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HIGH TEMPERATURE INTERACTIONS OF METAL OXIDES WITH NaCl

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Summary

The interaction of different metal oxides such as AL_2O_3, TiO_2, ZrO_2, SiO_2, Nb_2O_5, Ta_2O_5, Cr_2O_3, MoO_3, WO_3, Fe_2O_3, Co_3O_4 and NiO with NaCl in the temperature range 800-1200 K in flowing oxygen has been studied. These oxides are present on the scales formed on Na_2SO_4 or NaCl during the initiation stage of hot corrosion attack and react with Na_2SO_4 or NaCl during the propagation stage by a fluxing reaction. Thermogravimetric, optical metallography, scanning electron microscopy, EDAX and X-ray diffraction techniques were used to identify and to determine the structure of various phases present in the solid state reaction products. The concentration of soluble metal and chloride species in the aqueous solutions of the reaction products of NaCl and metal oxides was determined using atomic absorption spectrophotometry and ion selective electrode analysis respectively. The solid state products usually contain a three-phase structure, *i.e.* $Na_2O.M_2O_x$, MO and Cl^-. The concentration of various constituents varies according to the composition of interacting species, *e.g.* metal oxide and NaCl. The formation of $Na_2O.M_2O_x$ depends upon the solid state solubility of metal oxides in the salt at high temperature.

1. Introduction

High temperature alloys are susceptible to hot corrosion attack when used in hostile environments. The electrolytic deposits (ash or ionic salts) react with normally protective oxide layers on the alloy and give way to an accelerated corrosion attack known as hot corrosion. NaCl is one of the important hot corrosion causing agents of the salt deposits on metals or alloys. NaCl may be present in the air, in marine environments or in fuels. At high temperatures, the conventional alloys are invariably attacked by NaCl. The protective oxide scales of Cr_2O_3-Al_2O_3 are chemically attacked by molten NaCl and form a blistered and cracked surface on the alloy. The attack is more aggressive with NiO-Cr_2O_3 formers in comparison with Al_2O_3. Our information is limited on the role of oxides during the NaCl-induced hot corrosion of high temperature alloys. It is generally believed that NaCl attacks the alloy and forms volatile chlorides or oxychlorides.

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Conde and Wareham [1] carried out a series of chemical studies relating to the interaction of Al_2O_3 and Cr_2O_3 with Na_2SO_4 and NaCl in atmospheres of argon and air. The studies showed that little attack was observed with Al_2O_3 in either Na_2SO_4 or NaCl at temperatures up to 1000 °C, but Cr_2O_3 was found to react with NaCl in air to produce volatile products [2]. Stearns *et al.* [3], using high pressure mass spectrometric analysis, have identified the formation of a volatile species when NaCl in the gaseous phase reacts with Cr_2O_3 in an oxygen environment. The major chromium-containing species is a complex molecule, $(NaCl)_x.Cr_2O_3$ where $x = 1, 2$ or 3.

Deanhardt and Stearn [4, 5] measured the solubility products of NiO, Co_3O_4 and Y_2O_3 in molten NaCl (1100 K) by coulometric titration of the respective chlorides ($NiCl_2$, $CoCl_2$ and YCl_3) with electrochemically generated oxide ions, using a stabilized ZrO_2 electrode as an oxide pump. Activity coefficients for $NiCl_2$, $CoCl_2$, YCl_3 and sodium metal oxides in molten NaCl were computed.

The work presented in this paper deals with the high temperature studies on the interaction of NaCl with metal oxides. The main objective of the work is to investigate the nature of the chemical reaction between the metal oxide and NaCl on the basis of reaction kinetics and the morphology of the reaction products.

2. Experimental details

Co_3O_4, NiO, Al_2O_3, Cr_2O_3, Fe_2O_3, SiO_2, TiO_2, ZrO_2, Nb_2O_5, Ta_2O_5, MoO_3 and WO_3 were all A.R. grade products. NaCl (reagent grade) was dried in an oven at 200 °C for 48 h. Dried and powdered NaCl and the oxide (about 80 mesh size) were mixed in different molar ratios (1:2, 1:1 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 tons cm^{-2}).

The oxidation runs were carried out on a laboratory-fabricated helical thermal balance with a cathetometer arrangement using a nichrome-wound electric resistance furnace in a constant stream of pure and dried oxygen gas. An oxidation run of 24 h was found to be adequate to provide reaction products under steady state conditions which were indicated by no change in weight over a considerable period of exposure time. To obtain sufficient samples of the reaction products for a particular system, three silica boats, each containing compacts of the same ratio, were placed in a horizontal furnace and were oxidized under almost identical conditions. After completion of the oxidation run, the first one was mounted for morphological studies (metallographic, scanning electron microscopy (SEM) and EDAX), the second for X-ray diffraction (XRD) studies and the third was retained for quantitative estimation of soluble species.

