ABSTRACT
As a consequence of the industry’s motivation to achieve improved efficiency and enhanced performance, engineering components are required to operate in environments, which are becoming increasingly severe. Critical industrial components are, therefore, being degraded more aggressively due to surface/environment interactions such as simple oxidation, oxidation and sulfidation, oxidation and sulfidation with hot corrosion, erosion corrosion etc. The use of inorganic protective coatings on high temperature components to combat above mentioned degradation process is now well established. Amongst the various types of inorganic coatings, aluminum based coatings find wide applications in high temperature technologies such as marine aircraft gas turbines, fuel corrosion and generation systems, aerospace hardwares, chemical process and power plants etc. These coatings increase service life of the components, but fail to perform satisfactorily under aggressive environments. Recently, some advanced coatings like modified aluminide coatings i.e., aluminide coatings modified by noble metals, such as Pt, Pd or Cr, reactive elements such as Y, Ce or Hf or by rare-earth elements have been reported. Rare-earth addition, as it is well known improves the protective properties of the coatings. The improved high temperature oxidation and hot corrosion resistance of some rare-earth oxides modified aluminide coating on super alloys have recently been reported. However, the role of rare-earth oxides addition on the hot corrosion behaviour of aluminide coatings on mild steel is perhaps yet to be systematically studied. The problem is promising not only on academic point of view but also due to versatile technological applications.

The interaction of metallic materials with ionic salts or electrolytic deposits has been the subject of study for at least three decades. During this interaction, an accelerated attack called hot corrosion plays an important
role. In a hot corrosion attack, the electrolytic deposit (ash or ionic) and protective oxide scale on the metal interact and undergo a fluxing reaction resulting in accelerated oxidation rates. Hot corrosion attack is quite familiar in power generating units using low grade fossil fuel, fuel conversion or combustion units, fuel cell and incinerators etc. Amongst the salt inducing hot corrosion attack, \( \text{Na}_2\text{SO}_4 \) or less commonly \( \text{NaCl} \) are the salt, which are most frequently involved in such attacks. Many references are available dealing with the phenomenology of \( \text{Na}_2\text{SO}_4 \) or \( \text{NaCl} \) induced hot corrosion attack, but our knowledge regarding the actual chemical reactions taking place between molten salts and the scales on the alloy consisting of slow growing oxides of \( \text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3 \) or the oxides of the common, alloying additions, which are usually present in the outer oxide layer, is rather limited. Information regarding the reaction between the pertinent oxide and the ionic salts and proper identification of reaction products should be useful in understanding the occurrence and importance of fluxing reactions, and thus in the interpretation of hot corrosion mechanism and in the development of new protective materials. The dissolution behaviour of metal oxide is important in explaining the electrochemical mechanism of hot corrosion in which soluble metal species are involved. Following sections describe a brief summery of the work contained in different chapters of the thesis entitled, “High Temperature studies on some inorganic coatings and related reactions involving metal oxides and ionic salts”.

**Chapter 1**

General Introduction - I covers a literature survey on high temperature coatings and some aspects of oxidation behaviour of iron and iron-base alloys. The performance of aluminide and modified aluminide coatings has
been discussed in detail. Many new and latest techniques of coating preparation are also discussed.

General Introduction - II presents a literature survey on hot corrosion of metals and alloys. Special emphasis has been laid to the work, which has direct or indirect bearing on the studies described in this thesis.

Except for some early pioneering papers, the thesis includes literature survey from the selected research papers, reports, reviews and conference proceedings. It is possible that some results of important and remarkable studies might have left unquoted quite inadvertently yet there was absolutely no intention to undermine those works.

Chapter 2

The work presented in this chapter describes the results of an investigation carried out to study the oxidation behaviour of aluminide and CeO$_2$ and La$_2$O$_3$ modified aluminide coatings on mild steel in the temperature range of 700-900°C. The coatings on mild steel have been prepared by pack cementation process. The influence of CeO$_2$ and La$_2$O$_3$ additions on the oxidation rates of aluminide coatings has been investigated. The performance of coatings has also been studied by measuring oxidation kinetics, metallography, SEM and XRD analysis.

