

Hot Corrosion Behaviour of Protective Oxide Scales with Sodium Chloride in Chlorine Gas Environment

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ABSTRACT

Sodium chloride (NaCl) is one of the prominent hot corrosion inducing constituents of salt deposits that accumulate on the alloy surface in the field. In a marine environment NaCl is ingested into a gas turbine as an aerosol of sea salt along with intake air. At high temperatures, conventional alloys are severely attacked by NaCl and protective oxide scales like Cr₂O₃, Al₂O₃ and NiO invariably deteriorate. This paper deals with the high temperature reaction kinetics of such metal oxides with NaCl in a Cl₂ gas environment at atmospheric pressure. The kinetics of the reactions between NaCl and metal oxides were studied by monitoring them by thermo-gravimetric analysis. Reaction products were identified by XRD analysis and SEM studies. Water soluble metal species in the mixture were estimated with the help of atomic absorption spectroscopy and pH of aqueous solution was taken into account to establish the reaction mechanism. The result showed that the mixed oxide of the type (Na₂O.M₂O_x) and metal chlorides were the usual reaction products. Water soluble reaction products indicated the presence of metal oxy anions (CrO₂⁻; AlO₂⁻; and NiO₂⁻;) in the mixture. The aqueous solution of NaCl and Al₂O₃ in the system was found basic whereas for NiO and Cr₂O₃ it was acidic.

Key words: Hot corrosion, NaCl, metal oxide, chlorine, SEM, XRD

INTRODUCTION

Hot corrosion is an accelerated corrosion attack when electrolytic deposit reacts with normally protective oxide layers on the alloy. 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. An especially important characteristic of the hot corrosion attack is that, the combined effects of the deposit and gas results in much more severe corrosion than would have been induced, by the gas alone. NaCl is one of the important hot corrosion inducing constituents and its role during hot corrosion of alloys has been the subject of several investigations [1-5].

In developing world the investigation of NaCl induced hot corrosion failure of many operation units have become a major problem. It has been a challenge for researchers to find out a suitable material for such aggressive environment. Desalination plant in an arid area is an essential setup to fulfill the requirement of water in the region. Desalination plants are prone to high level corrosion risk. Operating conditions and processes in saline water treatment plants are very harsh that includes heat exchange, boiling, turbulent flow and distillation [6]. The corrosion resistance of super alloys can be improved by adding fair amounts of Al and Cr [7]. Hot corrosion behavior of Ni-Cr-Al based alloy in a mixture of Na₂SO₄-NaCl has been reported as good high temperature corrosion resistant material for gas purification [8, 9]. NaCl induced hot corrosion studies of Ti based alloy containing Al and Cr has received good results [10]. The stability and solubility measurements of protective oxide scales in NaCl-KCl-Na₂SO₄-K₂SO₄ suggested a reaction mechanism of corrosion in waste incineration environment for boiler tubes [11]. In cyclic oxidation weight gain of Cr containing steel (T-91) was found much lesser than that of in Ni containing steel (T-22) because NiO thus formed is said to be loose structured and not able to provide effective protection [12]. After pre-oxidation at 950°C in air for 20 h, a protective scale consisting of Cr₂O₃, Al₂O₃, NiO, NiCr₂O₄, and Ni₂Ti₄O formed on the DZ68 super-alloy surface. The pre-oxidation treatment improved the initial incubation stage of the alloy in the mixture of 75% Na₂SO₄+25% NaCl melts at 900°C [13].

The paper deals with the reaction of some protective oxide scales on alloy surface with NaCl in flowing chlorine gas atmosphere at temperature relevant to hot corrosion attack. The main objective of the work is to investigate the nature of chemical reaction between scale and NaCl on the basis of reaction kinetics, XRD analysis and the morphology of the reaction products.

EXPERIMENTAL PROCEDURE

Chemicals Used

Al₂O₃, Cr₂O₃ and NiO and NaCl (AR grade products, ~80 mesh size) were dried in an oven at 200°C for about 48 hours.

Preparation of the specimens

Dried and powdered NaCl and the metal oxides were mixed in different molar ratios of NaCl and oxide (1:2, 2:3, 1:1, 3:2 and 2:1) and the mixtures were put in a die (diameter 1.4 cm) and pressed into compact tablets using a hydraulic press (pressure: 10⁷ Kg m⁻²)

Oxidation Kinetics

The kinetics of the reaction between NaCl and metal oxide were studied by monitoring weight change as a function of time and mole fraction of NaCl at 1100 and 1200 K in a constant stream of pure Cl₂ gas. The reaction was performed on a hot stage Sartorius electronic microbalance. A 20-hour oxidation run was adequate to provide reaction products at steady state, which was indicated by a no change in weight for a considerable period of exposure time.

Three silica boats each containing compacts of the same ratio were placed in a horizontal furnace for oxidation under almost identical conditions. After completion of the oxidation, the compacts were taken out and quenched in air and weighed. Out of three samples, one was mounted for morphological studies (XRD and SEM), the second for qualitative chemical analysis, conductivity and pH determination and the third was retained for quantitative determination of soluble metal species.

