

Studies on Hot Corrosion Reactions Involving Nickel Oxide and Sodium Chloride in Cl_2 (g) Environment at 1100 and 1200K

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ABSTRACT

The work presented in this paper deals with the results of studies on reactions of Nickel oxide (NiO) with sodium chloride in flowing Cl_2 (g) at 1100 and 1200K. The main objective of the work was to investigate the nature of chemical reactions between nickel oxide and NaCl on the basis of reaction kinetics and the morphologies of the reaction products. The oxides taken into account for the studies were initial scaling products during oxidation of industrial alloys and invariably involved in hot corrosion reactions in presence of molten salts. The thermo gravimetric studies were carried out as a function of NaCl in the mixture. XRD analyses were used to identify the constituents present in the reaction products. Morphologies of the reaction products were discussed on the basis of scanning electron microscopic (SEM) studies. Quantitative estimation of soluble metal species was carried out using an atomic absorption spectrophotometer. The formation of products was investigated by thermodynamic computation of free energies of reaction.

Key words: Hot corrosion, Nickel oxide, XRD, SEM, Sodium chloride.

Introduction

Hot corrosion is a major and limiting problem in numerous industrial applications involving combustion processes e.g. energy production, waste incineration, gas turbine and recovery boilers etc. NaCl is one of the important hot corrosion inducing constituents and a major component of salt deposits that accumulate on the alloy surface in the field. The role of NaCl in the hot corrosion in the gas turbine operating in a marine environment has been the subject of several investigations [1- 4]. In harsh environments, such as heat engines and heat exchangers, the structural materials are subjected to high temperature corrosive gases and condensed phases such as NaCl and Na₂SO₄ [5]. Under the appropriate conditions these salts deposit on the substrate, leading to severe hot corrosion attack and accelerated degradation of materials [6].

At high temperature conventional alloys are invariably attacked by NaCl. Earlier published work [1, 7] had demonstrated that Cr₂O₃-forming alloys are particularly susceptible to attack in the presence of NaCl forming a blistered and cracked surface on the alloy. The corrosion rate generally increases with temperature. It is generally believed that NaCl attacks the alloy and form volatile chlorides and oxy-chlorides. Some studies on NaCl-induced hot corrosion of metal oxides in O₂ has been reported [8]. The presence of NaCl deposits accelerated the oxidation of TiAl; NaCl reacted with oxygen. The porous scales formed at the high temperature in the presence of NaCl deposits may have resulted from the growth of oxides in the form of whiskers or volatile phases. Deanhardt and Stern [9] measured the solubility products of Ni, Co and Y oxides in molten NaCl (1100K) by coulometric titration of the respective chlorides (NiCl₂, CoCl₂ and YCl₃) with electrochemically generated oxide ion, using a stabilized zirconia (SZ) electrode as an oxide pump. In some recent work the study of NaCl-induced hot corrosion of Fe-Mn-Al-

C alloys were carried out. The results showed that NaCl accelerated the oxidation of Fe–Mn–Al–C alloys. The hot corrosion behavior depends on the environment temperature and the contents of aluminum and chromium [10]. The mechanism of the NaCl-induced corrosion at high temperature and the effect of alloying elements were investigated in Nb-bearing ferritic stainless steels [11]. The results of study of the high temperature interactions of some transition and non transition metal oxides and carbides in an atmosphere of pure oxygen have been published [8, 12]. Corrosion behavior of electro-deposited Ni/Al₂O₃ composite coating covered with a NaCl salt film at 800 °C has recently been published [13, 14].

The work presented in this paper deals with the reaction of nickel oxides (NiO) 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 nickel oxide and NaCl on the basis of reaction kinetics and the morphology of the reaction products.

Experimental

Materials Methods

NiO and NaCl (AR grade products, ~80 mesh size) were dried in an oven at 200°C for about 48 hours. Dried and powdered NaCl and NiO 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: 10^7 Kg m⁻²)

Oxidation studies

The kinetics of the reaction between NaCl and nickel oxide was 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.

