Journal of Alloys and Compounds, 186 (1992) 1–14
JALCOM 254

Studies on the interactions of transition metal carbides and sodium chloride in the temperature range 900–1200 K in oxygen

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(Received April 6, 1991)

Abstract

The interaction of different metal carbides, namely Cr_7C_3, Fe_3C, TiC, ZrC, NbC, TaC, MoC, WC, VC and HfC with NaCl in a temperature range 900–1200 K in flowing oxygen has been studied. The thermogravimetric studies were carried out by measuring weight change as function of time and mole fraction of NaCl in the reaction mixture. The different constituents in the reaction products were identified by X-ray diffraction analysis and the morphologies of the reaction products were discussed on the basis of metallography, scanning electron microscopy and energy dispersive X-ray analysis. The concentration of water soluble metal species was determined using atomic absorption spectrophotometry.

The transition metal carbides on interaction with NaCl are decomposed into respective metal oxides which further interact with NaCl forming sodium metal oxide and/or metal chloride depending upon the local conditions prevailing during the interaction. The solubility measurements indicate the formation of water soluble metal species.

1. Introduction

The transition metal carbides are strong refractory compounds and their presence in engineering materials as a discrete phase provides excellent heat resistance and strengthening properties. Transition metal carbides are invariably present in heat resistant and high temperature corrosion resistant alloys, and have formidable resistance toward oxidation in low and high oxygen potential environments [1]. In high temperature applications based on fossil fuel energy generation or conversion, salt- or ash-containing environments often exist; the molten salt(s) deposits on the machinery components and initiates accelerated corrosion attack which is known as hot corrosion [2]. During a hot corrosion attack, molten salt reacts with the constructional material and causes a depletion of the alloying elements required to form a protective oxide film on the surface of the machine parts. 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 [3–7]. Some physicochemical studies relating to the interaction of Al_2O_3, Cr_2O_3, NiO, Co_3O_4 and Y_2O_3 with NaCl at high temperatures have been carried

0925-8388/92/$5.00

out [3–6, 8]. The results of a study of the high temperature interactions of some transition and non-transition metal oxide have recently been published [9]. It has been found that $Na_2O \cdot M_2O_x$ and metal chloride are the usual reaction products. Carbides present in the engineering materials or the alloys are preferentially attacked by NaCl during a hot corrosion attack [10]. Little is known about the chemical nature of the hot corrosion attack in presence of NaCl and the relative reactivities of the different carbides, although some information is available on the high temperature interactions of transition metal carbides with Na_2SO_4 [11]. The kinetic–thermogravimetric studies show that the weight losses are incurred due to the evolution of CO_2/SO_2 as a result of the degradation of Na_2SO_4 and carbide; the weight gains are due to the formation of sodium metal oxide and metal sulfide by the mutual interactions of metal oxide, Na_2O and Na_2S.

The present paper describes the interaction of NaCl with a number of transition metal carbides in oxygen at temperatures relevant to hot corrosion attack.

2. Experimental details

Transition metal carbides Cr_7C_3, Fe_3C, TiC, ZrC, NbC, TaC, MoC, WC, HfC and VC (99.9% purity), were CERAC, USA products. Analytical grade NaCl was dried in an oven at 473 K for about 48 h. Powdered NaCl and carbides were mixed separately in 1:2, 1:1 and 2:1 molar ratios of NaCl and carbide respectively and were compacted mechanically into tablets of 1.4 cm using a pressure of $\times 10^7$ kg m^{-2}.

The kinetics of solid-state reaction between NaCl and carbide were studied by carrying out weight change *vs.* time measurements in the temperature range 900–1200 K in a stream of pure and dried oxygen gas using a hot stage Sartorius electronic microbalance. An oxidation run of 20 h was adequate to provide reaction products under steady state, which was indicated by negligible 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, 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 3 samples, one was mounted for morphological studies (metallography, scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDAX), the second for X-ray diffraction analysis and the third was retained for quantitative determination of soluble species.

A computerized Leitz photometallurgical microscope (Metallux 2) was used for metallographic studies. The reaction products present in the form of compacts were mounted in a cold setting resin (Araldite). The mounted specimens were ground on 600 grit SiC papers followed by polishing with 6 μ diamond paste using kerosine as the lapping liquid. Appropriate etchants

TABLE 1

Etchants used in metallographic studies

System	Etchants
Cr_7C_3–NaCl	Aqueous lead acetate solution
Fe_3C–NaCl	Aqueous potassium ferrocyanide solution
TiC–NaCl	3% H_2O_2 in H_2O
ZrC–NaCl	1% aqueous solution of alizarin red S
NbC–NaCl	Aqueous pyrogallol-4-sulfonic acid solution
TaC–NaCl	Aqueous pyrogallol-4-sulfonic acid solution
MoC–NaCl	Potassium thiocyanate and stannous chloride
WC–NaCl	25% stannous chloride in conc. HCl

listed in Table 1 were used to identify the different phases in the microstructures.