X-ray diffraction studies

The X-ray diffraction studies were carried out using a Philips X-ray diffractometer (Model PW 1730 X-ray generator with PW 1710 microprocessor and KSR 43 printer) with Cu K_α target and appropriate filter.

Metallographic studies

Metallographic studies were carried out on a computerized Leitz photo-metallurgical microscope (Metallux-2). The reaction products present in the form of compacts were mounted in paper

moulds using Araldite as a cold setting resin. The mounted tablets were abraded sequentially on 320 and 600 grit SiC paper followed by polishing with 6 μ diamond paste using kerosene as the lapping liquid.

Scanning electron microscopic (SEM) studies

SEM studies were performed using a Philips 505 electron microscope. Polished specimens were coated with colloidal gold emulsion and their structures were examined through the microscope. The desired portions of the microstructure of specimen were photographed at various magnifications.

pH measurements

The compacts of reaction products were dissolved in demineralised water and the pH of aqueous solution of the reaction products were measured using Elico CM 180 pH meter.

Estimation of the soluble metals

An atomic absorption spectrophotometer (Model GBC 902) was used to determine the concentration of the different metals in the aqueous solution of the reaction products for NaCl-metal oxide systems. The compacts of the reaction products were weighed and dissolved in fixed volume of demineralised water. The mixture was heated near to boiling followed by filtration through Whatman filter paper. The filtrate, with appropriate dilution, was used to determine the concentration of metals in the solution.

Results and Discussion

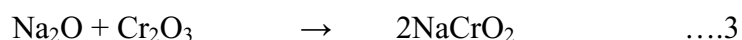
Thermo gravimetric studies

Reaction kinetics

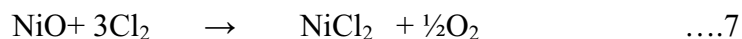
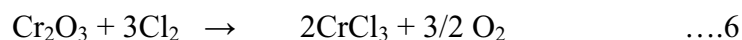
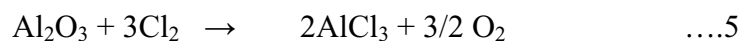
Figures-1-3 represent the percent weight loss versus time plots obtained for the reaction of 1:1 mixture of metal oxide and NaCl at 1100 and 1200 K, with the exception of NiO-NaCl system at 1100K there is a rapid and continuous weight loss up to 2-4 hours followed by a very small or no change in weight for Cr₂O₃ and Al₂O₃ systems. However, at 1200K, all the systems show a rapid and continuous weight loss up to a period of 10-12 hours followed by negligible weight loss up to a time period extending 20 hours. At 1200K the final weight loss for all the systems is invariably greater than that at 1100K.

The weight loss observed by metal oxide-NaCl system was mainly due to the evaporation of NaCl, thermal decomposition of NaCl to Na₂O with subsequent expulsion of Cl₂ gas, and evaporation of volatile metal chlorides formed during the reaction in certain cases. Several other factors such as the reaction temperature, thermodynamic feasibility of reactions, kinetic of the reaction and nature of the metal oxides play an important role in weight loss.

At high temperature, NaCl in presence of oxygen thermally decomposed to Na₂O to form reaction product Na₂O.M₂O_x which can be represented by the following reactions.



The chlorine gas may also react with metal oxide to form metal chlorides.



High temperature reaction of metal oxide and sodium chloride can be explained on the basis of oxygen activity at the surface leading to the formation of sodium metal oxides. However, in presence of flowing chlorine gas the activity of chlorine increased at the surface of the reaction mixture and formation of chloride was favored.

The formation of sodium metal oxide (Na₂O.M₂O_x) and metal chloride were inferred by X-ray diffraction analysis, photo micrographs of the reaction products showing phase structure of oxide/chloride/mixed oxide systems, standard free energy calculation (Table-1) and pH measurement.

Influence of salt

Figures-4-6 showed plots of total percent weight loss at steady state versus mole fraction of NaCl in the reaction mixture. The total weight loss represent the final reading recorded after 20 hours of heating a mixture consisting of metal oxide and NaCl in Cl₂ (g) environment at 1100 and 1200 K. In general no further loss in weight was observed after 20 hours exposure. The results of the study of

weight loss versus mole fraction of NaCl for different metal oxide-NaCl systems can be generalized as, at 1100K, NiO-NaCl system showed a linear trend whereas Al₂O₃-NaCl and Cr₂O₃-NaCl systems showed a minimum in weight loss curves. However, at 1200 K, there were linear trends in weight loss curves for all the systems.

Metallographic, SEM and XRD Studies

Figures 7-9 show some representative Scanning electron micrographs of the mounted reaction products. The different constituents as identified in the reaction product of 1:1 mixture of metal oxide and NaCl by X-ray diffraction analysis are listed in table-2. The salient features of the results obtained from the above studies are generalized as follows.

Al₂O₃-NaCl system

The appearance of multiphase structure is evident in a typical photomicrograph of Al₂O₃-NaCl reaction product (Figure-7). The light grey phase represents mixed oxide NaAlO₂ along with dark grey Al₂O₃ and whitish grey NaCl. The XRD analysis indicated the presence of Al₂O₃, NaAlO₂ and NaCl.

