on mildsteel oxidized at 750°C (250 X).
Fig. IVa SEM Cross-sectional view of Ni-Aluminide coating on mild steel oxidized at 800°C (180 X)

Fig. IVb SEM Cross-sectional view of Ni-aluminide coating on mild steel oxidized at 800°C (192 X)
Fig. V Optical photomicrograph of Ni-aluminide coating on mild steel oxidized at 850°C (125 X).
Fig. VI Optical photomicrograph of Ni-aluminide surface coating on mildsteel containing 2 % Sm$_2$O$_3$ (250 X).

Fig. VII Optical photomicrograph of Ni-aluminide surface coating on mildsteel containing 1 % Sm$_2$O$_3$ (250 X).
Fig. VIII SEM picture of Ni-aluminide surface coating on mildsteel containing 2% Sm$_2$O$_3$ (2000 X).

Fig. IX SEM Cross sectional view of Ni-aluminide coating on mildsteel containing 2% Sm$_2$O$_3$ oxidized 750°C (200 X)
Fig. XI Cross sectional view of Ni-aluminide coating on mildsteel containing 2% Sm$_2$O$_3$ oxidized at 850°C (125 X).
Fig. XII Cross sectional view of Ni-aluminide containing 4.7 wt. % Sm$_2$O$_3$ oxidized at 850°C (125 X).
Fig. XIII  Optical photomicrograph, Ni-aluminide surface coating containing 4.7 % Y₂O₃ on mildsteel (250 X).

Fig. XIV  SEM picture of Ni-aluminide surface coating on mildsteel containing 1 % Y₂O₃ (2000X).
Fig. XVa  SEM Cross sectional view of Ni-aluminide coating on mildsteel containing 2% Y$_2$O$_3$ oxidized at 750°C (180 X).

Fig. XVb  SEM Cross sectional view of Ni-aluminide coating on mildsteel containing 2% Y$_2$O$_3$ oxidized at 800°C (96 X).
Fig. XVIa Optical photomicrograph of Ni-aluminide surface coating containing 1% La$_2$O$_3$ on mild steel (150 X).

Fig. XVIb Cross sectional view of Ni-aluminide coating containing 4.7% Y$_2$O$_3$ on mild steel oxidized at 850°C (125 X).
Fig. XVII SEM picture of Ni-aluminide surface coating on mildsteel containing 1% La$_2$O$_3$ (1000 X).
Fig. XVIII Cross sectional view of Ni-aluminide coating on mildsteel containing 1% La$_2$O$_3$ Oxidized at 750°C (125 X).
Fig. XIX  Cross sectional view of ni-aluminide coating on mildsteel containing 1% La$_2$O$_3$ oxidized at 800°C (125 X).
Iron oxides

Fig. XXa SEM Cross sectional view of Ni-aluminide coating on mild steel containing 2% La$_2$O$_3$ oxidized at 800°C (200 X).

Fig. XXb SEM Cross sectional view of Ni-aluminide coating on mild steel containing 2% La$_2$O$_3$ oxidized at 800°C (200 X).
Fig. XXI Cross sectional view of Ni-aluminide coating on mildsteel containing 2% La2O3 oxidized at 850°C (125 X).
Fig. XXII SEM picture of Ni-aluminide surface coating on mild steel containing 2% Cd$_2$O$_3$ (1000 X).

Fig. XXIII SEM cross sectional view of Ni-aluminide coating on mild steel containing 2% Cd$_2$O$_3$ oxidized at 800°C (176 X).
Fig. XXIV SEM Cross sectional view of Ni-aluminide coating on mildsteel containing 2% Gd$_2$O$_3$ oxidized at 800°C (160 X).

Fig. XXV Optical photomicrograph of Ni-aluminide surface coating on mildsteel containing 2% Pr$_2$O$_3$ (625 X).
Fig. XXVI Optical photograph of Ni-aluminide surface coating on mild steel containing 2% Er$_2$O$_3$ (250 X).

Fig. XXVII Optical photomicrograph of Ni-aluminide surface coating on mild steel containing 2% Tb$_2$O$_3$ (250 X).
Chapter IV
CHAPTER - IV

A. OXIDATION BEHAVIOUR OF MILD STEEL IN PRESENCE OF Na₂SO₄

4.1 RESULTS

4.1.1 Hot Corrosion Studies

The hot corrosion behaviour of mild steel under a thin film of Na₂SO₄ (2 to 10 mg/cm²) has been studied in the temperature range of 700 to 900°C. These studies have been carried out in a limited supply of air and hot corrosion runs were usually of 1 hr, 6 hrs, 12 hrs and 24 hrs durations. The experimental details are provided in Chapter II.

4.1.2 Oxidation Studies

Figures 4.1 to 4.4 show the plots of weight gain versus amount of Na₂SO₄ deposited at 700, 800 and 900°C, respectively. The Na₂SO₄-deposited mild steel specimen were subjected to 1 hr, 6 hrs, 12 hrs and 24 hrs expositions. Interesting information is emerged from a study of these plots. There is little or no change in weight gain values on varying amount of Na₂SO₄ deposit on mild steel specimen at a particular temperature but on increasing temperature the weight gains values (or corrosion rate) increase rapidly. It appears that at a fixed temperature corrosion rates are independent of Na₂SO₄ concentration. Figures 4.5 to 4.10 show the plots of weight gain versus time for the oxidation of Na₂SO₄-coated mild steel specimen at varying concentration of Na₂SO₄ and at different temperatures.

61
At relatively low temperatures (700 and 800°C), the weight gain values are more or less the same in the presence of Na$_2$SO$_4$ depositions (range: 2-10 mg/cm$^2$) as indicated by Figs. 4.5 and 4.6. However, at a higher temperature (900°C) there is slight deviation from the normal behaviour (Fig. 4.7). The weight gain versus time plots indicate a rapid rise in the oxidation rates from 800 to 900°C (Figs. 4.8 to 4.10).

4.1.3 Microstructural Studies

Figure 4.11 shows a scanning electron photomicrograph of a cross section of mild steel specimen oxidized in presence of Na$_2$SO$_4$ at 700°C. A compact inner layer of FeO layer is present followed by relatively thick middle layer of Fe$_3$O$_4$ and outer most thin white layer of Fe$_2$O$_3$. A discreet thick layer containing crystalloid of Na$_2$SO$_4$ is distinct in the microstructure. Figure 4.12 shows an optical micrograph of the oxidized alloy. A thin white layer represents oxides of iron followed by coating of Na$_2$SO$_4$. It appears that there is very little or no reaction between Na$_2$SO$_4$ and the steel at this temperature.

Figures 4.13 to 4.15 show SEM pictures of the Na$_2$SO$_4$ coated mild steel specimen oxidized at 800°C. The multilayer thick scales containing FeS in the outer layers and the middle scale layer comprising the bulk of scale contain Na$_2$FeO$_2$/NaFeO$_2$ the inner layers contain FeO with inclusions of FeS. The
presence of Na$_2$FeO$_2$/NaFeO$_2$ and FeS is indicated by X-ray diffraction analysis. Figures 4.16 to 4.18 show optical micrographs of the oxidized specimens at 800°C. The scales are detached from the alloy in most of the cases as revealed by the micrographs perhaps due to decarburization. Na$_2$SO$_4$(l) reacted with the oxide layers on the steel and also penetrated inside the matrix along the grain boundaries. The presence of iron sulphide FeS and Na$_2$FeO$_2$ at the alloy/scale interface is indicated by X-ray diffraction analysis.

Figure 4.19 shows optical micrograph of a cross section of Na$_2$SO$_4$-coated mild steel oxidized at 900°C. The specimen is most aggressively attacked by Na$_2$SO$_4$ at this temperature as revealed by the appearance of the micrographs of scales and the matrix.

4.1.4 DISCUSSION

Interesting information is available from oxidation experiments involving weight gain/Na$_2$SO$_4$ deposited and weight gain/time measurements. It appears that the amount of Na$_2$SO$_4$ deposited is not an important parameter as far as corrosion rates are concerned specially at lower temperatures (≈ 700°C). At lower temperatures, the corrosion rates seem to be independent of the amount of salt deposited. After initial oxide formation, Na$_2$SO$_4$ seems to act as a barrier layer and practically there is little change in oxidation rate (or weight gain) with increasing salt deposition. Therefore, it is not
surprising to find that at low temperatures (upto 700°C), the oxidation rates of Na$_2$SO$_4$-coated mild steel are lower than the uncoated mild steel. Some variations in the oxidation rates are observed perhaps due to the gaps, cracks or discontinuity in the Na$_2$SO$_4$ layer, this may allow the air to review contact with the alloy resulting in oxidation of the alloy at a much faster rate. Temperature has a profound affect on the oxidation/hot corrosion behaviour of the alloy. At 700°C, no or very little hot corrosion attack is exhibited by Na$_2$SO$_4$. As stated above, after the formation of iron oxide layer, further oxidation depends entirely upon the integrity of Na$_2$SO$_4$ coating.