To obtain a sufficient number of samples of the reaction products for a particular system, 3 silica boats, and 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-NiO 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

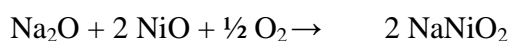
Reaction kinetics

Figure-1 represents the total weight change (in percent) versus time plots obtained during the reaction of 1:1 mixture of nickel oxide and NaCl at 1100 and 1200 K. The salient features of the results from reaction kinetics for the system were given as;

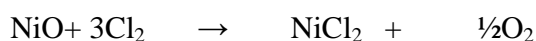
The system at 1100 K showed a rapid and continuous weight loss up to a period of 8 hours followed by negligible change and at 1200 K up to 13 hours weight loss was observed followed by negligible weight loss.

The weight loss incurred by NiO-NaCl system was mainly due to the evaporation of NaCl. The other processes which account for the weight loss were (i) thermal decomposition of NaCl to Na₂O and subsequent expulsion of Cl₂ gas, and (ii) evaporation of volatile nickel chlorides formed during the reaction. The magnitude of weight loss depends upon several factors e.g. the reaction temperature, thermodynamic feasibility of reactions, kinetics of the reaction and nature of the oxides.

At high temperature, NaCl in presence of oxygen thermally decomposed to Na₂O to form reaction product sodium nickelate NaNiO₂. It can be represented by the following reactions.



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



At high temperature the reaction of nickel oxide and sodium chloride can be explained as follows, initially the surface of the reaction mixture was the region of high oxygen activity and formation of sodium nickelate was therefore the predominant reaction. However, with the passage of chlorine gas the activity of chlorine increased at the surface of the reaction mixture and formation of chloride was favored.

The formation of sodium nickelate (NaNiO_2) and nickel chloride (NiCl_2) were inferred from the following results; (i) identification of solid reaction products by X-ray diffraction analysis, (ii) photo micrographs of the reaction products showing phase structure of oxide/chloride/mixed oxide systems, (iii) standard free energy calculation (Table-1) and (iv) pH studies.

Influence of salt

Figures-2 showed plots of total percent weight loss at steady state versus mole fraction of NaCl in the mixture of NaCl-NiO. The total weight change was recorded after heating for 20 hours, a mixture of NaCl and nickel oxide of known composition in Cl_2 (g) at 1100 and 1200 K. No further change in weight was observed after 20 hours. The results of the study of weight change versus mole fraction of NaCl for NaCl-NiO system can be generalized as, at 1100 and 1200 K, there were linear trends in weight loss curves.

Metallographic, SEM and XRD Studies

The representative scanning electron micrographs for the reaction products are shown in figure-3. The different constituents as identified in the reaction product of 1:1 mixture of nickel oxide and NaCl by X-ray diffraction analysis were NiO, NaNiO_2 and

NiCl₂. The salient features of the results obtained from the above studies are generalized as the photomicrographs of the equimolar reaction products at 1100 and 1200 K indicated the presence of Ni-rich multiphase structure, 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-4 showed the plot of the pH of the aqueous solution of the reaction products versus mole fraction of NaCl. The solution of the reaction products for this system was found acidic which indicated the presence of nickel chloride as a predominant species which overweighs the effect of the presence of sodium nickelate.

Estimation of soluble Metal Species

The concentration of water soluble metal species in the reaction products of NiO-NaCl was determined as a function of NaCl in the reaction mixture. Figure 5 showed the variation of concentration of soluble species versus mole fraction of NaCl. A decrease in the concentration of soluble metal species with increasing amount of NaCl in the reaction mixture was noticed till the minimum was reached. 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.

Conclusions

1. The high temperature reaction of sodium chloride and nickel oxide in Cl₂ gas environment lead to invariably weight loss due to evaporation NaCl, Thermal

- decomposition of NaCl with subsequent expulsion of Cl_2 gas and evaporation volatile NiCl_2 .
2. Water soluble species such as NaNiNO_2 and NiCl_2 were identified.
 3. The acidic nature of the aqueous solution of reaction products was assumed due to presence of nickel chloride as a predominant species.