Cr₂O₃-NaCl system

The photomicrographs of the equimolar reaction products at 1100K (Figure-8) indicated the presence whitish grey phase NaCl along with light grey flocculent product which could be a chromate together with Cr₂O₃. A very dark phase presumably CrCl₃ was also present in the micrograph. The XRD results indicated the presence of Cr₂O₃, CrCl₃ and NaCrO₂ in the 1:1 reaction product mixture of NaCl and Cr₂O₃ at 1100 and 1200K.

NiO-NaCl system

The photomicrographs of the equimolar reaction products of NiO-NaCl at 1100K indicated the presence of Ni-rich multiphase structure (Figure-9), namely NiO and/or NiCl₂ (dark grey) and NaNiO₂ (light grey). Some free NaCl were also present in the micrographs (whitish grey).

Variation in pH

Figure-10-12 showed the plot of the pH of the aqueous solution of the reaction products versus mole fraction of NaCl. A study of the plot indicated that the solutions are basic for Al₂O₃-NaCl system and acidic for Cr₂O₃-NaCl and NiO-NaCl systems. In case of Al₂O₃-NaCl the basic character decreased

with increasing NaCl concentration till a minimum was noticed followed by an increase in basic nature. In the aqueous solution of the reaction products many species are liable to hydrolyze and affect the pH of the solutions. The basic aqueous solution indicated the massive formation of NaAlO_2 in the reaction product. There is little possibility of the presence of AlCl_3 in reaction product. The high vapor pressure of AlCl_3 supports the above contention. An acidic solution for the systems NiO-NaCl indicated the presence of CrCl_3 and NiCl_2 respectively as predominant species which overweighs the presence of sodium metal oxides Na_2CrO_2 and NaNiO_2 . This may be explained on the basis of relatively low vapor pressure of metal chlorides formed during the reaction (Table-3).

Estimation of soluble Metal Species

The concentration of water soluble metal species in the reaction products of metal oxide-NaCl system was determined as a function of NaCl in the reaction mixture. Figures 13-15 showed the variation of concentration of soluble species versus mole fraction of NaCl. Three types of behavior were noticed. (i) An increase in the concentration of soluble metal species with increasing amount of NaCl for Cr_2O_3 -NaCl; at 1100 & 1200K. (ii) A decrease in the concentration of soluble metal species with increasing NaCl amount till a minimum was obtained which includes NiO-NaCl system and (iii) The system Al_2O_3 -NaCl showed a maximum at 0.5 mole fraction of NaCl at both 1100 and 1200K. The soluble metal species present in the solution were either in the form of metal chlorides and/or in the form of mixed oxides. The solubility of nickel oxide was presumed due to oxide fluxing. In case of NiO-NaCl system (at 1100 and 1200 K) maximum oxide fluxing was noticed at lower concentration of NaCl where as fluxing terminated at 0.5 mole fraction of NaCl in case of Al_2O_3 ; this may be attributed to the precipitation of oxide on enhancing the amount of NaCl. In case of Cr_2O_3 , fluxing reaction continued with increasing NaCl amount.

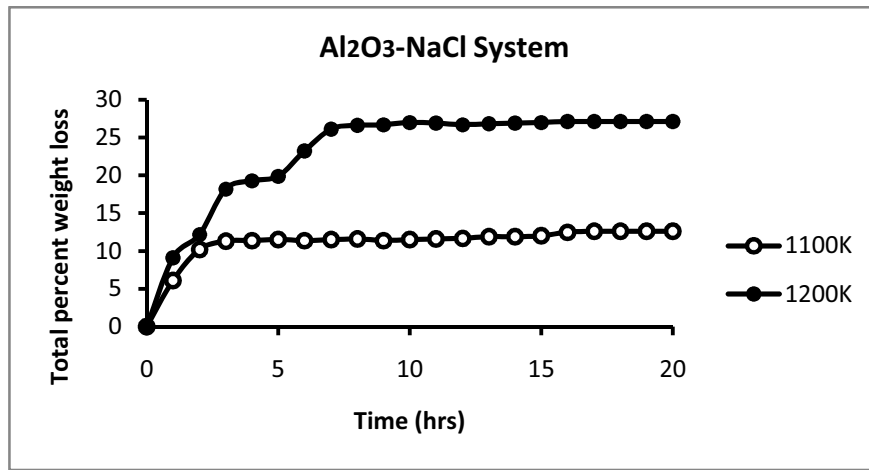


Figure 1 Total percent weight loss versus Time plot for Al₂O₃-NaCl system (molar ratio 1:1) at 1100 and 1200K