At 800°C, Na$_2$SO$_4$(t) attacks the multi oxide scales already present on the steel. A salt fluxing reaction takes place resulting in the formation of NaFeO$_2$ and/or Na$_2$FeO$_2$.

\[
\text{Na}_2\text{SO}_4 \rightarrow \text{Na}_2\text{O} + \text{SO}_2 + 0
\]
\[
2\text{FeO} + 0 \rightarrow \text{Fe}_2\text{O}_3
\]
\[
\text{Na}_2\text{O} + \text{Fe}_2\text{O}_3 \rightarrow \text{Na}_2\text{Fe}_2\text{O}_4 \text{ (or 2NaFeO$_2$)}
\]
\[
\text{Na}_2\text{O} + \text{FeO} \rightarrow \text{Na}_2\text{FeO}_2
\]

Consumption of oxygen at the salt/scale interface results in an increasing S-activity and in consequence, sulfide is formed in the outer layers. Na$_2$SO$_4$(t) also penetrates into the alloy and there is some sulfidation in the regions of the vicinity of alloy/scale interface. The reaction is more pro-
nounced at 900°C as is evident from weight gain versus time measurements and microstructural studies.

At 800°C and 900°C, the scales are detached from the steel due to evolution of carbonaceous gases (CO/CO₂) which exert stresses on the already fragile scales. The photomicrographs therefore, do not show scales.
FIG 4.1

![Graph showing weight gain vs. Na$_2$SO$_4$ deposited in mg/cm$^2$ for different temperatures.]

FIG 4.2 Plots of weight change versus amounts of Na$_2$SO$_4$ deposited on mild steel, Oxidized at 700°C, 800°C and 900°C for 1 hr and 6 hrs.
**FIG. 4.3** Plots of weight change versus amounts of Na$_2$SO$_4$ deposited on mild steel, Oxidized at 700°, 800° and 900°C for 12 hrs.
FIG. 4.4 Plots of weight change versus amounts of Na$_2$SO$_4$ deposited on mild steel, oxidized at 700°, 800° and 900°C for 24 hrs.
FIG 4.5

FIG 4.6 Plots of weight change versus time for Na₂SO₄ deposited on mild steel at different concentrations, oxidized at 700°C and 800°C for 24 hrs.
FIG. 4.7 Plots of weight change versus time for Na$_2$SO$_4$ deposited on mild steel at different concentrations, oxidized at 900°C for 24 hrs.
FIG. 4-8 Plots of weight change versus time for 2 mg. \( \text{Na}_2\text{SO}_4 \) deposited on mild steel, oxidized at 700\(^\circ\), 800\(^\circ\) and 900\(^\circ\)C for 24 hrs.
FIGURE 4.9 Plots of weight change versus time for 5 mg. Na$_2$SO$_4$ deposited on mild steel, oxidized at 700$^\circ$, 800$^\circ$ and 900$^\circ$C for 24 hrs.
FIG. 4.10 Plots of weight change versus time for 10 mg. Na$_2$SO$_4$ deposited on mild steel, oxidized at 700$^\circ$, 800$^\circ$ and 900$^\circ$C for 24 hrs.
Fig. 4.11 Scanning Electron Micrograph of a cross section of mild steel specimen in presence of 5 mg Na\textsubscript{2}SO\textsubscript{4} oxidized at 700°C for 6 hrs (470 X)

Fig. 4.12 Optical photomicrograph of cross section of mild steel specimen in presence of 5 mg of Na\textsubscript{2}SO\textsubscript{4} oxidized at 700°C for 12 hrs (125 X)
Fig. 4.13 Scanning Electron Micrograph of a cross section of mild steel specimen in presence of 5 mg Na$_2$SO$_4$ oxidized at 800°C for 24 hrs (200 X)

Fig. 4.14 Scanning Electron Micrograph of a cross section of mild steel specimen in presence of 10 mg Na$_2$SO$_4$ oxidized at 800°C for 12 hrs (360 X)
Fig. 4.15 Scanning Electron Micrograph of a cross section of mild steel specimen in presence of 2 mg Na$_2$SO$_4$ oxidized at 800°C for 1 hr (2400 X)

Fig. 4.17 Optical photomicrograph of a cross section of mild steel specimen in presence of 10 mg Na$_2$SO$_4$ oxidized at 800°C for 1 hr (125 X)
Fig. 4.16 Optical photomicrograph of a cross section of mild steel specimen in presence of 5 mg Na₂SO₄ oxidized at 800°C for 6 hrs (125 X)
Fig. 4.18 Optical photomicrograph of a cross section of mild steel specimen in presence of 2 mg Na$_2$SO$_4$ oxidized at 800°C for 12 hrs (125 x)
Fig. 4.19 Optical photomicrograph of cross section of mild steel specimen in presence of 5 mg Na$_2$SO$_4$ oxidized at $900^\circ$C for 6 hrs ($125 \times$)
B. OXIDATION OF BOROSILICATE COATING ON MILD STEEL

4.2.1a Oxidation Kinetics

The oxidation kinetics of the borosilicate coated steel was measured at 700°, 800° and 900°C in a stream of dried air. The weight changes with time were measured using a helical thermal balance attached with a cathetometer.

4.2.1b X-ray Diffraction Analysis

The identification of coating phases and those of the constituents present in the scales was determined by X-ray diffraction analysis using a philips X-ray diffractometer model APD 1700.

4.2.1c Microstructural Studies

The metallographic studies were carried out using a Leitz Metallux-2 photomicroturgical microscope. The samples were mounted on paper moulds using araldite as a cold setting compound. The mounted specimens were abraded sequentially on 180, 380 and 600 SiC grit papers followed by polishing on 40 μ, 8 μ, 6 μ and 1 μ diamond pastes.

SEM studies were carried out using a JEOL scanning electron microscope. Polished specimen were coated with colloidal gold emulsion and their structures were examined through the microscope.

The X-ray concentration profiles or X-ray mapping of
the various elements in the alloys were determined using Energy Dispersive X-ray Analysis (EDAX).

4.2.2 EXPERIMENTAL

4.2.2a Materials

Commercial mild steel of the composition C-0.2, Si-0.5, S-0.03 and Mn-0.1 was used during the experiments. Strips of about 20 x 10 x 1 mm size were cut from the sheet of mild steel. The specimen were sealed in an evacuated quartz tube and were annealed at 900°C for 4 hrs. The annealed specimen were abraded with 180 and 600 grits SiC papers and were subsequently washed with alcohol and degreased with CCl₄.

Al₂O₃, B₂O₃, SiO₂ and H₃PO₄ used were analytical grade (AR) reagents. The rare earth oxides : La₂O₃, Sm₂O₃, Gd₂O₃, Y₂O₃, Yb₂O₃, Ce₂O₃, Nd₂O₃, Er₂O₃, Pr₂O₃, Tb₂O₃ and Ho₂O₃, used were all spectroscopically pure chemicals.

4.2.2b Preparation of Borosilicate Coating

A mixture was prepared by mixing 30 mesh size powders of SiO₂, B₂O₃ and Al₂O₃ in the ratio of 1:2:3 (by weight), respectively. The mixture powder was slurried in 10 % H₃PO₄ solution. The slurry was applied on the mild steel strips using a brush. The coated strips were heated at 100⁰-150⁰C in air for about 15 mts, the strips having non-uniform or uneven coating were rejected. The coated strips were then
treated at 800°C for 3 hrs in Ar(g) followed by annealing. A thin dark grey coating was formed on the mild steel having an excellent adhesion.

Rare earth oxide-containing borosilicate coating was prepared by using a slurry containing SiO₂, B₂O₃, Al₂O₃ and RE₂O₃ in the ratio of 1:2:3:1 or 2, (by weight) respectively. The method of application and heat treatment were similar to those used for borosilicate coating.

4.2.3 RESULTS

4.2.4 Oxidation Kinetics

The oxidation kinetics studies on borosilicate coating on mild steel in presence of varying concentration of rare earth oxides, were carried out at 3 different temperatures e.g., 700°C, 800°C and 900°C in air. Some typical weight gain vs time plots are shown in Figures 4.20 to 4.22). In general the oxidation kinetic plots are parabolic at 700°C and 800°C as indicated by the linear nature of weight gain² vs time plots (Figs. 4.23 and 4.24). However, weight gain² vs time plots at 900°C show breaks in most cases after exposure time varying from 6 to 10 hrs (Fig. 4.25). Table 4.2.7 lists the values of the parabolic rate constant, Kp for the oxidation of borosilicate coated steel at 700°C, 800°C and 900°C. Figures 4.26a and b show the effect of increasing rare earth oxide concentration on the oxidation rates of borosilicate coatings on mild steel. The weight gain vs time plots are given for
14, 25 and 32 weight % of \( \text{RE}_2\text{O}_3 \) at 700° and 900°C. In general, an increase in \( \text{RE}_2\text{O}_3 \) concentration in the coating enhances the oxidation rate slightly. Arrhenius plots (log \( K_p \) vs \( 1/T \)) for the oxidation of borosilicate-coated steel in presence of different rare earth oxides are shown in Figure 4.27. Only in a few cases a linear relationship seems to exist.