A computerized Leitz photometallurgical microscope (Metallux-2) was used for the metallographic studies. The compacts of the reaction products were mounted in a cold setting resin (Araldite) and were abraded sequentially on different grit SiC papers followed by polishing with 6 μm diamond paste using kerosine oil as the lapping liquid. Appropriate etchants (Table 1) were used to identify the different phases in the microstructures.

TABLE 1

Etchants used in the metallographic studies

System	*Etchants*
Co_3O_4–NaCl	Aqueous sodium thiosulfate solution
NiO–NaCl	1% dimethyl glyoxime in alcohol (ammonical solution)
Al_2O_3–NaCl	Quinalizarin in pyridine and acetic acid
Cr_2O_3–NaCl	Aqueous lead acetate solution
Fe_2O_3–NaCl	Aqueous potassium ferrocyanide solution
SiO_2–NaCl	Ammonium molybdate and benzidine
TiO_2–NaCl	3% H_2O_2 in H_2O
ZrO_2–NaCl	1% aqueous solution of alizarin red S
Nb_2O_5–NaCl	Aqueous pyrogallol-4-sulfonic acid solution
Ta_2O_5–NaCl	Aqueous pyrogallol-4-sulfonic acid solution
MoO_3–NaCl	Potassium thiocyanate and stannous chloride
WO_3–NaCl	25% stannous chloride in concentrated HCl

SEM and EDAX studies were performed using a Jeol electron microscope with an EDAX attachment. XRD analysis was carried out using a Philips X-ray diffractometer with Co Kα, Mo Kα or Fe Kα targets and appropriate filters.

The water soluble species in the reaction product mixtures of different molar ratios were estimated by dissolving a weighed amount of each ratio in a fixed amount of doubly distilled 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 different soluble species in the solution. An atomic absorption spectrophotometer was used to determine the concentration of metals while an Orion Research microprocessor ionalyzer was used to determine the concentration of chloride ions in the solution.

3. Results

3.1. Thermogravimetric studies

3.1.1. Oxidation kinetics

Figures 1(a) and 1(b) represent the weight loss (in per cent) *vs.* time curves for metal oxide–NaCl systems. With the exceptions of the MoO_3–NaCl, Nb_2O_5–NaCl and Ta_2O_5–NaCl systems, where there is a rapid weight loss up to a period of 2 h only, all the other systems show a rapid and continuous weight loss up to 8–14 h followed by a very small or no change in weight.

3.1.2. Influence of salt

Figure 2 shows plots of per cent total weight loss *vs.* mole fraction of NaCl in the reaction mixture. The total weight loss represents the final reading recorded after 24 h of heating a mixture consisting of NaCl and metal oxide at selected temperature in the range 800–1200 K in flowing oxygen. In general, no further