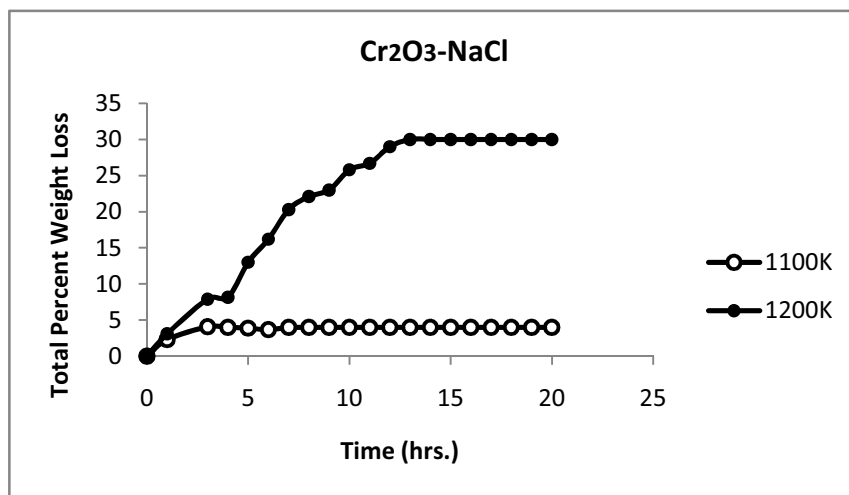


Figure 2 Total percent weight loss versus Time plot for Cr₂O₃-NaCl system (molar ratio 1:1) at 1100 and 1200K

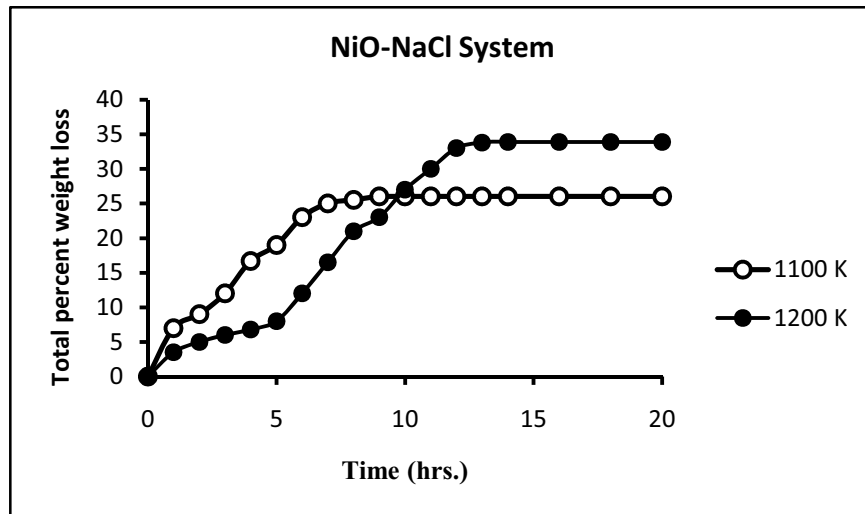


Figure 3 Total percent weight loss versus Time plot for NiO-NaCl system (molar ratio 1:1) at 1100 and 1200K

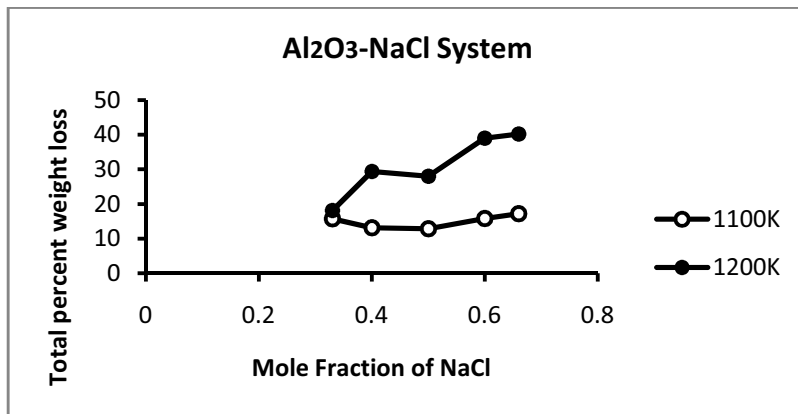


Figure- 4. Total percent weight loss versus mole fraction of NaCl in the reaction mixture at 1100K and 1200K for 20 h

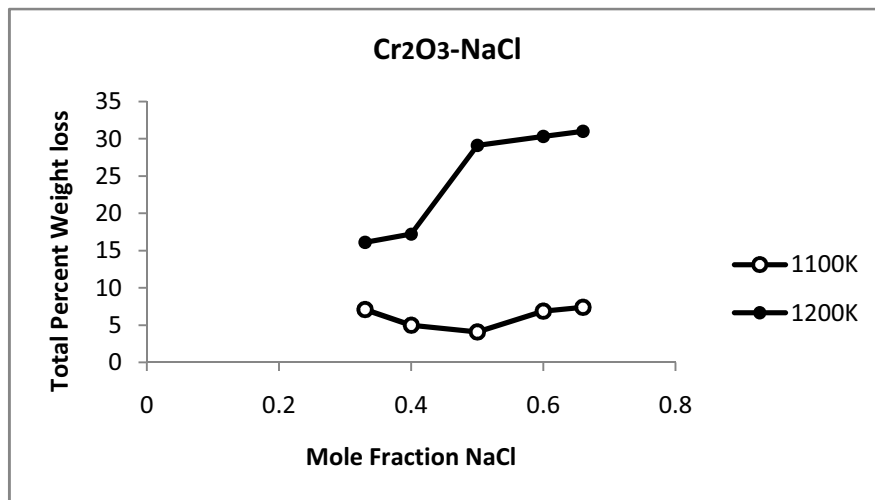


Figure-5.Total percent weight loss versus mole fraction of NaCl in the reaction mixture at 1100K and 1200K for 20 h.