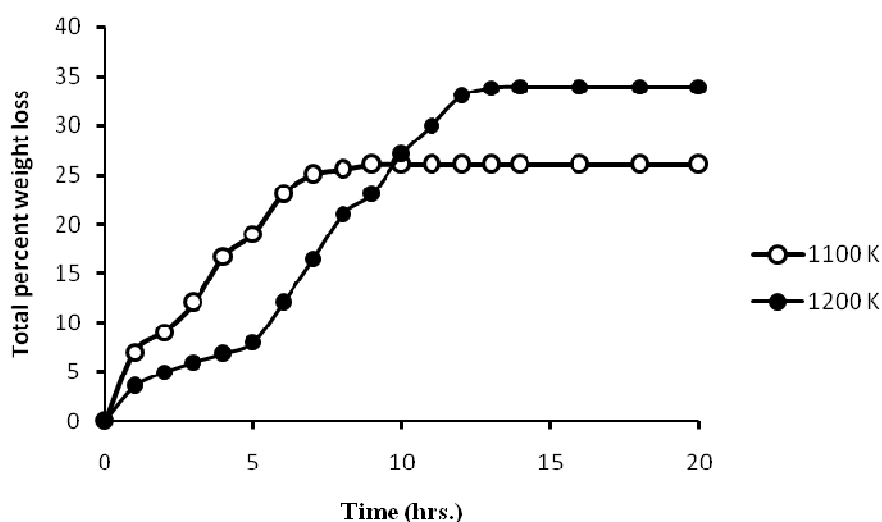


Figure-1 Plot of total percent weight loss versus time for NiO-NaCl system (molar ratio 1:1) at 1100 and 1200K.

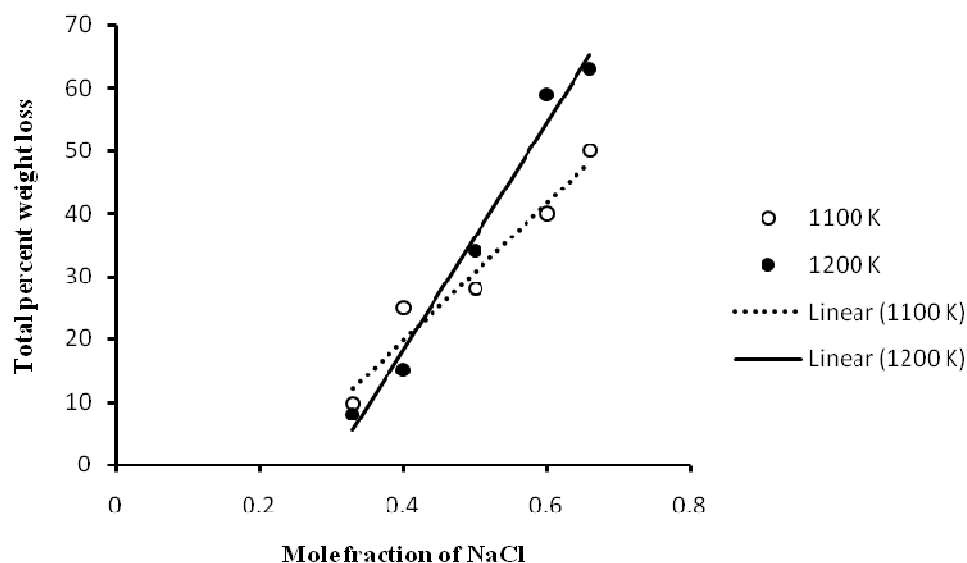


Figure-2 Plots of total percent weight loss versus mole fraction of NaCl in the reaction mixture at 1100 and 1200K.