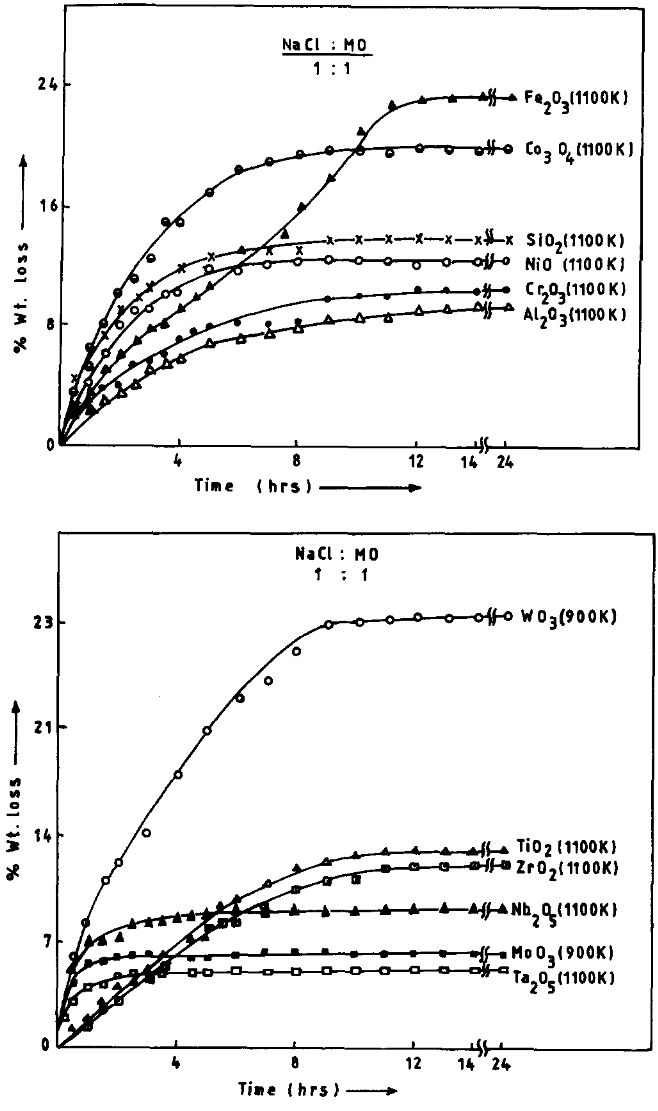

Fig. 1. Plots of weight loss *vs.* time for 1:1 (molar ratio) NaCl–metal oxide systems.

weight loss was observed after 24 h. Thus, the weight loss incurred during an oxidation run of 24 h represents the total weight loss at steady state.

A study of the weight loss *vs.* mole fraction of NaCl plots indicates four types of behaviour during the interaction. The first type shows no significnt change in total weight loss on varying NaCl concentration in the reaction mixture: Co_3O_4–NaCl (1000 K), Al_2O_3–NaCl (1000 K), Cr_2O_3–NaCl (1000 K), Fe_2O_3–NaCl (1000 K), SiO_2–NaCl (1000 K), TiO_2–NaCl (1000 K) and WO_3–NaCl (800 K). The second type is characterized by a maxima in the weight loss curves

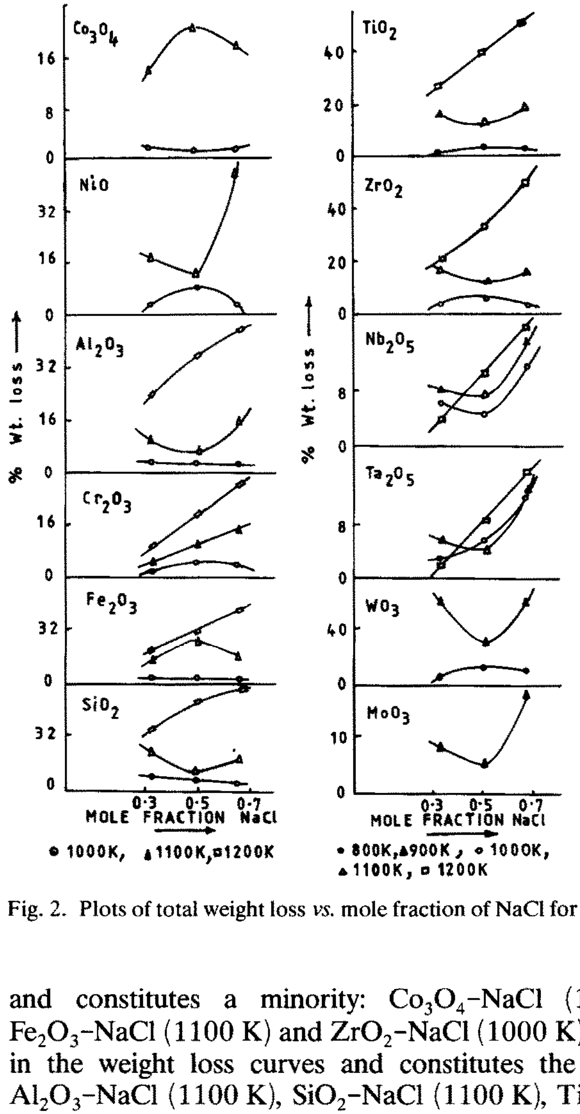

Fig. 2. Plots of total weight loss *vs.* mole fraction of NaCl for different NaCl–metal oxide systems.

and constitutes a minority: Co_3O_4–NaCl (1100 K), NiO–NaCl (1000 K), Fe_2O_3–NaCl (1100 K) and ZrO_2–NaCl (1000 K). The third type shows a minima in the weight loss curves and constitutes the majority: NiO–NaCl (1100 K), Al_2O_3–NaCl (1100 K), SiO_2–NaCl (1100 K), TiO_2–NaCl (1100 K), ZrO_2–NaCl (1100 K), Nb_2O_5–NaCl (1000 and 1100 K), Ta_2O_5–NaCl (1100 K), WO_3–NaCl (900 K) and MoO_3–NaCl (900 K). Lastly, the fourth type, showing a linear trend in the weight loss curves: Al_2O_3–NaCl (1200 K), Cr_2O_3–NaCl (1100 and 1200 K), Fe_2O_3–NaCl (1200 K), SiO_2–NaCl (1200 K), TiO_2–NaCl (1200 K), ZrO_2–NaCl (1200 K), Nb_2O_5–NaCl (1200 K) and Ta_2O_5–NaCl (1000 and 1200 K).