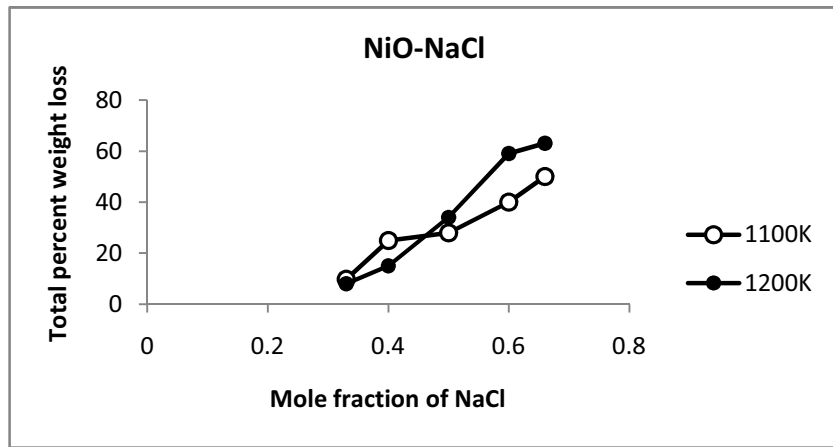
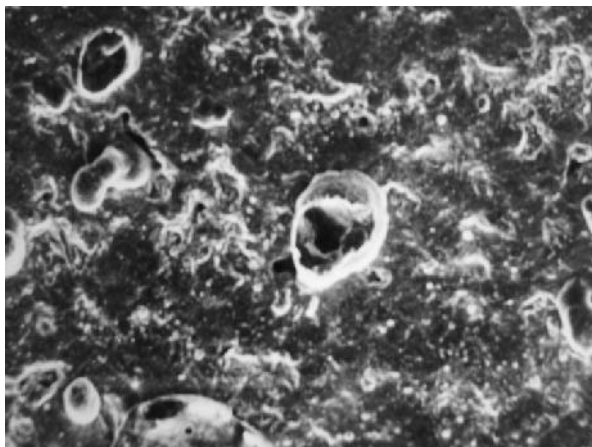


Figure-6. Total percent weight loss versus mole fraction of NaCl in the reaction mixture at 1100K and 1200K for 20 h.



a.

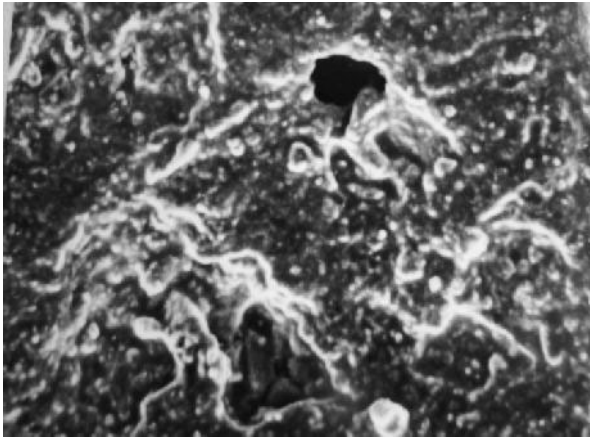


b.

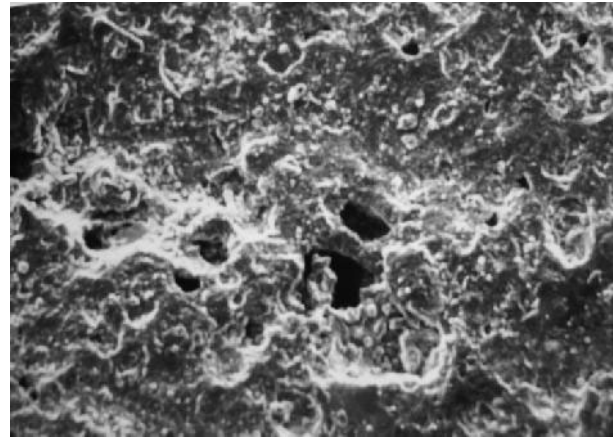
Figure-7: SEM picture of the reaction product of Al₂O₃-NaCl system (molar ration 1:1), oxidized at

a. 1100K

b. 1200K



a.



b.