4.2.5 **Microstructural Studies**

The surface and cross-sectional views of the coated steels were examined by optical and scanning electron microscopy. Figure 4.28 shows optical micrograph of borosilicate coating on mild steel (surface view); 3 phase appeared in the microstructure namely, \( \text{Al}_2\text{O}_3 \) (light), \( \text{FeB}_2\text{SiO}_4 \) (dark grey) and elongated grains of \( \text{SiO}_2 \). The presence of all the three phases is confirmed by X-ray diffraction analysis. SEM picture of the same alloy shows the presence of polygonal \( \text{Al}_2\text{O}_3 \) grains in a dark grey matrix of \( \text{FeB}_2\text{SiO}_4 \) (Fig. 4.29). Figure 4.30 shows an optical micrograph of the borosilicate-coated mild steel oxidized at 800°C. The borosilicate coating is fairly compact and appears to be intact. During oxidation, at the alloy/coating interface, extremely thin scales of FeO grew along with FeO. \( \text{Fe}_2\text{O}_3 \) formed outermost scales at the top of the borosilicate coating. The coating is detached from the substrate alloy due to decarburization. Figure 4.31 shows SEM picture of the same specimen, it provides more details about the morphology of the scales and the coating.
The coating is detached from the alloy substrate otherwise it is quite compact.

Figures 4.32 and 4.33 show optical and scanning photomicrographs of borosilicate-coated mild steel containing 14 % La$_2$O$_3$. The surface view shows the dispersion of extremely fine La$_2$O$_3$ in an iron borosilicate matrix containing coarse particulates of Al$_2$O$_3$ as inclusions. Figure 4.34 shows a cross-sectional view of the same alloy oxidized at 800°C. While the coating is somewhat disrupted but is intact, the oxide scales are detached.

Figures 4.35 and 4.36 show optical and scanning photomicrographs of the surface of the borosilicate coating on mild steel containing 14 weight % Sm$_2$O$_3$. The three phase structure shows the dispersion of dark grey Sm$_2$O$_3$ particles in light grey matrix of iron boro-silicate, FeB$_2$SiO$_4$. Figure 4.37 shows an optical micrograph of a cross section of borosilicate-coated mild steel containing 14 weight % Sm$_2$O$_3$ and oxidized at 800°C. The coating though compact is somewhat porous and is detached from the substrate perhaps due to decarburization. The outer layers are rich in iron oxides existing with relatively thick borosilicate coating. Figure 4.38 shows SEM picture of the oxidized borosilicate alloy containing 25 weight % Sm$_2$O$_3$. The features are similar as those of 14 weight % Sm$_2$O$_3$ alloy however, in this case Sm$_2$O$_3$ is present not only as dispersion in the matrix but also at
the coating/alloy interface.

Figures 4.39 and 4.40 show optical photomicrographs of borosilicate coating containing 14 and 25 weight % $Y_2O_3$, respectively. The structure is similar to the other rare earth oxide containing borosilicate coating. Dark grey $Y_2O_3$ dispersoids are present in a light grey iron-borosilicate, light $Al_2O_3$ particles are also present as a discrete phase. SEM picture (Fig. 4.41) shows similar features in much more detail, the presence of polygonal coarsened $Al_2O_3$ particles can be seen. Figure 4.42 shows an optical micrograph of borosilicate-coated mild steel containing 14 weight % $Y_2O_3$ and oxidized at 800°C. The coating seems to be intact although separated from the substrate due to decarburization. $Y_2O_3$ particles are dispersed in a coating matrix constituting mainly iron borosilicate. The outer layers of coating contain $Fe_2O_3$ whereas the alloy/coating interface $FeO$ is present along with $Al_2O_3$.

Figures 4.43 to 4.49 show optical and scanning photomicrographs of borosilicate-coated mild steel containing 14 weight % of $Gd_2O_3$, $Nd_2O_3$, $Ca_2O_3$, $Tb_2O_3$ or $Pr_2O_3$ in unoxidized and oxidized conditions. The surface morphologies of the coating and the oxide scales are very similar to those described for $La_2O_3$, $Sm_2O_3$ and $Y_2O_3$ containing borosilicate coatings. The coating in general constitutes iron borosilicate $FeB_2SiO_4$ matrix in which grey rare earth oxide, $RE_2O_3$ are dis-
persed along with light $\text{Al}_2\text{O}_3$ particles. Upon oxidation, the integrity of borosilicate coating by and large remain maintained but is separated from the matrix due to decarburization.

4.2.6 DISCUSSION

The oxidation of borosilicate coating on mild steel in air at $700^\circ$ and $800^\circ$C proceeds by a diffusion controlled mechanism as indicated by the parabolic nature of the weight gain vs time plots. However, at $900^\circ$C, there is deviation from the parabolic behaviour after exposure time ranging from 6 to 10 hrs as evident from the breaks in the weight gain vs time plots. The breaks perhaps represent the disruption of coating due to decarburization or thermal effect and in consequence, fresh metal is exposed to air and the oxidation proceeds by a faster rate.

Considering the effect of rare earth oxide addition on the oxidation rate of borosilicate alloy, at $700^\circ$C the presence of rare earth oxide has a negative effect i.e. oxidation rate increases. In fact borosilicate coated-steel has the lowest oxidation rate (except $\text{Nd}_2\text{O}_3$ addition) and in some cases, it is one magnitude lower than the $\text{RE}_2\text{O}_3$-containing borosilicate-coated alloy. However, at higher temperatures ($800^\circ$ and $900^\circ$C), the addition of $\text{RE}_2\text{O}_3$ considerably lowers the oxidation rate of borosilicate coated alloy. Considering the effect of rare earth size on the
oxidation rate of the borosilicate-coated alloy, (Figs. 4.50 to 4.52) a similar behaviour can not be generalized at these temperatures but the rates seem to be maximum in the middle of the lanthanide series e.g., Gd$^{3+}$ or Tb$^{3+}$. At 800° and 900°C there is a progressive increase in oxidation rate with increasing ionic radius of rare earth reaching a maximum at Gd$^{3+}$ and then the rate progressively decreases having a minimum around Nd$^{3+}$; the difference between different oxidation rates is though nominal.

The X-ray diffraction analysis of the borosilicate coating on mild steel indicates the presence of three phases: Al$_2$O$_3$, iron borosilicate FeB$_2$SiO$_4$ and SiO$_2$. The microstructure shows the presence of Al$_2$O$_3$ as polygonal grains and SiO$_2$ as inclusions in a dark or light grey matrix of iron borosilicate matrix. The formation of borosilicate coating on mild steel can be explained on the basis of following reaction mechanism.

I In the initial step, FeO is formed on steel by cation diffusion:

$$\text{Fe}^{++} + \text{O}^{--} \rightarrow \text{FeO}$$

II The inner oxide layer of FeO reacts with B$_2$O$_3$ to form iron borate, FeB$_2$O$_4$

$$\text{FeO} + \text{B}_2\text{O}_3 \rightarrow \text{FeB}_2\text{O}_4$$

III Iron borate, FeB$_2$O$_4$ reacts with SiO$_2$ to form iron
borosilicate, \( \text{FeB}_2\text{SiO}_4 \)

\[ \text{FeB}_2\text{O}_4 + \text{SiO}_2 + 2\text{Fe} \rightarrow \text{FeB}_2\text{SiO}_4 + 2\text{FeO} \]

Thus a layer of FeO is invariably present at the alloy/coating interface along with \( \text{Al}_2\text{O}_3 \).

The addition of rare earth oxide results in the introduction of a new phase thus \( \text{RE}_2\text{O}_3 \) is present as a dispersoid in the iron borosilicate matrix and some of the \( \text{RE}_2\text{O}_3 \) is concentrated at the alloy/coating interface along with FeO. During disruption of the coating either due to decarburization or thermal effect, \( \text{Fe}_2\text{O}_3 \) is formed as result of anion diffusion as is usually present as a thick layer.

The role of rare earth oxide in consolidating the oxide scales and increasing the adherence is well established. The rare earth oxide dissolves in the protective scales of \( \text{Al}_2\text{O}_3 \), \( \text{Cr}_2\text{O}_3 \) (or FeO) and traps the cationic defects of these oxides and therefore, decreases the diffusion rate of component alloy. In aluminide coating, the effect of rare earth oxide addition on the oxidation rates of the steel is more prominent where it shows invariably the lowering of oxidation rates and has been attributed to vacancy sinks provided by rare earth oxide particles thus preventing void formation at the alloy/scale interface.

During the oxidation of borosilicate coated steel containing \( \text{RE}_2\text{O}_3 \), the scales are usually compact and adherent.
with low porosity and the adherence seems to be improved by
the presence of rare earth oxide. The presence of small pegs
or ridges of RE₂O₃ at the alloy/scale interface in some cases
acts as fastner between Al₂O₃ and the alloy substrate. But
separation between metal and scales is frequently observed
due to decarburization inspite of the compactness of the
scales and the coating.
Table 4.2.7

Parabolic rate constant, $K_p$ for the oxidation of borosilicate coated-mild steel in presence of different rare earth oxides (14 weight %).