3.2. Metallographic, SEM, EDAX and XRD studies

Figures 3–8 show some representative optical and scanning micrographs, and EDAX concentration profiles of the mounted reaction products. Table 2 lists the different constituents as identified in the reaction product of an equimolar mixture of NaCl and metal oxide at 1100 K (900 K in case of WO_3 and MoO_3–NaCl

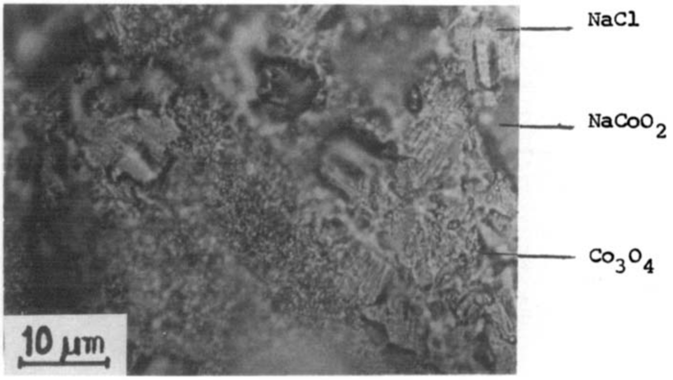

Fig. 3. Optical photomicrograph of the reaction product of the 1:1 NaCl–Co_3O_4 system, oxidized at 1000 K.

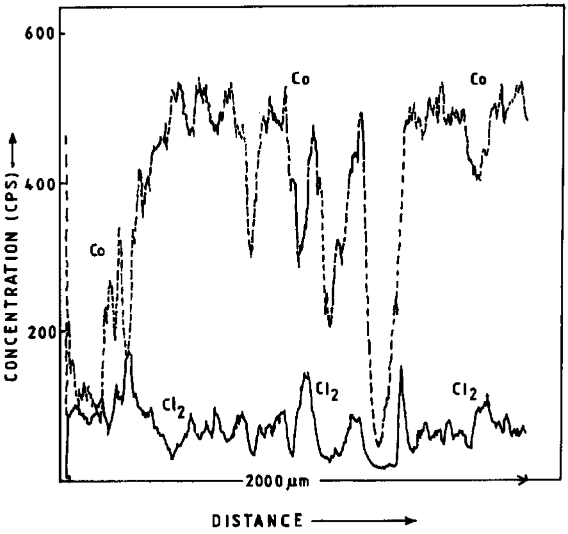

Fig. 4. EDAX concentration profiles of the 1:2 NaCl–Co_3O_4 reaction product, oxidized at 1100 K.

systems) by XRD analysis. In general, the presence of multiphase structures containing oxide, mixed oxide $Na_2O.M_2O_x$ and metal chloride is evident from the metallographic and SEM studies. The EDAX studies are particularly useful in determining the compounds containing sodium and chlorine in the reaction products.

3.3. *Estimation of soluble metal and chloride ions*

The concentration of water soluble metal and chloride species in the reaction products of NaCl and metal oxides was determined as a function of NaCl in the reaction mixture. Figure 9 shows plots of the concentration of soluble metal *vs.*

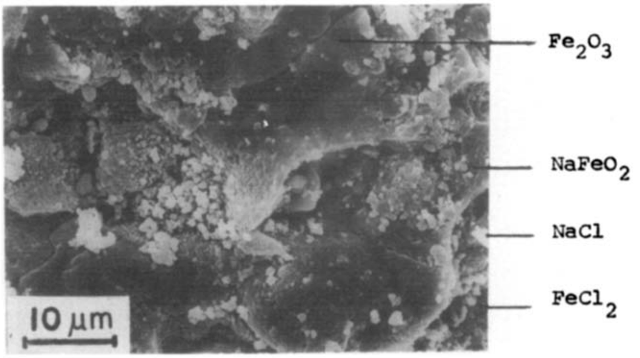

Fig. 5. Scanning electron micrograph of the reaction product of the 1:1 NaCl–Fe_2O_3 system, oxidized at 1100 K.