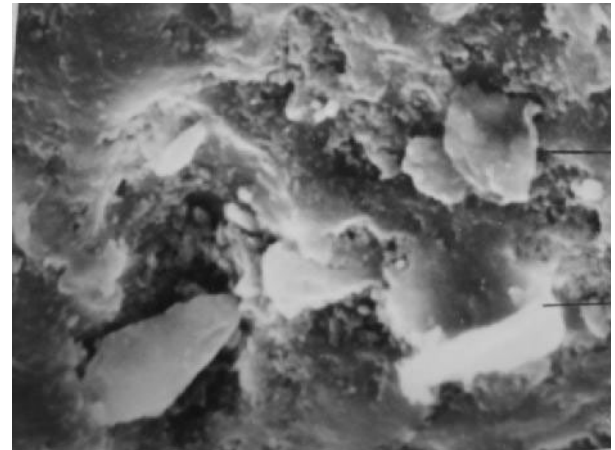
Figure-8: SEM picture of the reaction product of $\text{Cr}_2\text{O}_3\text{-NaCl}$ system (molar ratio 1:1), oxidized at

a. 1100K

b. 1200K



a.



b.

Figure-9: SEM picture of the reaction product of NiO-NaCl system (molar ratio 1:1), oxidized at

1100K.

a. molar ratio 1:1 b. molar ratio 1:2

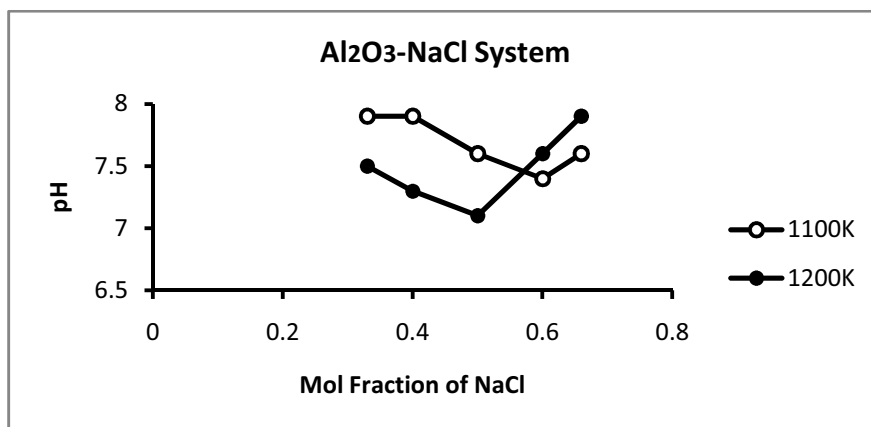


Figure- 10: Plots of the pH of aqueous solution of the reaction products versus mole fraction of NaCl for Al₂O₃-NaCl system at 1100 and 1200K.

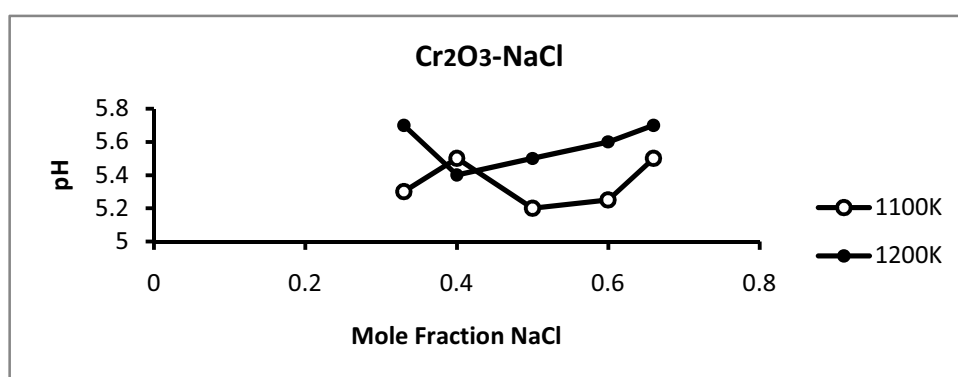


Figure- 11: Plots of the pH of aqueous solution of the reaction products versus mole fraction of NaCl for Cr₂O₃-NaCl system at 1100 and 1200K.

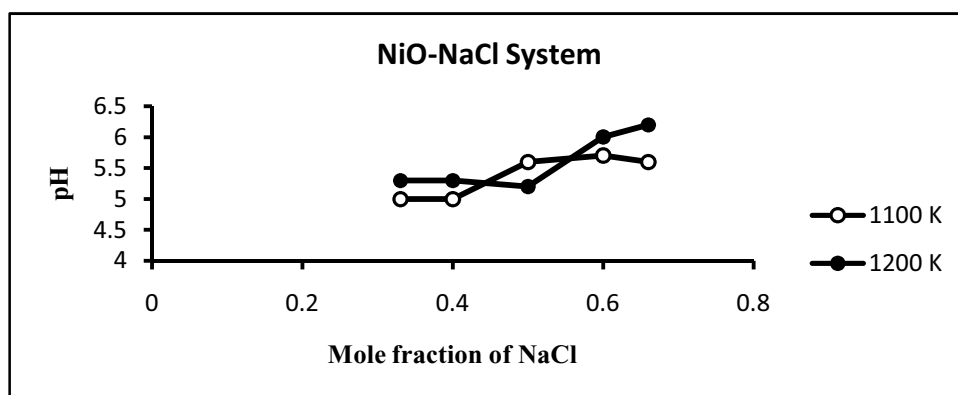


Figure -12: Plots of the pH of aqueous solution of the reaction products versus mole fraction of NaCl for NiO-NaCl system at 1100 and 1200K.