<table>
<thead>
<tr>
<th>RE$_2$O$_3$ addition</th>
<th>Parabolic rate constant, $K_p$, g$^2$cm$^{-4}$s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>700°C</td>
</tr>
<tr>
<td>Yb$_2$O$_3$</td>
<td>1.5 x 10$^{-9}$</td>
</tr>
<tr>
<td>Er$_2$O$_3$</td>
<td>2.1</td>
</tr>
<tr>
<td>Ho$_2$O$_3$</td>
<td>0.6</td>
</tr>
<tr>
<td>Tb$_2$O$_3$</td>
<td>0.7</td>
</tr>
<tr>
<td>Gd$_2$O$_3$</td>
<td>0.4</td>
</tr>
<tr>
<td>Sm$_2$O$_3$</td>
<td>0.7</td>
</tr>
<tr>
<td>Y$_2$O$_3$</td>
<td>0.6</td>
</tr>
<tr>
<td>Nd$_2$O$_3$</td>
<td>0.3</td>
</tr>
<tr>
<td>Pr$_2$O$_3$</td>
<td>0.7</td>
</tr>
<tr>
<td>Ce$_2$O$_3$</td>
<td>0.4</td>
</tr>
<tr>
<td>La$_2$O$_3$</td>
<td>0.1</td>
</tr>
<tr>
<td>No addition</td>
<td>0.3</td>
</tr>
</tbody>
</table>
FIG. 4.20 Borosilicate coating on mild steel containing 14 wt % RE₂O₃ oxidized at 700°C.
FIG. 4.21 Borosilicate coating containing 14 wt. % RE₂O₃ oxidized at 800°C.
FIG 4.22 Borosilicate coating containing 14 wt% RE₂O₃ oxidized at 900°C.
FIG. 4.23 Borosilicate coating containing 14 wt% RE₂O₃ oxidized at 700°C.
FIG. 4.24(a) Borosilicate coating containing 14 wt.% RE$_2$O$_3$ oxidized at 800°C.
FIG. 4.24(b) Borosilicate coating containing 14 wt.% RE₂O₃ oxidized at 800°C.
FIG. 4.25 Borosilicate coating containing 14 wt % RE₂O₃ oxidized at 900°C.
FIG. 4.26 (a) Borosilicate coating containing different wt % RE$_2$O$_3$ oxidized at 900°C.
FIG. 4.26(b) Borosilicate coating containing different wt. % RE₂O₃ oxidized at 700°C.
FIG 4.27 Arrhenium plots for the oxidation of 14 wt% RE$_2$O$_3$ containing Borosilicate coating.
FIG 4.50 Ionic radii Vs Kp plots of Borosilicate coating containing different RE₂O₃ oxidized at 700°C.
FIG. 4.51 Ionic radii Vs Kp plots of Borosilicate coating containing different RE$_2$O$_3$ oxidized at 800°C.
FIG. 4.52 Ionic radii Vs Kp plots of Borosilicate coating containing different RE$_2$O$_3$ oxidized at 900°C.
Fig. 4.28 Optical photomicrograph of the surface of Borosilicate coating on mild steel (250 x)

Fig. 4.29 SEM picture of the surface of Borosilicate coating on mild steel (1000 X)
Fig. 4.30 Optical Photomicrograph of a cross section of Borosilicate coating on mild steel oxidized at 800°C (125 X)
Fig. 4.31 SEM picture of a cross section of Borosilicate coating on mild steel oxidized at 800°C (120X).
Fig. 4.32a Optical photomicrograph of the surface of Borosilicate coating on mild steel containing 14 wt % of La$_2$O$_3$ (125 X)

Fig. 4.33 SEM picture of the surface of Borosilicate coating on mild steel containing 14 wt % of La$_2$O$_3$ (1500 X)
Fig. 4.32b Optical photomicrograph of the surface of Borosilicate coating on mild steel containing 14 wt % of La$_2$O$_3$ (250 X)

Fig. 4.34 SEM picture of a cross section of Borosilicate coating on mild steel containing 14 wt % of La$_2$O$_3$ oxidized at 800°C (180 X)
Fig. 4.35a Optical photomicrograph of the surface of Borosilicate coating on mild steel containing 14 wt % of Sm$_2$O$_3$ (125 X)

Fig. 4.35b Optical photomicrograph of the surface of Borosilicate coating on mild steel containing 25 wt % of Sm$_2$O$_3$ (250 X)
Fig. 4.36 SEM picture of the surface of Borosilicate coating on mild steel containing 14 wt % of Sm$_2$O$_3$ (1500 X)

Dispersion of light
Sm$_2$O$_3$ (light grey)

FeB$_2$SiO$_4$ (dark grey)

Al$_2$O$_3$ (light)

Fig. 4.38 SEM picture of a cross section of Borosilicate coating on mild steel containing 25 wt % of Sm$_2$O$_3$ oxidized at 800°C (300 X)

Grey dispersion of Sm$_2$O$_3$

Al$_2$O$_3$

Al$_2$O$_3$ + FeB$_2$SiO$_4$

Sm$_2$O$_3$

Oxide of iron
Fig. 4.37 Optical photomicrograph of a cross section of Borosilicate coating on mild steel containing 14 wt % of Sm$_2$O$_3$ oxidized at 800°C (125 X)
Fig. 4.39 Optical photomicrograph of the surface of Borosilicate coating on mild steel containing 14 wt % of $Y_2O_3$ (125 X)

Fig. 4.40 Optical photomicrograph of the surface of Borosilicate coating on mild steel containing 25 wt % of $Y_2O_3$ (250 X)
Fig. 4.41 SEM picture of the surface of Borosilicate coating on mild steel containing 14 wt % of $Y_2O_3$ (1500 X)
Fig. 4.42 Optical photomicrograph of a cross section of Borosilicate coating on mild steel containing 14 wt% of $Y_2O_3$ oxidized at 800°C (125 X)
Fig. 4.43 SEM picture of the surface of Borosilicate coating on mild steel containing 14 wt % of Gd$_2$O$_3$ (1200 X)

- Gd$_2$O$_3$ (grey)
- FeB$_2$SiO$_4$ (dark)
- Al$_2$O$_3$ (light)

Substrate
FeO + Al$_2$O$_3$
Al$_2$O$_3$ + Gd$_2$O$_3$
Gd$_2$O$_3$ dispersoids
Fe$_2$O$_3$
Oxides of iron

Fig. 4.44 SEM picture of a cross section of Borosilicate coating on mild steel containing 14 wt % of Gd$_2$O$_3$ oxidized at 800°C (200 X)
Fig. 4.45 SEM picture of surface of borosilicate coating on mild steel containing 14 wt % of Nd$_2$O$_3$ (1500 X).

Fig. 4.46 SEM picture of a cross section of borosilicate coating on mild steel containing 14 wt % of Nd$_2$O$_3$ oxidized at 800°C (180 X).
Fig. 4.47 Optical photomicrograph of the surface of Borosilicate coating on mild steel containing 14 wt % of Ce₂O₃(125 X)

Fig. 4.48 Optical photomicrograph of the surface of Borosilicate coating on mild steel containing 14 wt % of Tb₂O₃(250 X)
Fig. 4.49 Optical photomicrograph of the surface of Borosilicate coating on mild steel containing 14 wt % of Pr$_2$O$_3$ (250 X)
C. BEHAVIOUR OF BOROSILICATE COATED MILD STEEL IN PRESENCE OF Na$_2$SO$_4$

4.3 RESULTS

4.3.1 Hot Corrosion Studies

Hot corrosion studies on borosilicate coated mild steel was carried out in presence of varying concentration of Na$_2$SO$_4$ in the temperature range of 700$^\circ$ to 900$^\circ$C, in a limited supply of air. Hot corrosion runs were of time periods varying from 1 hr to 24 hrs. The experimental details of specimen preparations and coating procedures have already been described in Chapter II.

4.3.2 Oxidation Studies

Figures 4.53 to 4.56 show weight gain versus Na$_2$SO$_4$ concentration plots at 700$^\circ$, 800$^\circ$ and 900$^\circ$C for 1 hr, 6 hrs, 12 hrs, and 24 hrs, respectively. There is an increase in weight gain values with increasing temperature, increasing Na$_2$SO$_4$ concentration and increasing exposure time. In general corrosion rates at low concentrations of Na$_2$SO$_4$ are faster but as the concentration of Na$_2$SO$_4$ is increased the rates become slower. Figures 4.57 to 4.59 show weight gain versus time plots for the borosilicate-coated steel in presence of varying concentration of Na$_2$SO$_4$ (2, 5 and 10 mg/cm$^2$) and at 3 different temperatures viz 700$^\circ$, 800$^\circ$ and 900$^\circ$C. The oxidation rates of uncoated (plain) mild steel specimen
in presence of Na$_2$SO$_4$ are higher than the borosilicate coated mild steel in the temperature range of 700° to 900° C.