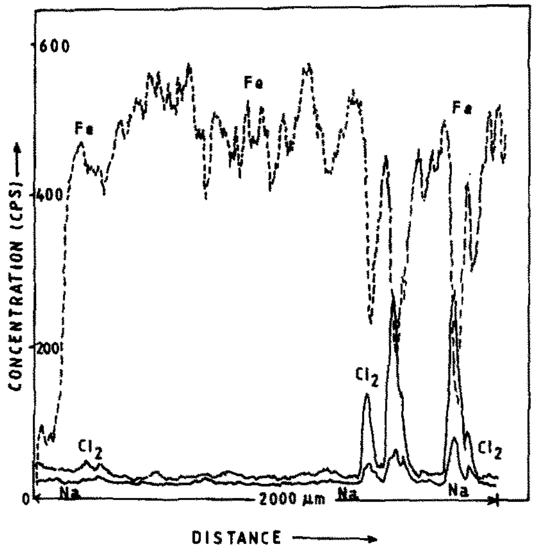

Fig. 6. EDAX concentration profiles of the 1:2 NaCl–Fe_2O_3 reaction product, oxidized at 1200 K.

mole fraction of NaCl in the reaction product mixture of NaCl and metal oxides at 1100 K (900 K in case of MoO_3–NaCl). Two types of behaviour were mainly noted.

(1) An increase in the concentration of soluble metal species with increasing amount of NaCl in the reaction mixture followed by a decrease. Systems showing this behaviour include: Co_3O_4–NaCl (1100 K), Al_2O_3–NaCl (1100 K) and Cr_2O_3–NaCl (1100 K).

(2) A continuous increase in the concentration of soluble metal species with increasing amount of NaCl in the reaction mixture. Systems showing this behaviour include: Fe_2O_3–NaCl (1100 K) and MoO_3–NaCl (900 K). The system NiO–NaCl (1100 K) shows singularly a minimum at 0.5 mole of NaCl in the solubility curve.

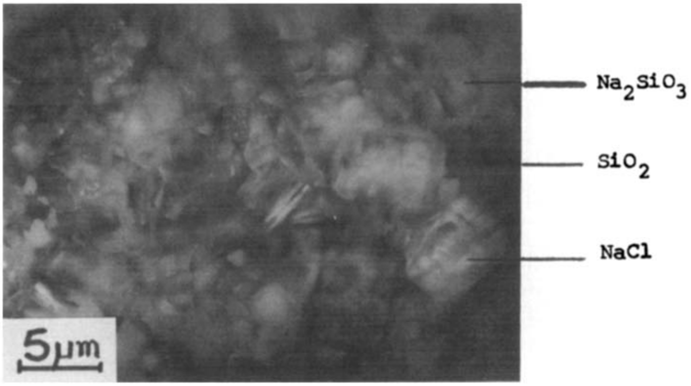

Fig. 7. Optical photomicrograph of the reaction products of the 2:1 NaCl–SiO_2 system, oxidized at 1100 K.

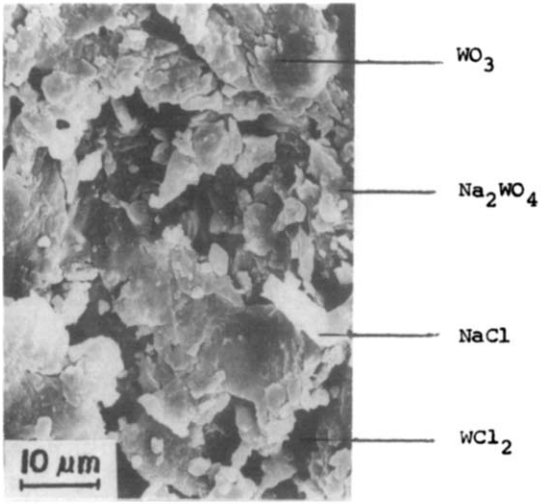

Fig. 8. Scanning electron micrograph of the 1:2 NaCl–WO_3 reaction product, oxidized at 900 K.

The plots of the mole fraction of NaCl *vs.* concentration of chloride in NaCl–metal oxide mixtures are shown in Fig. 10. Two types of curves are distinguishable:

(i) Curves showing an upward trend in chloride content in the solution with increasing concentration of NaCl in the reaction mixture and include the following systems: Co_3O_4–NaCl (1100 K), Cr_2O_3–NaCl (1100 K) and Fe_2O_3–NaCl (1100 K).

(ii) Curves exhibiting a maxima at 0.5 mole of NaCl and include the systems: NiO–NaCl (1100 K), Al_2O_3–NaCl (1100 K), SiO_2–NaCl (1100 K) and MoO_3–NaCl (900 K).