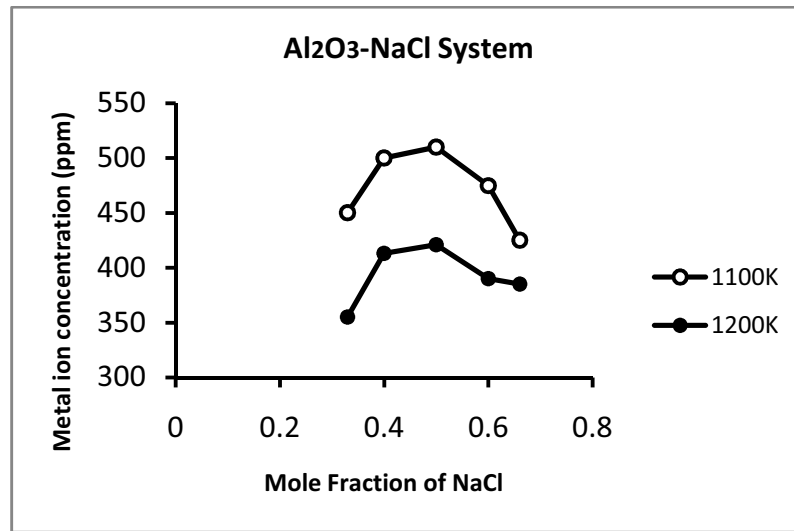


Figure-13: Variation of metal ion concentration (ppm) versus mole fraction of NaCl for Al₂O₃-NaCl system

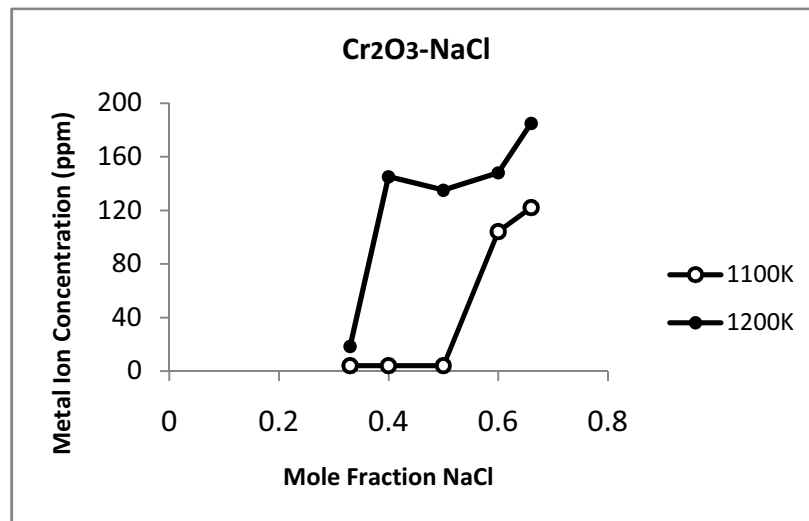


Figure-14: Variation of metal ion concentration (ppm) versus mole fraction of NaCl for Cr₂O₃-NaCl system

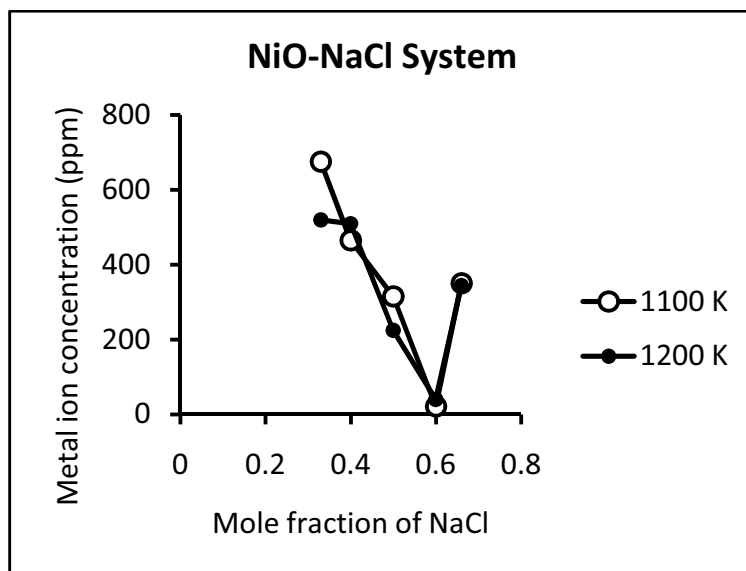


Figure-15: Variation of metal ion concentration (ppm) versus mole fraction of NaCl for NiO-NaCl system

Reaction	ΔG° kcal mol ⁻¹
$\text{Al}_2\text{O}_3 + 3\text{Cl}_2 \rightarrow 2\text{AlCl}_3 + 3/2 \text{O}_2$	-53.183
$\text{Cr}_2\text{O}_3 + 3\text{Cl}_2 \rightarrow 2\text{CrCl}_3 + 3/2 \text{O}_2$	-55.490
$\text{NiO} + 3\text{Cl}_2 \rightarrow \text{NiCl}_2 + 1/2 \text{O}_2$	-37.129
$\text{Na}_2\text{O} + \text{Al}_2\text{O}_3 \rightarrow 2\text{NaAlO}_2$	-45.359
$\text{Na}_2\text{O} + \text{Cr}_2\text{O}_3 \rightarrow 2\text{NaCrO}_2$	-18.187
$\text{Na}_2\text{O} + 2 \text{NiO} + 1/2 \text{O}_2 \rightarrow 2 \text{NaNiO}_2$	-10.394

Table-1: Standard free energy of the reaction, ΔG° at 1200K.