4.3.3 Morphological Studies

Figures 4.60 to 4.69 show some typical photomicrographs of the cross sections of the borosilicate coated mild steel corroded in presence of Na$_2$SO$_4$ at different temperatures and time periods. The main features of the microstructures of the corroded borosilicate coated steels are as follows:

(i) At 700°C, relatively thin scales are formed and there is very limited attack on the grain boundaries (Figs. 4.60 to 4.62). The borosilicate coating seems to remain intact.

(ii) At 800°C, considerable attack on the Na$_2$SO$_4$-coated alloy is observed. Besides thicker scale formation, the grain boundaries are also affected by corrosion attack (Figs. 4.63 to 4.69).

(iii) At 900°C, the attack is maximum and thicker sulfide scales are formed, the inner scales contain mainly Na$_2$FeO$_2$ as revealed by X-ray diffraction analysis. The Na$_2$SO$_4(\beta)$ has also penetrated along the grain boundaries at the vicinity of alloy/scale interface (Figs. 4.70 to 4.72). The borosilicate coating seems to be disrupted completely at this temperature.
4.3.4 DISCUSSION

The weight gain versus $\text{Na}_2\text{SO}_4$ concentration measurements for the borosilicate coated steel indicate that the specimen exposed for relatively short periods (1 to 6 hrs) exhibit a steep increase in weight gain with increasing $\text{Na}_2\text{SO}_4$ deposition. However, for borosilicate coated specimens exposed for relatively long periods (12 to 24 hrs), after an initial weight gain at lower $\text{Na}_2\text{SO}_4$ concentrations, there is little or no change in weight gain values. This behaviour is followed at all the three temperatures viz., 700°, 800° and 900°C but is more pronounced at 700° and 800°C.

Weight gain versus time curves at 700°, 800° and 900°C show that the oxidation behaviour of $\text{Na}_2\text{SO}_4$-coated borosilicate coatings is not simple. At 700°C, the behaviour is parabolic during the entire 24 hrs oxidation run but at 800°C, the parabolic behaviour is exhibited up to 12 hrs followed by faster oxidation rate. At 900°C, the behaviour is approximately linear. Interestingly the net weight gains after 24 hrs exposures are independent of amount of $\text{Na}_2\text{SO}_4$ deposition but strongly dependent on temperature. It appears that after initial reactions between the coating and $\text{Na}_2\text{SO}_4$ on one hand and the alloy and $\text{Na}_2\text{SO}_4$ on the other hand, the $\text{Na}_2\text{SO}_4$ coating remains inert as a top coat on borosilicate coating independent of the amount of $\text{Na}_2\text{SO}_4$ deposition.

The attack of $\text{Na}_2\text{SO}_4$ on borosilicate coated steel is
not significant at 700°C but quite appreciable at 800°C. Na₂SO₄ is very aggressive at 900°C, Na₂SO₄(ℓ) penetrated through borosilicate coating and attacked the alloy. Na₂SO₄(ℓ) and FeO in the inner scales undergo fluxing reaction forming Na₂FeO₃. With decreasing O₂-activity and a corresponding increase in S-activity at the alloy/scale interface result in the formation of iron sulfide, FeS. Na₂SO₄ also penetrated along the grain boundaries.

The results of the hot corrosion studies (Na₂SO₄-induced corrosion) on borosilicate coated-steel indicate that at 700°C there is manifestation of little or no attack on the alloy and the boro-silicate coating by and large remains intact. At 800°C, the attack is appreciable and the integrity of borosilicate coating is partly disturbed. At higher temperature (900°C), a pronounced hot corrosion attack is noted and this attack is a combination of fluxing and sulfidation reactions.
FIG. 4.53 Plots of weight change versus amounts of Na$_2$SO$_4$ deposited on Borosilicate coated mild steel, oxidized at 700°, 800° and 900°C for 1 hr and 6 hrs.
FIG. 4.55 Plots of weight change versus amount of Na$_2$SO$_4$ deposited on Borosilicate coated mild steel, oxidized at 700°, 800° and 900°C for 12 hrs.
FIG. 4.56 Plots of weight change versus amount of Na$_2$SO$_4$ deposited on Borosilicate coated mild steel, oxidized at 700°, 800° and 900°C for 24 hrs.
FIG. 4.57 Plots of weight change versus time for 2 mg Na$_2$SO$_4$ deposited on Borosilicate coated mild steel, oxidized at 700°, 800° and 900°C for 24 hrs.
FIG. 4.58 Plots of weight change versus time for 5 mg \( \text{Na}_2\text{SO}_4 \) deposited on Borosilicate coated mild steel, oxidized at 700°, 800° and 900°C for 24 hrs.
FIG. 4.59 Plots of weight change versus time for 10 mg Na$_2$SO$_4$ deposited on Borosilicate coated mild steel, oxidized at 700°, 800° and 900°C for 24 hrs.
Fig. 4.60 Optical photomicrograph of a cross section of Borosilicate-coated mild steel specimen in presence of 5 mg Na$_2$SO$_4$ oxidized at 700°C for 12 hrs (250 X)

Fig. 4.61 Optical photomicrograph of a cross section of Borosilicate coated mild steel specimen in presence of 10 mg Na$_2$SO$_4$ oxidized at 700°C for 12 hrs (250 X)
Fig. 4.62 Scanning Electron Micrograph of a cross section of Borosilicate-coated mild steel specimen in presence of 5 mg Na$_2$SO$_4$ oxidized at 700°C for 12 hrs (360 X)

Fig. 4.63 Optical photomicrograph of a cross section of Borosilicate-coated mild steel specimen in presence of 2 mg Na$_2$SO$_4$ oxidized at 800°C for 1 hr (125 X)
Fig. 4.64 Scanning Electron Micrograph of a cross section of Borosilicate coated mild steel specimen in presence of 2 mg Na$_2$SO$_4$ oxidized at 800°C for 1 hr (600 X)

Fig. 4.65 Optical photomicrograph of cross section of Borosilicate coated mild steel specimen in presence of 2 mg Na$_2$SO$_4$ oxidized at 800°C for 6 hrs (125 X)
Fig. 4.66 Optical photomicrograph of a cross section of Borosilicate coated mild steel specimen in presence of 2 mg Na$_2$SO$_4$ oxidized at 800°C for 12 hrs (125 X)

Fig. 4.67 Scanning Electron Micrograph of a cross section of Borosilicate coated mild steel specimen in presence of 10 mg Na$_2$SO$_4$ oxidized at 800°C for 12 hrs (800 X)
Fig. 4.68 Optical Photomicrograph of a cross section of Borosilicate coated mild steel specimen in presence of 10 mg Na₂SO₄ oxidized at 800°C for 12 hrs (250 X)
Fig. 4.69 Scanning Electron Micrograph of a cross section of Borosilicate-coated mild steel specimen in presence of 10 mg Na₂SO₄ oxidized at 800°C for 24 hrs (270 X)

Fig. 4.70 Optical photomicrograph of a cross section of Borosilicate coated mild steel specimen in presence of 5 mg Na₂SO₄ oxidized at 900°C for 6 hrs (125 X)
Fig. 4.71 Scanning Electron Micrograph of a cross section of Borosilicate coated mild steel specimen in presence of 5 mg Na$_2$SO$_4$ oxidized at 900°C for 6 hrs (150 X)

Fig. 4.72 Optical photomicrograph of cross section of Borosilicate coated mild steel specimen in presence of 5 mg Na$_2$SO$_4$ oxidized at 900°C for 12 hrs (125 X)
Chapter V
CHAPTER - V

A. HIGH TEMPERATURE OXIDATION BEHAVIOUR OF INCONEL 600 ALLOY IN PRESENCE OF Na₂SO₄

5.1 RESULTS

5.1.1 Hot Corrosion Studies

High temperature oxidation behaviour of Inconel 600 was studied in presence of varying amount of Na₂SO₄ (upto 10 mg/cm²) at three different temperatures viz. 800°, 900°, and 1000°C. The oxidation runs were usually of 24 hrs durations but some runs were limited to short duration also.

Figure 5.1 shows a typical weight gain versus amount of Na₂SO₄ deposited plot at 800°, 900° and 1000°C. It appears from the plots that initially there is an increase in corrosion rate with increasing Na₂SO₄ deposition but when the concentration exceeds to a certain limit the corrosion rate starts falling steeply. Figures 5.2 and 5.3 show weight gain versus time plots for the oxidation of Inconel 600 in presence of varying amounts of Na₂SO₄ deposited at 800° and 1000°C. The plots do not exhibit a regular behaviour. At 800°C, in the initial stages (about 30 mts or so) a maximum weight gain is noted this is followed by a rapid decrease in weight gain values upto about 6 hrs and then steep increase upto 12 hrs. After 12 hrs there are very nominal variations in weight gain values. At 1000°C there is a steep increase in weight gain.
values up to about 12 hours followed by a gradual decrease in weight gain values. Weight gain values at 1000°C are the highest for the lowest salt deposition (2 mg/cm²) and lowest for the highest salt deposition (10 mg/cm²). Figures 5.4 to 5.6 show weights gain versus time plots for the oxidation of Na₂SO₄-deposited Inconel 600 at different temperatures. There is no regular pattern in oxidation behaviour but invariably there is a loss in weight after 12 hours of exposition.