TABLE 2

Different constituents identified in the reaction product by XRD analysis

System	*Molar ratio*	*Temperature* (K)	*Constituents identified*
NaCl-Co_3O_4	1:1	1100	NaCl, Co_3O_4, $NaCoO_2$
NaCl-NiO	1:1	1100	NaCl, NiO, $NaNiO_2$
NaCl-Al_2O_3	1:1	1100	NaCl, Al_2O_3, $NaAlO_2$
NaCl-Cr_2O_3	1:1	1100	Cr_2O_3, $CrCl_3$, Na_2CrO_4
NaCl-Fe_2O_3	1:1	1100	Fe_2O_3, $FeCl_2$, $NaFeO_2$
NaCl-SiO_2	1:1	1100	SiO_2, NaCl, Na_2SiO_3
NaCl-TiO_2	1:1	1100	TiO_2, $TiCl_2$, $TiCl_3$
NaCl-ZrO_2	1:1	1100	ZrO_2, $ZrCl_2$, Na_2ZrO_3
NaCl-Nb_2O_5	1:1	1100	Nb_2O_5, $NbCl_2$, Na_2NbO_3
NaCl-Ta_2O_5	1:1	1100	Ta_2O_5, $TaCl_4$, $NaTaO_3$, NaCl
NaCl-MoO_3	1:1	900	MoO_3, $MoCl_2$, Na_2MoO_4
NaCl-WO_3	1:1	900	WO_3, Na_2WO_4

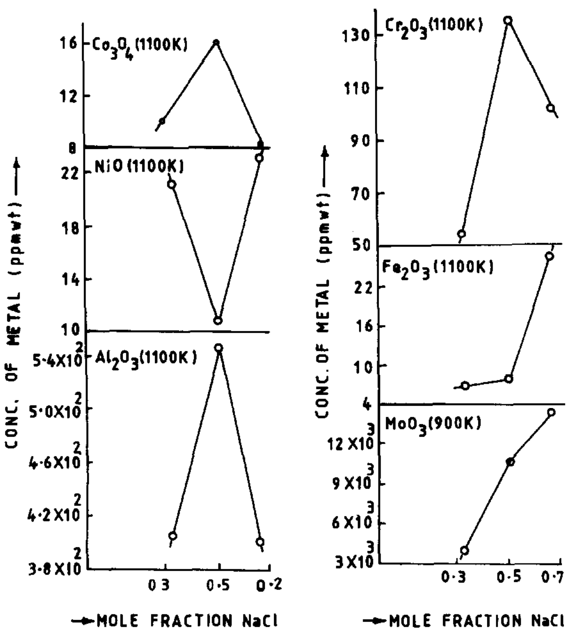

Fig. 9. Plots of the metal concentration in the aqueous solution of the reaction mixtures *vs.* mole fraction of NaCl for the different NaCl-metal oxide systems.

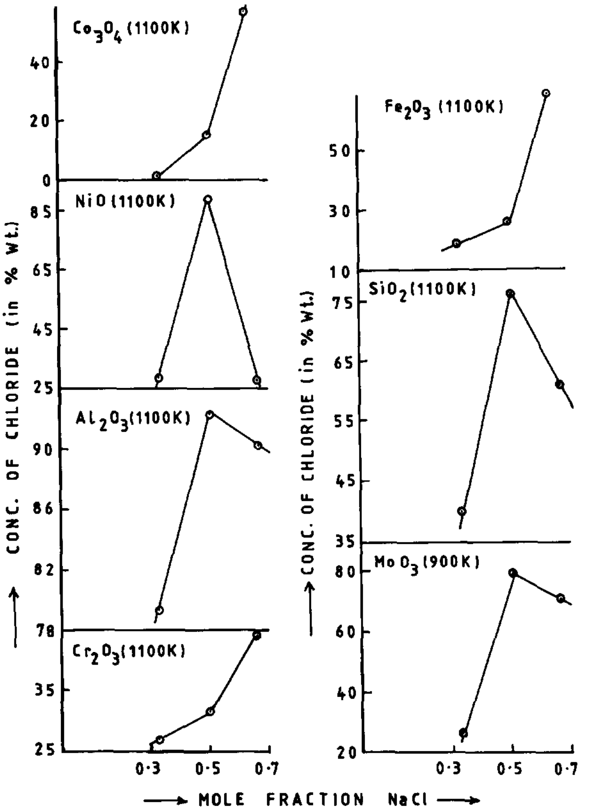

Fig. 10. Plots of the chloride concentration in the aqueous solution of the reaction mixtures *vs.* mole fraction of NaCl for the different NaCl–metal oxide systems.

4. Discussion

The interaction of NaCl and metal oxides at high temperatures results in weight losses, indicating the expulsion of volatile metal chloride/$Cl_2(g)$/NaCl which are the usual products during the interaction of NaCl and metal oxides. The total weight loss for different NaCl–metal oxide systems was measured under a steady state condition realized by a constant weight with increasing exposure time. We consider the weight loss as a function of mole fraction of NaCl in the reaction mixture of NaCl and metal oxide. At 1200 K, there is a continuous increase in the weight loss values with increasing NaCl concentration in the mixture. This behaviour is exhibited by all the systems.

