

OXIDATION BEHAVIOUR OF MILD STEEL IN MOLTEN ALKALI METAL SALTS DEPOSITS

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ABSTRACT

The oxidation behaviour of commercial mild steel has been investigated in presence of alkali metal salts viz. NaCl, Na₂CO₃, KCl, K₂CO₃ in the temperature at 750°C for the period of 36 h in atmospheric condition. The low temperature oxidation kinetic and effect of alkali metal salts deposition on the corrosion rate were studied. The Na₂CO₃- & K₂CO₃- coated steel seems to be aggressive than NaCl & KCl, being an active oxidizing agent providing additional oxygen during fluxing reaction. However, due to profuse evolution of CO/CO₂ heavy mass losses are observed during corrosion and scales are porous. The tests included mass change monitoring and surface morphology examination were characterized by scanning electron microscopy (SEM) techniques.

Key Words : *Chloride Salts; Carbonate Salts; Steel; Oxidation; SEM*

1. INTRODUCTION

The intensification of process engineering in almost every branch of modern technology, and development of new technologies make increasingly higher requirements for metallic construction materials, especially for their heat and scaling resistance. The increase in operating efficiency of certain installation or plants is generally achieved by the application of higher temperatures and pressures and higher flow velocities of gases and vapours which creates gas corrosion hazard for the construction materials^{1,2}.

The corrosion process under hot gases or vapours being a mixture of many aggressive components proceeds usually many times faster and is characteristic by non-uniform attack of metal surface. It became obvious that sulphur, always present in such industrial gases, is one of the most dangerous aggressive components of the above mentioned atmospheres³⁻⁵. The importance of low temperature oxidation is indicated by the fact that although much of the progress relating to the research on this subject is limited to the period of about 20 years or so the literature is abound with references covering multifarious aspects of this type of corrosion. The influence of chloride salts separately or in combination with transition metal sulphate salts has been

studied but not in so much details^{6,7}. Only a limited amount of Na_2CO_3 and other salts in inducing corrosion attack⁸ is reported. Alkali/alkaline earth metal salts on the alloy scale can result in cracking and spalling of oxide to reveal a fresh alloy surface, with the result that protection is lost either permanently or temporarily.

The present investigation was undertaken to determine the effect of alkali metal chlorides as well as carbonates on oxidation behaviour of commercial mild steel at 750°C for the periods of 36 h.

2. MATERIALS AND METHOD

Specimens ($20 \times 10 \times 2$ mm) of commercial grade mild steel (C-0.2%; Si-0.05%; P-0.05%; Mn-0.26%; S-0.04% and Fe-rest) were cut from plate. The alloy specimens were grounded 180, 320 and 600 grit size of SiC papers, washed with water and degreased with acetone. The specimens were uniformly coated with thin film of NaCl, Na_2CO_3 , KCl and K_2CO_3 and then oxidized at 750°C for 36 h. Sometimes more than one spraying operation were used to get uniform coating (about 1 mm thick) of the salt (s) described previously⁹. The oxidation experiments were carried out in a high temperature furnace for 36 h. Variation in mass change was recorded at 6 h intervals throughout the 36 h. The investigation was based upon oxidation kinetics and morphologies of scales were characterized by Scanning Electron Microscopy (SEM) using SEM Joel 840A. The mounted specimens were abraded and polished by conventional means using SiC papers and diamond pastes of various grades respectively. The oxidized polished specimens were subjected to gold plating in order to make the surface conducting and fill the pores for SEM examinations.

3. RESULTS AND DISCUSSION

The oxidation kinetics data are shown in Fig. 1 for mild steel at 750° for 36 h. The NaCl- and KCl-coated steel exhibit mass gain with increasing time up to 30 h followed by a decrease in mass gain while the Na_2CO_3 - and K_2CO_3 - induced alloy appear to be continuous mass losses throughout the experiments.

The chlorides might be entrapped between inner oxide layers of the steel and get condensed on cooling and appear as distinct and discrete¹⁰ phase (s) in the scales. The alkali metal carbonate salts coated steel seems to be more aggressive, being an active oxidizing agent during fluxing reaction. However, due to profuse evolution¹¹ of CO/ CO_2 heavy mass losses are noted and scales are porous. The evolution of gases exhibiting the cracking or disruption of the scales.

Fig. 2 (a & b) show scanning electron micrograph of a cross section of NaCl- and KCl-coated mild steel specimen corroded at 750°C for 36 h. The scales are separated from substrate at some regions, possibly due to polishing artifacts.

The inner scales constitute of magnetite, Fe_3O_4 with Na_2O inclusions. The outer scales are predominantly concentrated in Fe_2O_3 with FeO_2Cl_2 inclusions. There is evidence of internal oxidation. This might be due to the formation of intermediate volatile species FeO_2Cl_2 , some of which evaporates and condenses on the wall of the reaction tube and some of it decomposes and accumulates at the alloy/salt interface in the form of Fe_2O_3 .