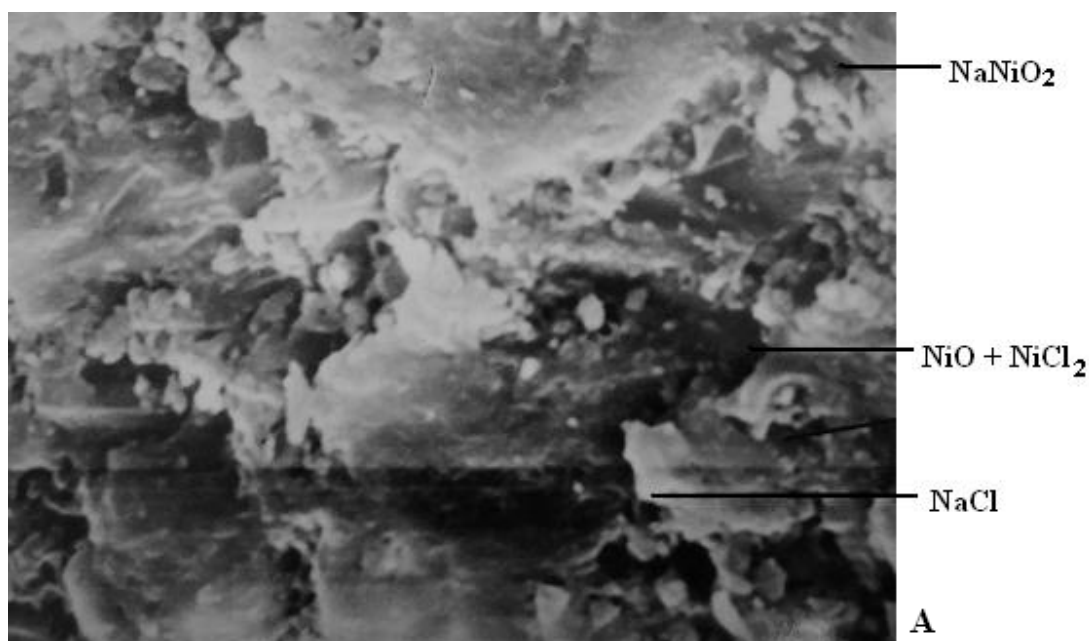


Figure-3 A SEM pictures of the reaction products of NiO-NaCl system oxidized for 20 hours at 1100K (2500 X)

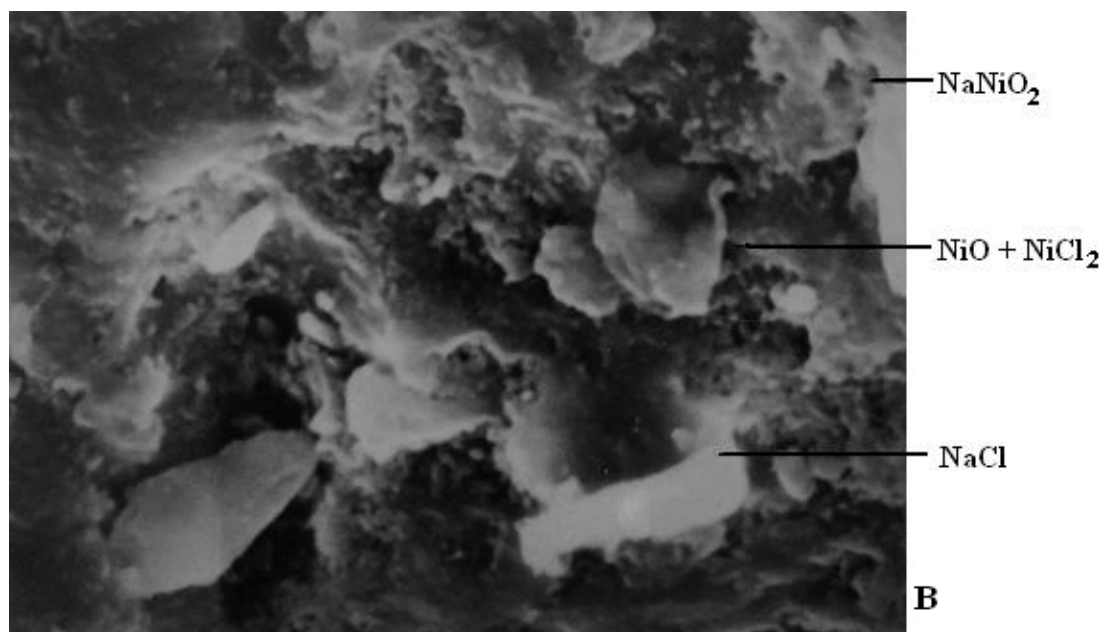


Figure-4 B SEM pictures of the reaction products of NiO-NaCl system oxidized for 20 hours at 1200K (1550 X)