The weight loss incurred by NaCl–metal oxide systems is accounted by the following processes: (i) evaporation of NaCl, (ii) evaporation of volatile metal chlorides formed during the reaction, (iii) release of chlorine during the reaction of metal chlorides with oxygen and (iv) evaporation of volatile metal oxides. The magnitude of the weight loss depends upon several factors, namely, the reaction temperature, the nature of the oxides, the thermodynamic feasibility of the reactions and the kinetics of the reactions. These factors decide the relative contribution of processes (i) to (iv) responsible for weight losses during the oxidation.

In general, during the interaction of NaCl and a metal oxide, NaCl reacts with oxygen to give Na_2O and $Cl_2(g)$. The metal oxide dissolves in Na_2O to form $Na_2O.M_2O_x$ where the $Cl_2(g)$ reacts with the metal oxide to give the metal chloride. It can be represented as follows:

$$2NaCl+\tfrac{1}{2}O_2 \rightleftharpoons Na_2O+Cl_2$$

$$Na_2O+M_2O_x \rightleftharpoons Na_2O.M_2O_x$$

$$M_2O_x+Cl_2 \rightleftharpoons 2MCl_x+\tfrac{1}{2}O_2$$

Various species formed during the interaction can be written with the help of the above equations and their formation is accounted for by the following experimental evidences. (i) The continuous weight loss with time on exposure to oxygen. (ii) The optical and scanning photomicrographs of the reaction products show phase structures typical of oxide/chloride/mixed oxide systems. (iii) The XRD patterns identify the presence of most of the products depicted in the above reactions. (iv) The EDAX concentration profiles indicate the presence of metal chloride and/or sodium metal oxide in the reaction products.

A qualitative interpretation of the data obtained from the determinations of soluble metal and chloride species in aqueous solutions of the metal–oxide reaction products provides information regarding the formation of different oxyanion and chloride species (Fig. 9 and Table 3). The concentration of soluble metal species varies from a few parts per million of NiO, Fe_2O_3 and Co_3O_4 to several thousands parts per million of MoO_3; Al_2O_3 occupying a middle position (several hundred parts per million). Obviously, the soluble metal species present in the solution are either in the form of metal chlorides and/or in the form of MO_2^{2-}, MO_2^- or MO_4^{2-}. Owing to the volatility of most of the metal chlorides within the temperature range (1000–1200 K) selected for this study there is little likelihood of the presence of metal chlorides in the reaction products. Therefore, in systems containing relatively low levels of soluble metal species the formation of complex species, *e.g.* CoO_2^-, NiO_2^-, CrO_2^- or CrO_4^{2-} and FeO_2^-, can be presumed in the respective metal oxide–NaCl systems. The evidence for the formation of these species has been obtained by XRD and EDAX analysis. The metallographic studies also indicate the presence of a mixed oxide phase.

In the Al_2O_3–NaCl system, the concentration of soluble aluminium-containing species and chloride species in the reaction products is much higher than in other systems. In such circumstances, the formation of $NaAlO_2$ along with some chloride of aluminium is very likely. Similarly, a relatively high concentration of soluble molybdenum-containing species in the MoO_3–NaCl system is an indication of the massive formation of Na_2MoO_4. There is strong XRD and EDAX evidence for the presence of Na_2MoO_4 in the reaction products.

Under molten conditions, in a metal oxide–NaCl system, the behaviour can be generalized as follows. Under low oxide solubility conditions, the regions

TABLE 3

System	*Molar ratio*	*Weight of the reaction product* (g)	*Theoretical weight of the reacting mixture* (g)		*Concentration of soluble metals* (ppm wt.)	*Concentration of chloride in the solution* (wt.%)	*Temperature* (K)
			NaCl	*Metal oxide*			
NaCl-Co_3O_4	1:2	0.446	0.048	0.398	10.137	0.459	1100
	1:1	0.189	0.036	0.153	16.071	15.217	
	2:1	0.274	0.089	0.185	8.148	65.063	
NaCl-NiO	1:2	0.598	0.167	0.431	21.005	28.26	1100
	1:1	0.389	0.170	0.219	10.818	89.54	
	2:1	0.283	0.172	0.111	23.255	27.44	
NaCl-Al_2O_3	1:2	0.619	0.137	0.482	403.54	79.37	1100
	1:1	0.376	0.137	0.239	547.61	92.36	
	2:1	0.487	0.260	0.227	400.00	90.29	
NaCl-Cr_2O_3	1:2	0.584	0.094	0.490	54.179	26.82	1100
	1:1	0.312	0.086	0.226	135.714	31.61	
	2:1	0.396	0.172	0.224	102.614	44.97	
NaCl-Fe_2O_3	1:2	0.506	0.078	0.428	7.023	18.79	
	1:1	0.236	0.063	0.173	7.851	25.61	
	2:1	0.357	0.151	0.206	26.38	77.74	
NaCl-SiO_2	1:2	0.559	0.181	0.378	–	39.73	1100
	1:1	0.377	0.185	0.192	–	76.27	
	2:1	0.618	0.406	0.212	–	60.90	
NaCl-MoO_3	1:2	0.514	0.086	0.428	3810	26.15	900
	1:1	0.329	0.095	0.234	10640	79.43	
	2:1	0.355	0.159	0.196	14370	71.18	