5.1.2 Microstructural Studies

Figures 5.7 to 5.9 show photomicrographs of the cross sections of Inconel 600 alloy corroded in presence of Na₂SO₄ at 800°C for 6 hrs. Little change in the microstructure of the alloy, which consisted of Cr-rich Ni phase (dark) and Ni-rich iron phase (light), is found after exposures of 6 hrs and 12 hrs, respectively. A limited change is observed at the alloy interface specially for the specimens exposed to longer durations (12 hrs). Figures 5.10 to 5.17 show photomicrographs of the cross section of Inconel 600 alloy corroded in presence of Na₂SO₄ at 900°C. Although no scales are found but there is significant attack on the alloy and the salt is penetrated along the grain boundaries, the Cr-rich dark phase seems to be more attacked. Cr₂S₃ and NiS are formed along with Na₂CrO₄/Na₂Cr₂O₄, this has been confirmed by X-ray diffraction analysis. Figure 5.18 shows a SEM photomicrograph of a cross section of Inconel 600 oxidized at 900°C for 24 hrs.
The outermost layers contain Fe$_2$O$_3$ and the inner layers are rich in Cr$_2$O$_3$. Presence of Ni-rich iron phase in the form of polygonal grains can be seen. Figures 5.19 to 5.21 show scanning electron micrographs of the cross sections of Na$_2$SO$_4$ coated Inconel 600 alloy oxidized at 900°C. The structures of the scales and the matrix can be seen in much more detail. Na$_2$SO$_4$ has preferentially attacked the Cr-rich Ni phase forming NiS and Cr$_2$S$_3$ along with Na$_2$CrO$_4$ and Na$_2$Cr$_2$O$_4$. The outer layer rich in iron oxide is also observed. The attack is most severe in Na$_2$SO$_4$-coated specimen oxidized for a longer duration.

5.1.3 DISCUSSION

The weight gain vs amount of Na$_2$SO$_4$ plots show an increase in corrosion rate with increasing Na$_2$SO$_4$ at 800°C, 900°C and 1000°C. However, this is valid up to a certain concentration of Na$_2$SO$_4$, on exceeding this concentration the corrosion rate starts diminishing. It appears that Na$_2$SO$_4$(1) reacts with the metal undergoing fluxing and sulfidation reaction and when the reaction is completed or amount of Na$_2$SO$_4$ is much more than the required for the reaction, Na$_2$SO$_4$ acts as a protective layer resulting in no or very little change in weight. The weight losses occurred during corrosion of Inconel 600 is attributed to the loss of some reaction products due to volatilization or evolution of some gases. This behaviour is more obvious at 900°C and can be explained as follows:
Inconel 600 forms a protective film of $\text{Cr}_2\text{O}_3$. $\text{Na}_2\text{SO}_4(l)$ decomposes according to following reaction:

$$\text{Na}_2\text{SO}_4 \rightarrow \text{Na}_2\text{O} + \text{SO}_2 + \frac{1}{2}\text{O}_2$$

$$\text{Na}_2\text{SO}_4 \rightarrow \text{Na}_2\text{S} + 2\text{O}_2$$

$\text{Na}_2\text{S}$ reacts with $\text{Cr}_2\text{O}_3$ to form $\text{Cr}_2\text{S}_3$

$$\text{Na}_2\text{S} + \text{Cr}_2\text{O}_3 \rightarrow \text{Cr}_2\text{S}_3 + \text{Na}_2\text{O} + \text{O}_2$$

With decrease in $S$-activity at the alloy/salt interface, $\text{Na}_2\text{O}$ will react with $\text{Cr}_2\text{O}_3$ and other oxide present on the alloy surface

$$\text{Na}_2\text{O} + \text{Cr}_2\text{O}_3 \rightarrow \text{Na}_2\text{Cr}_2\text{O}_4$$

Once the protective $\text{Cr}_2\text{O}_3$ layer is broken, $\text{Na}_2\text{O}$ can react with Ni and Fe present in the alloy to undergo fluxing reactions when the fluxing reaction is completed there will be depletion of $\text{O}^{2-}$ ions and an increase in $S^{2-}$ concentration at the alloy interface this would result in the sulfidation of Cr, Ni and Fe in the alloy itself. The scale morphologies support this point of view. The weight losses during oxidation could be attributed to the volatilization of $\text{Na}_2\text{Cr}_2\text{O}_4$/ $\text{Na}_2\text{CrO}_4$ and evolution of $\text{SO}_2$ and $\text{O}_2$.

It appears that there is very limited reaction at $800^\circ\text{C}$ but at $900^\circ\text{C}$, significant morphological changes are observed during the oxidation of Inconel 600 in presence of $\text{Na}_2\text{SO}_4$. 
FIG. 5.1 Plots of weight change versus amounts of \( \text{Na}_2\text{SO}_4 \) deposited on Inconel-600 alloy, oxidized at 800\(^\circ\), 900\(^\circ\) and 1000\(^\circ\)C for 6 hrs.
FIG. 5.2 Plots of weight change versus time for Na₂SO₄ deposited on Inconel-600 alloy at different concentrations oxidized at 800°C for 24 hrs.
FIG. 5.3 Plots of weight change versus time for Na$_2$SO$_4$ deposited on Inconel-600 alloy at different concentrations oxidized at 1000°C for 24 hrs.
FIG. 5.4 Plots of weight change versus time for 2 mg. Na$_2$SO$_4$ deposited on Inconel-600 alloy, oxidized at 800°C and 1000°C for 24 hrs.
FIG. 5.5 Plots of weight change versus time for 5 mg Na₂SO₄ deposited on Inconel-600 alloy, oxidized at 800°C and 1000°C for 24 hrs.
FIG. 5.6 Plots of weight change versus time for 10 mg. Na$_2$SO$_4$ deposited on Inconel-600 alloy, oxidized at 800°C and 1000°C for 24 hrs.
Fig. 5.7 Photomicrograph of a cross section of Inconel 600 in presence of 5 mg Na$_2$SO$_4$, oxidized at 800°C for 6 hrs (125 X)

Fig. 5.8 Photomicrograph of a cross section of Inconel 600 in presence of 10 mg Na$_2$SO$_4$, oxidized at 800°C for 6 hrs (125 X)
Fig. 5.9 Photomicrograph of a cross section of Inconel 600 in presence of 10 mg Na$_2$SO$_4$, oxidized at 800°C for 12 hrs (250 X)

Fig. 5.10 Photomicrograph of a cross section of Inconel 600 in presence of 2 mg Na$_2$SO$_4$, oxidized at 900°C for 1 hr (250 X)
Fig. 5.11 Photomicrograph of a cross section of Inconel 600 in presence of 2 mg Na$_2$SO$_4$, oxidized at 900°C for 12 hrs (125 X)

Fig. 5.12 Photomicrograph of a cross section of Inconel 600 in presence of 2 mg Na$_2$SO$_4$, oxidized at 900°C for 12 hrs (250 X)
Fig. 5.13 Photomicrograph of a cross section of Inconel-600 in presence of 2 mg Na₂SO₄, oxidized at 900°C for 24 hrs (125 X)

Fig. 5.14 Photomicrograph of a cross section of Inconel-600 in presence of 5 mg Na₂SO₄, oxidized at 1000°C for 12 hrs (125 X)
Fig. 5.15 Photomicrograph of a cross section of Inconel-600 in presence of 5 mg Na₂SO₄ oxidized at 900°C for 24 hrs (1250X)

Fig. 5.16 Photomicrograph of a cross section of Inconel-600 in presence of 10 mg Na₂SO₄ oxidized at 900°C for 1 hr (250X)
Fig. 5.17 Photomicrograph of a cross section of Inconel-600 in presence of 10 mg Na$_2$SO$_4$ oxidized at 900°C for 6 hrs (250 X)

Fig. 5.18 Scanning Electron Micrograph of a cross section of Inconel-600 oxidized at 900°C for 24 hrs (1200 X)
Fig. 5.19 Scanning Electron Micrograph of a cross section of Inconel-600 in presence of 5 mg Na$_2$SO$_4$, oxidized at 900°C for 1 hr (5000 X)

Fig. 5.20 Scanning Electron Micrograph of a cross section of Inconel-600 in presence of 10 mg Na$_2$SO$_4$, oxidized at 900°C for 12 hrs (1000 X)
Fig. 5.21 Scanning Electron Micrograph of a cross section of Inconel-600 in presence of 2 mg Na$_2$SO$_4$, oxidized at 900°C for 24 hrs (1600 X)
B. HIGH TEMPERATURE OXIDATION BEHAVIOUR OF BOROSILICATE COATED INCONEL 600 ALLOY

The details about specimen and coating preparation and coating application are given in Chapter II.