The kinetics of the oxidation proceeds by a diffusion controlled mechanism as revealed by the parabolic nature of weight gain vs time plots. The oxidation resistance coated mild steel is discussed on the basis of a decrease in oxidation rates as well as adherence of oxide scales. The oxidation rates of mild steel and aluminide coatings are lowered down markedly in presence of CeO$_2$ and La$_2$O$_3$ in the temperature range of 700-900°C. The oxide scales are formed by outward diffusion of iron ions. This
results in the formation of voids at the scale/alloy interface and adherence of scale is degraded. The presence of CeO$_2$ and La$_2$O$_3$ in the coatings suppresses the voids formation at the scale alloy interface and thus improves the adherence of oxide scales. The presence of rare-earth oxides in the coatings also results in significant reduction in weight gains by promoting the formation of a continuous layer of Al$_2$O$_3$, which blocks the outward diffusion of iron ions to the outer scale.

The oxidation rates are significantly affected by the morphology of the oxides scales. In case where the structure of oxide scales is not seriously disrupted due to decarburization, the oxidations rates are significantly reduced.

**Chapter 3**

The work presented in this chapter describes the results of an investigation carried out to study the Na$_2$SO$_4$-induced hot corrosion behaviour of aluminide and CeO$_2$ and La$_2$O$_3$ modified aluminide coatings on mild steel in the temperature range of 700-900°C. The study involves reaction kinetics, influence of the salt, methodology, SEM and XRD analysis of corroded and uncorroded alloys.

An analysis of the results from oxidation/hot corrosion curves indicates that pure aluminide coatings show better corrosion resistance than mild steel at 700°C. At 800 and 900°C, aluminide coatings show higher weight gains. It could be attributed to the fluxing of protective alumina and increased formation of sulfide at the inner region of scale. The addition of CeO$_2$ and La$_2$O$_3$ in the aluminide coatings has significantly improved its hot corrosion performance. This is presumably due to the presence of CeO$_2$ and La$_2$O$_3$ in the grain boundaries of Al$_2$O$_3$ and boundaries between Al$_2$O$_3$ and
FeAl spinel which effectively prohibit fast diffusion of oxidants (sulfur and oxygen) and aluminum along grain boundaries. Consequently, it may induce slow diffusion through matrix, preventing internal sulfidation and oxidation and thus increasing hot corrosion resistance subsequently.

The results from metallographic and SEM studies indicate that at 700°C, the scales are relatively thin and adhered to the coatings. There is very limited attack on the grain boundaries. At and above 800°C, besides thicker oxide scale formation, the grain boundaries are also affected by Na₂SO₄ attack. The scales are detached from the substrate due to evolution of CO/CO₂ (g) which exert stress on the already fragile scale. As a result of dismemberment of scales, fresh alloy is exposed to the oxidants and alloy oxidizes at a faster rate.

**Chapter 4**

The work presented in this chapter contains the results of the studies concerning with reaction of metal oxides such as NiO, Cr₂O₃, Fe₂O₃ and Al₂O₃ with Na₂SO₄ in flowing SO₂ (g) at a temperature of 1100 and 1200K. The oxides chosen for the studies are the initial scaling products during the oxidation of industrial alloys and are invariably involved in hot corrosion reactions in presence of molten salt. The thermogavimetric studies for each metal oxide-Na₂SO₄ system were carried out measuring weight change as a function of time and mole fraction of Na₂SO₄ in the reaction mixture. The presence of different constituents in the reaction products were identified by X-ray diffraction analysis and the morphologies of the reaction products were characterized using metallography and scanning electron microscopy (SEM). The formation of the products was also investigated by thermodynamic computation of free energies of the reactions and the study
of relevant thermodynamic phase stability diagrams. The conductivity, pH metric and solubility measurements were carried out to characterize the soluble species in the reaction products.

The reaction of metal oxides with Na$_2$SO$_4$ at high temperatures results in weight gains or weight losses. The total weight change at steady state was measured which is indicated by a constant weight with increasing exposure time.