beneath the surface of the oxide–NaCl film would have a higher activity of chlorine (or low oxygen activity); therefore, the formation of the chloride is the most favourable. Since most of the metallic chlorides formed have a high vapour pressure, they would have an inherent tendency to vapourize, resulting in a surface with a porous appearance. Some of the metal chlorides may remain as a condensed phase. With the formation of chloride, the activity of sodium increases and oxygen penetrates inwardly through the pores, this results in conditions that favour the formation of sodium metal oxides. Some of the chlorides which are formed might be converted into oxides by oxygen at the surface (or underneath) when they come into contact with diffused oxygen. The formation of oxides from metal chlorides results in the production of $Cl_2(g)$. If the chlorine gas is produced at the surface there is little possibility of chloride formation due to the low partial pressure of the gas; however, beneath the surface high chlorine activity persists which favours the formation of metallic chlorides. This mechanism is shown schematically in Fig. 11.

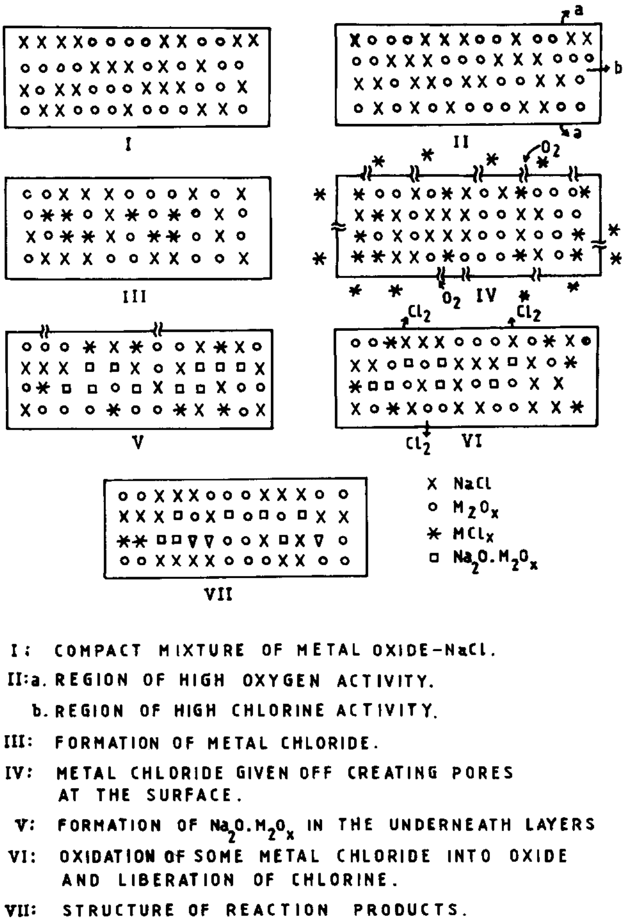

Fig. 11. Schematic diagram representing cross-section, showing different species formed during the interaction of NaCl and metal oxides.

5. Conclusions

(1) The high temperature interaction of NaCl and metal oxides results invariably in weight losses indicating the expulsion of volatile metal chloride/ $Cl_2(g)$/NaCl.

(2) During the interaction, $Na_2O.M_2O_x$ and metal chlorides are the usual reaction products.

(3) Determination of soluble metal and chloride species in the aqueous solutions of the metal oxide reaction products indicate the presence of soluble species CoO_2^-, NiO_2^-, CrO_2^- or CrO_4^{2-} and FeO_2^- in respective metal oxide–NaCl systems, whereas in the NaCl–MoO_3 and NaCl–Al_2O_3 systems there is evidence of the presence of metal chlorides in addition to oxyanion species MoO_4^{2-} and AlO_2^-.

Acknowledgment

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