5.2 RESULTS

Figure 5.22 shows weight gain vs time plots for the oxidation of uncoated and borosilicate-coated Inconel 600 Ni-base alloy at 800°, 900° and 1000°C for 24 hrs in air. The weight gain vs time plots are linear although in case of uncoated alloy oxidized at 900° and 1000°C a break is noted after 6 hrs and 8 hrs of oxidation respectively (Fig. 5.23). In general, the oxidation behaviour is parabolic and seems to proceed by a diffusion controlled mechanism. Table 5.2 lists the parabolic rate constant, Kp for the oxidation of uncoated and borosilicate-coated inconel 600 alloy. The oxidation rates of coated alloys at 900° and 1000°C are invariably about one order of magnitude lower than the uncoated alloy.

5.2.1 Microstructural Studies

Figure 5.24 presents a cross sectional view of uncoated Inconel 600 alloy oxidized at 900°C for 2 hours. The alloy matrix contains uniformly dispersed γ precipitate (white) in which large discontinuous M23C6/MC particles (black) are accumulated at the grain boundaries. Relatively their oxide scales in the form of a band are formed. The scales which are
constituted mainly of Cr₂O₃ are detached from the matrix perhaps during polishing. No change in the structure of matrix occurred during oxidation.

Figures 5.25a and b show photomicrographs representing cross sectional views of borosilicate-coated Inconel 600 oxidized at 900°C for 24 hrs. Due to interaction of coating with the matrix, iron borosilicate FeB₂SiO₄ (light grey) is formed which is present as a discrete phase along with γ' phase (white). Coarsened carbide particles are also dispersed in the matrix. Figure 5.26 shows a twinned structure of the borosilicate-coated alloy oxidized at 1000°C. γ' phase (white) coexists with light grey Ni₃Al and dark grey FeB₂SiO₄ phases. The oxide scales forms are separated from the matrix during polishing.

5.2.2 DISCUSSION

High temperature oxidation studies carried out on borosilicate-coated Inconel 600 alloy in air indicate lowering in oxidation rates of the alloy due to the presence of coating. The effect of coating is much more pronounced at 900°C and 1000°C where the borosilicate alloys have oxidation rates one order of magnitude lower than the uncoated Inconel 600 alloy.

The Ni-base Inconel 600 alloy is a corrosion and heat resistant alloy, however, in presence of borosilicate coating the oxidation resistance is further improved.

During oxidation of coated alloy, the oxidation of
Inconel 600 proceeds by cation diffusion, Fe\(^{2+}\) ions diffuse out reacting with borate and silicate ions present in the coating to form iron borosilicate. The reactions can be represented as follows:

From alloy: \[ \text{Fe} \rightarrow \text{Fe}^{++} + 2e; \text{Ni} \rightarrow \text{Ni}^{++} + 2e \]

From air: \[ \text{O}_2 + e \rightarrow 2 \text{O}^{--} \]

Coating alloy: \[ \text{Fe}^{++} + \text{O}^{--} \rightarrow \text{FeO} \]

Coating: \[ \text{FeO} + \text{B}_2\text{O}_3 + \text{SiO}_2 \rightarrow \text{FeB}_2\text{SiO}_4 + \text{O}_2 \]

Coating/air: \[ \text{Ni}^{++} + \text{O}^{--} \rightarrow \text{NiO} \]

At the alloy coating: \[ 2\text{Cr}^{+++} + 3 \text{O}^{--} \rightarrow \text{Cr}_2\text{O}_3 \]

Iron borosilicate along with Al\(_2\)O\(_3\) acts as a barrier layer against oxidation and therefore, it considerably slows down the diffusion of cationic species, resulting in reduced oxidation rates.
Table 5.2

Parabolic rate constant $K_p \left( \text{gm}^2\text{cm}^{-4}\text{S}^{-1} \right)$ of plain and boro-silicate coated-inconel 600 alloy oxidized in the temperature range 800°, 900° and 1000°C ($x \times 10^{-10}$ \text{gm}^2\text{cm}^{-4}\text{S}^{-1}$)

<table>
<thead>
<tr>
<th>System</th>
<th>Temperature range</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>800°C</td>
</tr>
<tr>
<td>Uncoated</td>
<td>3.8</td>
</tr>
<tr>
<td>Coated</td>
<td>2.0</td>
</tr>
</tbody>
</table>
FIG. 5.22 Uncoated and Borosilicate coated-Inconel-600 alloy oxidized at different temperatures.
FIG. 5.23 Uncoated and Borosilicate coated-Inconel-600 alloy oxidized at different temperatures.
Fig. 5.24 Photomicrograph of a cross section of uncoated Inconel-600, oxidized at 900°C for 24 hrs. (125 X)

Fig. 5.25a Photomicrograph of a cross section of Borosilicate-coated Inconel-600, oxidized at 900°C for 24 hrs. (125 X)
Fig. 5.25b Photomicrograph of a cross section of Borosilicate-coated Inconel-600, oxidized at 900°C for 24 hrs. (250 X)

Fig. 5.26 Photomicrograph of a cross section of Borosilicate-coated Inconel-600, oxidized at 1000°C for 24 hrs.
C. HIGH TEMPERATURE OXIDATION BEHAVIOUR OF BOROSILICATE-COATED INCONEL 600 ALLOY IN PRESENCE OF Na₂SO₄

5.3 RESULTS

The high temperature oxidation behaviour of borosilicate-coated Inconel 600 alloy has been studied in presence of Na₂SO₄ at 800°C, 900°C and 1000°C in flowing air. Parallel oxidation studies were also carried out on uncoated alloys in presence of salt coating.

5.3.1 Oxidation Kinetics

Figures 5.27 to 5.29 show weight gain vs time plots for the oxidation of borosilicate-coated Inconel alloy in presence of 2, 5 and 10 mg of Na₂SO₄ at 800°C, 900°C and 1000°C, respectively. Figures 5.30 to 5.36 show weight gain vs time plots for the oxidation of alloy at 800°C, 900°C and 1000°C in presence of 2, 5 and 10 mg/cm² of Na₂SO₄ coating respectively. Although no uniform or regular behaviour has been observed in weight gain vs time plots but some generalization can be made from the study of the curves.

(i) At a particular temperature and exposure time, the weight gain increases with increasing amount of salt coating till a maxima is obtained. This is followed by the lowering in weight gain values with further increase in the salt deposition on the metal coupans. 1-2 mg/cm² is the usual
amount of the coated salt to achieve a maximum weight gain.

(ii) At a particular Na$_2$SO$_4$ concentration and temperature, maximum weight gain value is observed usually at an exposure time of about 12 hrs. (at 900$^\circ$ or 1000$^\circ$C) and 6 hrs (800$^\circ$C).

(iii) With a few exceptions, the corrosion rate (or weight gain values) increases with increasing temperature, the rate at 1000$^\circ$C being the highest.

5.3.2 Microstructural Studies

Figures 5.37 and 5.38 show photomicrographs of borosilicate-coated Inconel 600 alloy coated with 10 mg of Na$_2$SO$_4$ and oxidized at 800$^\circ$C. A typical microstructure of borosilicate-coated alloy is exhibited. $\gamma'$ phase (white) exists with dark grey iron borosilicate, FeB$_2$SiO$_4$ phase, black carbide particles can also be seen. During oxidation in presence of Na$_2$SO$_4$, the borosilicate coated alloy is affected only marginally and only at the metal interface some attack is noticed.

Figures 5.39 to 5.46 show optical micrographs of borosilicate-coated Inconel 600 specimen corroded at 900$^\circ$C in presence of varying amounts of Na$_2$SO$_4$ and at varying exposure times. The study of the microstructures shows varying degree of attack depending upon the exposure time and the amount of salt deposition. The attack propagates by penetration along the grain boundaries. The analysis of the corrosion products by X-ray identifies the presence of Na$_2$FeO$_2$, Fe$_2$CrO$_4$, Na$_2$CrO$_4$,
NiCrO$_4$ and some sulfides e.g., (Fe,Cr)$_2$S$_3$, NiS, FeS etc. Figures 5.47 to 5.50 show SEM pictures of the Na$_2$SO$_4$ induced corroded borosilicate-coated Inconel 600 alloy. Multiscales are formed, the borosilicate seems to disintegrate during attack. Figures 5.51 and 5.52 show optical photomicrographs of the borosilicate-coated alloy oxidized at 1000°C for 12 hrs in presence of 5 mg/cm$^2$ of Na$_2$SO$_4$. While borosilicate-coating seems to be dismembered during hot corrosion attack, the attack is also quite severe at the alloy interface. The corrosion attack seems to proceed along the grain boundaries and at some sites, resulting in the fragmentation of the alloy at the edges as indicated by the scanning electron micrographs (Figs. 5.53 and 5.54). The corrosion products as identified by X-ray diffraction analysis include sulfides (Fe,Cr)$_2$S$_3$, NiS, FeS and mixed oxides like NaFeO$_2$, FeCrO$_4$, Na$_2$CrO$_4$, NaNiO$_2$ etc.