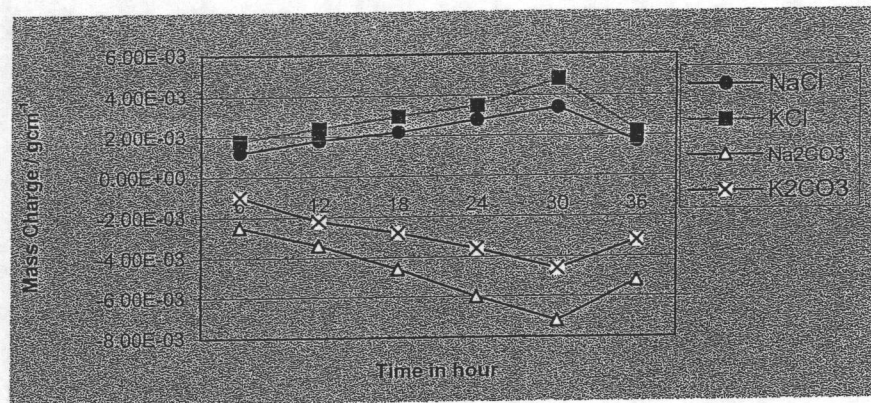
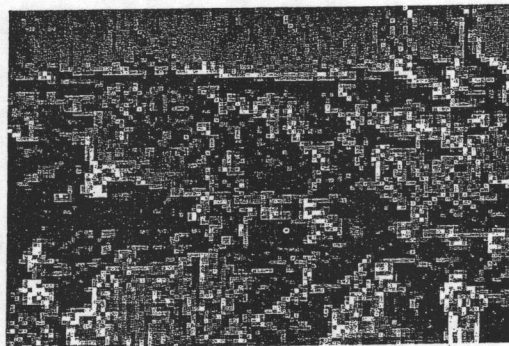
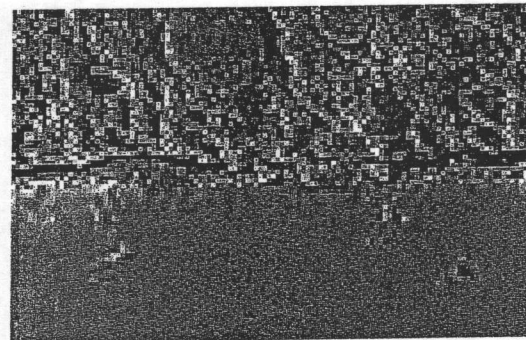


Figure 1 : Oxidation Kinetics (mass charge vs time) of mild steel coated with NaCl, KCl, Na₂CO₃ and K₂CO₃, oxidised at 750°C for a period of 36 hours



(a) NaCl coated, Mag. × 500



(b) KCl coated, Mag. × 200

Figure 2 : (a & b) Scale morphologies of mild steel coated with NaCl and KCl, oxidised at 750°C for 36 h.

Fig. 3 (a & b) represents SEM micrographs of Na₂CO₃- and K₂CO₃- induced mild steel, oxidised at 750°C. The inner layers of the scales seem to contain light crystalloids of Fe₂O₃ followed by light coloured FeO in the form of a thin layer, middle layers constitute of fluxing products like FeNa₂O₃ & Na₂FeO₄ followed by containing crystalloids of Fe₂O₃. The scale structure shows presence of voids and pores specially in the outer layers of the scales. These pores are produced due to expulsion of CO/CO₂.

4. CONCLUSION

The low temperature behaviour of industrially commercial mild steel has been investigated in presence of alkali metal chloride as well as carbonate salts at 750°C in atmospheric condition. During the reaction of molten NaCl and KCl with oxide scales, metallic chlorides and fluxing products are formed such as FeO₂Cl₂, Na₂FeO₄ & FeCl₃ which exert sufficient vapour pressure so as to break the protective scales.

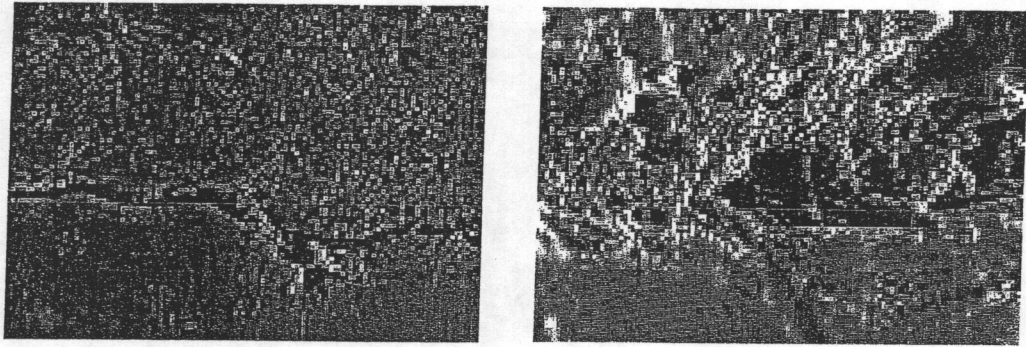
(a) Na_2CO_3 coated, Mag. $\times 200$ (b) K_2CO_3 coated, Mag. $\times 400$

Figure 3 : (a & b) Scale morphologies of mild steel coated with Na_2CO_3 and K_2CO_3 , oxidised at 750°C for 36 h.

In Na_2CO_3 - and K_2CO_3 -induced corrosion, the appearance of porous and copious scales is attributed due to the profuse evolution of CO/CO_2 and fluxing of protective oxide scales.

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