Considering the reaction kinetics, there is a weight loss in a very initial stages of reaction for all the metal oxide-Na$_2$SO$_4$ systems (region I of the kinetic curves) followed invariably by weight gain. The initial weight loss for all the systems is due to the thermal decomposition of Na$_2$SO$_4$ to Na$_2$O and subsequent expulsion of SO$_2$ / SO$_3$(g).

\[
\text{Na}_2\text{SO}_4(s) \rightleftharpoons \text{Na}_2\text{O}(s) + \text{SO}_2(g) + \frac{1}{2} \text{O}_2(s)
\]

\[
\text{Na}_2\text{SO}_4(s) \rightleftharpoons \text{Na}_2\text{O}(s) + \text{SO}_3(g)
\]

The weight gain after initial weight loss in the kinetic curves for all the system (region II of the kinetic curves) is due to the formation of sodium metal oxide (Na$_2$O.MO) and metal sulfide and/or metal sulfate. The Na$_2$O formed may dissolve metal oxide to form sodium metal oxide and sulfur oxide gases may react with metal oxide to form metal sulfide and/or metal sulfate. This is represented by the following general reactions:

\[
\text{Na}_2\text{O} + \text{MO} \rightarrow \text{Na}_2\text{O}.\text{MO}
\]

\[
\text{MO} + \text{SO}_3 \rightarrow \text{MSO}_3
\]

\[
\text{MO} + 4\text{SO}_2 \rightarrow \text{MS} + 3\text{SO}_3
\]

The evidence for the formation of above reaction products is inferred from the following results: (i) identification of solid reaction products by XRD, (ii) standard free energy calculations favourable for most of the proposed
reactions, and (iii) weight gain after initial weight loss in the kinetics curves for all the metal oxide-Na$_2$SO$_4$ systems. In some systems there is a sudden interruption in weight gain curves and a decrease in weight gain is observed till net weight change is weight loss (region III of the kinetic curves). The vaporization of some reaction products and release of SO$_2$/SO$_3$(g) seemed to be the prime cause of the decrease in weight gain values in the kinetic curves.

Considering the weight change as a function of mole fraction of Na$_2$SO$_4$ in the reaction mixture, two types of behaviour are noted. In the first type, there is an increase in weight gain (or decrease in weight loss) values with increasing amount of Na$_2$SO$_4$. This is followed by a decrease in weight gain (or increase in weight loss) values with increase in the concentration of Na$_2$SO$_4$. This behaviour is exhibited by a majority of the systems and includes Cr$_2$O$_3$-Na$_2$SO$_4$, Fe$_2$O$_3$-Na$_2$SO$_4$, and Al$_2$O$_3$-Na$_2$SO$_4$. An increase in the weight gain values with increasing Na$_2$SO$_4$ concentration is because of the formation of Na$_2$O-MO and binding of sulfur in the form of metal sulfide and/or metal sulfate. A decrease in the weight gain values with increasing Na$_2$SO$_4$ concentration is because of the release of SO$_2$/SO$_3$(g), precipitation of metal oxide from Na$_2$O-MO and volatility of some reaction products.

In case of NiO-Na$_2$SO$_4$ system, there is a decrease in weight gain values with increasing Na$_2$SO$_4$ concentration till a maximum is noticed, this is followed by an increase in weight gain values with increasing Na$_2$SO$_4$ concentration. A decrease in weight gain values with increasing Na$_2$SO$_4$ concentration is due to the evaporation of sulfur oxides gasses which overweighs the formation of metal sulfide and/or sulfate. When concentration of Na$_2$SO$_4$ increases above 0.5 or 0.6 mole fraction, formation of
metal sulfide and/or metal sulfate takes place, which is responsible for weight gain.

The optical metallographic and SEM studies show the presence of multiphase structure in the reaction products. Each phase represents a constituent usually identified by XRD and is predicted by the proposed reactions. In general, an oxide phase or Na₂SO₄ appears as whitish grey, sulfide or sulfate as dark grey and Na₂O.MO as light grey.