5.3.3 DISCUSSION

Borosilicate-coated Inconel 600 alloy oxidizes by a parabolic rate law. It appears that borosilicate coating acts as a barrier layer to lower the oxidation rate of Inconel 600 by one order of magnitude at 900° and 1000°C. But in presence of Na$_2$SO$_4$, the coating is deleteriously attacked by the salt at 900° and 1000°C whilst there is little or no attack at 800°C. Maximum weight gains of the order of 10 mg/cm$^2$ are obtained for borosilicate coated alloys corroded at 1000°C for 24 hrs in presence of Na$_2$SO$_4$, comparing this value with
that obtained in case of uncoated Inconel 600 alloy (20 mg/cm²) it appears that the presence of borosilicate lowers down the corrosion rate significantly. This goes to show that during hot corrosion attack borosilicate coating is quite effective up 800°C but above this temperature it loses its protectivity. It is difficult to envisage the mechanism of attack between coating and the Na₂SO₄ but the identification of the corrosion products by X-ray analysis points out a sulfidation and salt fluxing mechanism operate during the hot corrosion attack.
Plots of weight change versus time for Na$_2$SO$_4$ deposited on Borosilicate coated Inconel-600 alloy at different concentrations, oxidized at 800°C and 900°C for 24 hrs.
FIG. 5.29 Plots of weight change versus time for Na$_2$SO$_4$ deposited on Borosilicate coated Inconel-600 alloy at different concentrations, oxidized at 1000°C for 24 hrs.
FIG 5.30

FIG 5.31 Plots of weight change versus time for 2 mg and 5 mg Na$_2$SO$_4$ deposited on Borosilicate coated Inconel-600 alloy, oxidized at 800°, 900° and 1000°C for 24 hrs.
FIG. 5.32 Plots of weight change versus time for 10 mg Na₂SO₄ deposited on Borosilicate coated Inconel-600 alloy, oxidized at 1000°C for 24 hrs.
Plots of weight change versus amounts of Na₂SO₄ deposited on Borosilicate coated Inconel-600 alloy, oxidized at 900°C and 1000°C for 1 hr and 6 hrs.
FIG 5.35

FIG 5.36 Plots of weight change versus amounts of Na$_2$SO$_4$ deposited on Borosilicate coated Inconel-600 alloy, oxidized at 800°, 900° and 1000°C for 12 hrs and 24 hrs.
Fig. 5.37 Photomicrograph of a cross section of Borosilicate coated Inconel-600 in presence of 10 mg Na$_2$SO$_4$, oxidized at 800°C for 6 hrs (250 X)

Fig. 5.38 Photomicrograph of a cross section of Borosilicate coated Inconel-600 in presence of 10 mg Na$_2$SO$_4$, oxidized at 800°C for 12 hrs (250 X)
Fig. 5.39 Photomicrograph of a cross section of Boro-
silicate coated Inconel-600 in presence of
2 mg Na$_2$SO$_4$, oxidized at 900°C for 24 hrs
(125 X)

Fig. 5.40 Photomicrograph of a cross section of Boro-
silicate coated Inconel-600 in presence of
5 mg Na$_2$SO$_4$, oxidized at 900°C for 6 hrs
(125 X)
Fig. 5.41 Photomicrograph of cross section of Boro-silicate coated Inconel-600 in presence of 5 mg Na$_2$SO$_4$, oxidized at 900°C for 6 hrs (250 X)

Fig. 5.42 Photomicrograph of a cross section of Boro-silicate coated Inconel-600 in presence of 5 mg Na$_2$SO$_4$, oxidized at 900°C for 12 hrs (125 X)
Fig. 5.43 Photomicrograph of cross section of Borosilicate coated Inconel-600 in presence of 5 mg Na$_2$SO$_4$, oxidized at 900°C for 24 hrs (125 X)

Fig. 5.44 Photomicrograph of cross section of Borosilicate coated Inconel-600 in presence of 10 mg Na$_2$SO$_4$, oxidized at 900°C for 24 hrs (250 X)
Fig. 5.45 Photomicrograph of cross section of Borosilicate coated Inconel-600 in presence of 10 mg Na₂SO₄, oxidized at 900°C for 24 hrs (250 X)

Fig. 5.46 Photomicrograph of cross section of Borosilicate coated Inconel-600 in presence of 10 mg Na₂SO₄, oxidized at 900°C for 1 hr (125 X)
Fig. 5.47 Scanning Electron Micrograph of a cross section of Borosilicate coated Inconel-600 in presence of 2 mg Na$_2$SO$_4$, oxidized at 900°C for 1 hr (1300 X)

Fig. 5.48 Scanning Electron Micrograph of a cross section of Borosilicate coated Inconel-600 in presence of 5 mg Na$_2$SO$_4$, oxidized at 900°C for 6 hrs (1300 X)
Fig. 5.49 Scanning Electron Micrograph of a cross section of Borosilicate coated Inconel-600 in presence of 10 mg Na$_2$SO$_4$, oxidized at 900°C for 12 hrs (1500 X)

Fig. 5.50 Scanning Electron Micrograph of a cross section of Borosilicate coated Inconel-600 in presence of 5 mg Na$_2$SO$_4$ 900°C for 24 hrs (1800 X)
Fig. 5.51 Photomicrograph of a cross section of Boro-
silicate coated Inconel-600 in presence of
5 mg Na$_2$SO$_4$, oxidized at 1000°C for 12 hrs
(125 X)

Fig. 5.52 Photomicrograph of a cross section of Boro-
silicate coated Inconel-600 in presence of
5 mg Na$_2$SO$_4$, oxidized at 1000°C for 12 hrs
(250 X)
Fig. 5.53 Scanning Electron Micrograph of a cross section of Borosilicate coated Inconel-600 in presence of 5 mg Na$_2$SO$_4$, oxidized at 1000°C for 12 hrs (1000 X)

Fig. 5.54 Scanning Electron Micrograph of a cross section of Borosilicate coated Inconel 600 and oxidized at 1000°C for 24 hrs (1300 X)
Chapter VI
CHAPTER VI

CONCLUSIONS

The following conclusions can be drawn from the high temperature oxidation and hot corrosion studies carried out on nickel aluminide and borosilicate coatings.

CHAPTER III: High temperature oxidation behaviour of nickel aluminide coatings on mild steel

(i) The oxidation rates of mild steel are markedly lowered in presence of a nickel aluminide coating.

(ii) The presence of rare earth oxides (RE$_2$O$_3$) provides grain refinement of the structure.

(iii) At relatively low temperatures (upto 800°C) and low concentrations of RE$_2$O$_3$, the presence of RE$_2$O$_3$ generally results in a slight increase in the oxidation rates.

(iv) At higher temperatures (above 800°C), the addition of RE$_2$O$_3$ lowers considerably the oxidation rates of nickel aluminide coated steels.

(v) In quite a large number of cases, there is evidence of the presence of small pegs or ridges at alumina scale/alloy interface which acts as fastners between alloy and the scales.

(vi) Decarburization during oxidation seems to upset the beneficial effects of rare earth oxide additions.
CHAPTER IV: High temperature corrosion of borosilicate coatings on mild steel

(i) The oxidation of borosilicate coating on mild steel, in the temperature range of 700°-900°C, proceeds by a diffusion controlled mechanism.

(ii) The presence of borosilicate coating lowers down the oxidation rate of the alloy significantly especially at higher temperatures e.g., 800° and 900°C.

(iii) The presence of RE₂O₃ in the borosilicate coating lowers down the oxidation rates considerably at 800° and 900°C.

(iv) The size of the rare earths influences the oxidation rates of borosilicate coated steel. A maxima is noted in the middle of lanthanide series and a minima at about the largest ionic size (Nd³⁺).

(v) There is apparently no effect of Na₂SO₄-induced hot corrosion attack on borosilicate coated steels at 700°C.

(vi) At 800°C and above, the borosilicate-coated steel is subjected to hot corrosion attack and the integrity of the borosilicate coating is destroyed.

(vii) The Na₂SO₄ induced hot corrosion attack proceeds by fluxing and sulfidation mechanisms.
CHAPTER V: High temperature oxidation and hot corrosion of borosilicate coated Inconel 600 alloy

(i) The presence of borosilicate coating on Inconel 600 alloy lowers the oxidation rates of the substrate alloy by one order of magnitude at 900° and 1000°C.

(ii) Very little Na$_2$SO$_4$-induced hot corrosion attack is observed on borosilicate coated Inconel 600 alloy at 800°C and the corrosion rates are similar to those without Na$_2$SO$_4$ deposition.

(iii) At 900° and 1000°C, the borosilicate coating on Inconel 600 is severely attacked by Na$_2$SO$_4$ and loses its integrity.

(iv) The Na$_2$SO$_4$ induced hot corrosion attack is most presumably propagated by fluxing and sulfidation mechanisms.
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