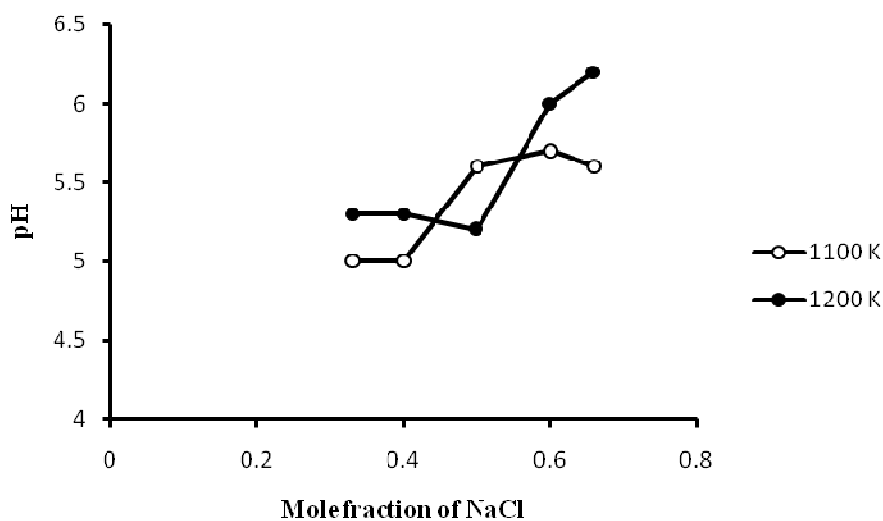


Figure-4 Plots of the pH of the aqueous solution of the reaction product versus mole fraction of NaCl for NiO-NaCl system at 1100 and 1200K.

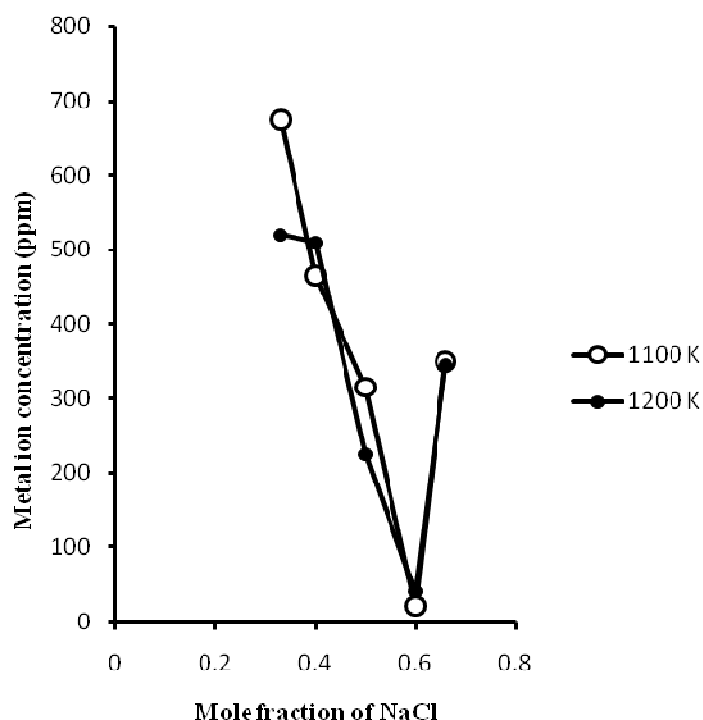


Figure-5 Plots of the metal ion concentration (ppm weight) versus mole fraction of NaCl for NiO-NaCl system at 1100 and 1200K.

Reaction	ΔG° (Kcal mol ⁻¹)
$\text{NiO (s)} + \text{Cl}_2(\text{g}) \rightarrow \text{NiCl}_2 (\text{s}) + \frac{1}{2} \text{O}_2 (\text{g})$	- 37.129
$\text{Na}_2\text{O (s)} + 2\text{NiO (s)} + \frac{1}{2}\text{O}_2 \rightarrow \text{NaNiO}_2 (\text{s})$	- 53.183

Table-1 Standard free energy of the reaction, ΔG° at 1200K [15].

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