The XRD analysis identifies most of the constituents of the reaction products as envisaged from the above proposed reactions.

From the solubility data there is ample evidence of the presence of water soluble metal containing species in the reaction products, which may be in the form of MO₂⁻, MO₄⁻² or MSO₄⁻. Equimolar mixtures of metal oxides and Na₂SO₄ at 1200K show largest solubility in case of NiO and lowest in case of Cr₂O₃, Al₂O₃ and Fe₂O₃ occupying middle position.

From the pH studies, an acidic aqueous solution of the metal oxide-Na₂SO₄ reaction indicates the presence of metal ions as acid salts. The conductivity measurements of metal oxides-Na₂SO₄ reaction products at varying concentration of Na₂SO₄ show the presence of breaks in conductance curves indicating the formation of soluble complex species at certain mole fractions of Na₂SO₄ in the reaction mixture.

Chapter 5

The work presented in this chapter deals with the reaction of metal oxides with NaCl in flowing Cl₂(g) at 1100 and 1200K. The oxides chosen for the studies are NiO, Al₂O₃, Cr₂O₃ and Fe₂O₃.

The reaction of metal oxides and NaCl at high temperature results invariably in weight losses for all the MO-NaCl systems under study. The
weight loss incurred by MO-NaCl systems is mainly due to the evaporation of NaCl. The other processes which account for weight losses are evaporation of volatile metal chlorides formed during the reaction and release of Cl\textsubscript{2} during the reaction of NaCl with oxygen. The magnitude of the weight loss depends upon the several factors, namely, the reaction temperature, nature of the oxide, thermodynamic feasibility of the reactions and kinetic of the reactions.

The different reaction occurring during the reaction of metal oxide with NaCl are represented as follows:

i. In presence of oxygen, NaCl thermally decomposes to Na\textsubscript{2}O and subsequently releases chlorine gas.

\[ 2\text{NaCl} + \frac{1}{2} \text{O}_2 \rightleftharpoons \text{Na}_2\text{O} + \text{Cl}_2 \]

ii. The metal oxide reacts with Na\textsubscript{2}O to form Na\textsubscript{2}O.MO

\[ \text{Na}_2\text{O} + \text{MO} \rightarrow \text{Na}_2\text{O.MO} \]

\[ \text{Na}_2\text{O} + \text{Fe}_2\text{O}_3 \rightarrow 2\text{NaFeO}_2 \]

iii. The chlorine gas reacts with metal oxide to form metal chlorides

\[ \text{MO} + \frac{1}{2} \text{Cl}_2 \rightarrow \text{MCl} + \frac{1}{2} \text{O}_2 \]

\[ \text{Fe}_2\text{O}_3 + 2\text{Cl}_2 \rightarrow 2\text{FeCl}_2 + 3/2\text{O}_2 \]

\[ \text{Fe}_2\text{O}_3 + 3\text{Cl}_2 \rightarrow 2\text{FeCl}_3 + 3/2\text{O}_2 \]

The formation of various species during the reaction is accounted by the following experimental evidences:

(i) Identification of solid reaction products by XRD, (ii) optical and scanning photomicrographs of the reaction products showing phase structure typical of oxide/chloride/mixed oxide system, (iii) standard free energy calculations of the proposed reactions and (iv) pH studies.
The solubility data provide ample evidence of the presence of water soluble metal containing species in the reaction products which are in the form of metal chlorides and/or mixed oxide Na₂O:MO. The solubility behaviour of metal oxides in molten NaCl is generalized as follows:

(i) An increase in the solubility (continued fluxing) with increasing NaCl concentration and include: Cr₂O₃-NaCl (1100 and 1200K) and Fe₂O₃-NaCl (1100 and 1200K).

(ii) A maximum in the solubility curve at 0.5 mole fraction of NaCl and include Al₂O₃-NaCl (1100 and 1200K); this may be attributed to the precipitation of oxide on enhancing the amount of NaCl above 0.5 mole fraction.

(iii) A minimum in the solubility curve and include NiO-NaCl (1100 and 1200K), maximum oxide solubility is noticed at lower concentration of NaCl.