Systems	Temperature (K)	Constituents Identified
Al ₂ O ₃ -NaCl	1100	Al ₂ O ₃ , NaCl, NaAlO ₂
	1200	Al ₂ O ₃ , NaAlO ₂
Cr ₂ O ₃ -NaCl	1100	Cr ₂ O ₃ , NaCrO ₂ , CrCl ₃
	1200	Cr ₂ O ₃ , NaCrO ₂ , CrCl ₃
NiO-NaCl	1100	NiO, NaNiO ₂ , NiCl ₂

Table-2: Different constituents identified in the reaction products by X-ray diffraction analysis.

Chlorides	Temperature at which vapor pressure is 760 mm (K)	Melting point (K)	Boiling point (K)
AlCl ₃	453.2 (s)	465 (under pressure)	720 (under oressure)
CrCl ₂	--	1088	1577
CrCl ₃	--	1220 (s)	--
NiCl ₂	1260 (s)	1274	--
NaCl	1738	1073	1656

Table-3: Thermodynamic data (K) for the chlorides. (s) = sublime

CONCLUSIONS

The high temperature reaction of NaCl and metal oxide results invariably in weight losses. The weight losses observed during the reaction were due to evaporation of NaCl, thermal decomposition of NaCl and subsequent release of Chlorine gas and evaporation of volatile metal chlorides in certain cases. Mixed oxide (Na₂O.M₂O_x) and metal chlorides were the usual reaction products. Determination of soluble metal species in the reaction products indicated the presence of AlO₂⁻, CrO₂⁻ and NiO₂⁻.

References

1. R. C. Hurst, J. B. Johnson, M. Davies and P. Hancock, in A. B. Hart and A. J. B. Cutler (eds.) Deposition and corrosion in gas turbines, Halstead Press, (1973)173.
2. C. A. Stearns, F. J. Cohl and G. C. Fryburg, NASA Technical Memorandum TMX-73476, Electrochem. Soc. Meeting on properties of high temperature alloys, Las Vegas, NV, (1976), Oct., 17,.
3. M. L. deanhardt and K. H. Stern, J. Electrochem. Soc., 128 (1981) 2577,.
4. M. L. deanhardt and K. H. Stern, J. Electrochem. Acta, 29 (1982), 2228,.
5. Y. Shinta and Y. Nishi, Oxid. Met. 26, (1986) 201,.

6. P. R. Roberge, Corrosion Engineering Principles and Practice, Seawater, New York NY, McGraw Hill, (2008), 274-280.
7. F. Wang, H. Lou, L. Bai and W. Wu, Hot Corrosion of Yttrium-Modified Aluminide Coatings, Mater. Sci. Engg. A-Struct., 121(1989) 387-389.
8. LI Weijie, LIU Yong , WANG Yan , HAN Chao , TANG Huiping, Hot corrosion behavior of Ni-16Cr-xAl based alloys in mixture of Na₂SO₄-NaCl at 600 °C, Trans. Nonferrous Met. Soc. China, 21, (2011), 2617-2625
9. R L. TERPSTRA, I E. ANDERSON, B. GLEESON, Development of metallic hot gas filters, International Conference on Powder Metallurgy and Particulate Materials. New Orleans, USA: Metal Powder Industries Federation, (2001): 84-97.
10. Y. Xiong, X. Xiong, S. Zhub and F. Wang, Hot Corrosion of Ti-Based Intermetallics with Coatings in NaCl+ (Na,K)₂SO₄ Melts at 750°C, The Open Corrosion Journal, (2009), 2, 157-163.
11. T. Ishitsuka, K. Nose, Stability of protective oxide films in waste incineration environment-Solubility measurement of oxides in molten chlorides, Corrosion Science 44, (2002), 247-263.
12. D. Gonda, V. Chawlab, D. Puria, S. Prakash, High Temperature Corrosion Behaviour of T-91 and T-22 Bare Steel in 75wt.%Na₂SO₄+25wt.%NaCl Molten Salt Environment at 900°C, Journal of Minerals & Materials Characterization & Engineering, Vol. 9, No.7, (2010) pp.593-606.
13. E. Liuy, Z. Zheng, X. Guan, J. Tong, L. Ning and Y. Yu, Influence of Pre-oxidation on the Hot Corrosion of DZ68 Superalloy in the Mixture of Na₂SO₄-NaCl, J. Mater. Sci. Technol., (2010), 26(10), 895-899.