The SEM and EDAX studies were conducted using a JOEL electron microscope JSM840.

The X-ray diffraction studies were carried out using a Philips X-ray diffractometer model APD 1700 with Cu Kα or Mo Kα targets and appropriate filters.

The concentration of metals in the aqueous solution of the reaction products for the system NaCl–Cr_7C_3, NaCl–MoC and NaCl–VC was determined with the help of a Varian atomic absorption spectrometer model AA975. The compacts of the reaction products were weighed and dissolved in fixed volume of demineralized water. The mixture was heated near to boiling followed by filtration through a Whatman filter paper. The filtrate was diluted accordingly, and the concentration of metal was determined.

3. Results

3.1. *Thermogravimetric studies*

3.1.1. *Reaction kinetic*

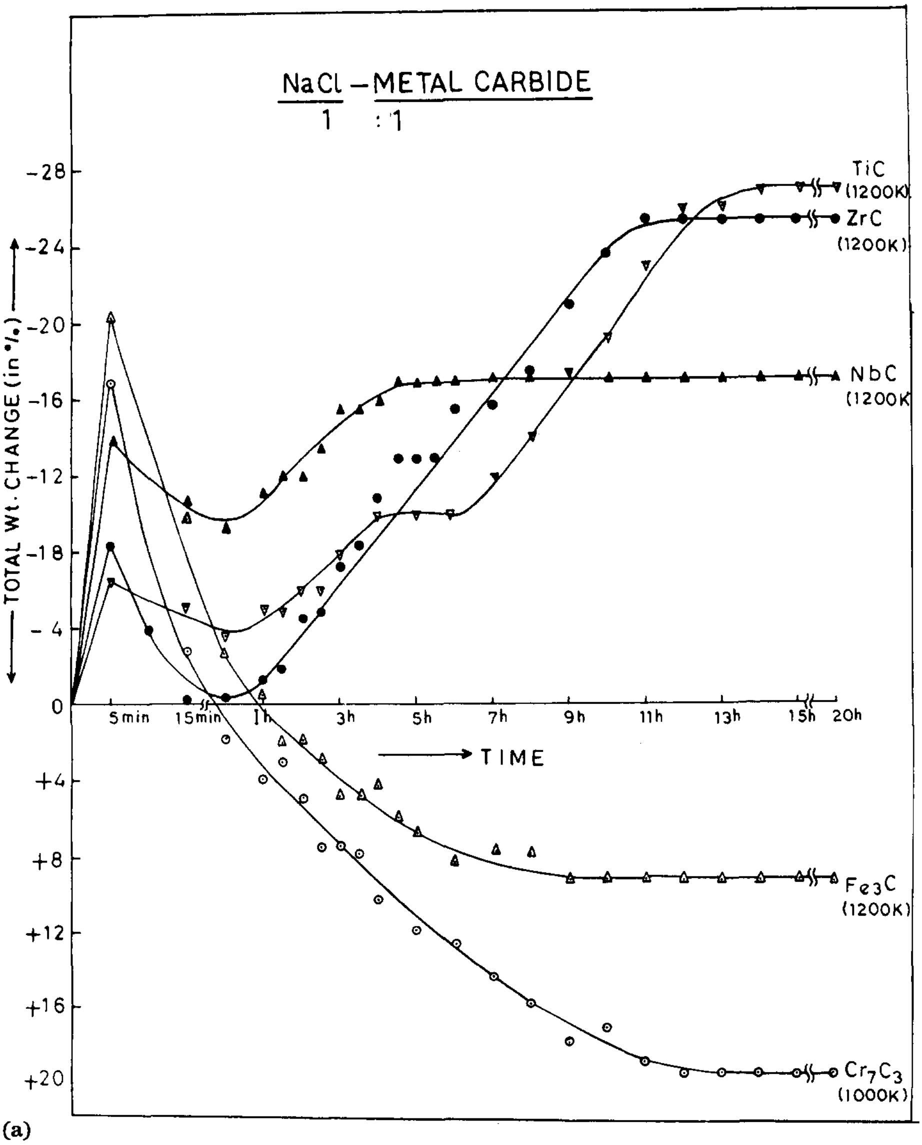
Weight change *vs.* time plots obtained during the reaction of 1:1 mixture of transition metal carbides and NaCl in oxygen at 900, 1000 and 1200 K are shown in Fig. 1(a) and (b). In general, all the systems showed a rapid weight loss in the very initial stages of the reaction followed by a gradual gain in weight. Two types of behaviour were observed: (i) a net weight loss, which included the following systems: NaCl–TiC, NaCl–ZrC, NaCl–NbC, NaCl–WC and NaCl–HfC; (ii) a net weight gain which included the following systems: NaCl–Cr_7C_3, NaCl–Fe_3C, NaCl–TaC, NaCl–MoC and NaCl–VC.

3.1.2. *Influence of salt*

Figure 2 shows some typical plots of total weight change versus mole fraction of NaCl in the mixture of NaCl and transition metal carbide. The total weight change represents the final reading recorded after heating for

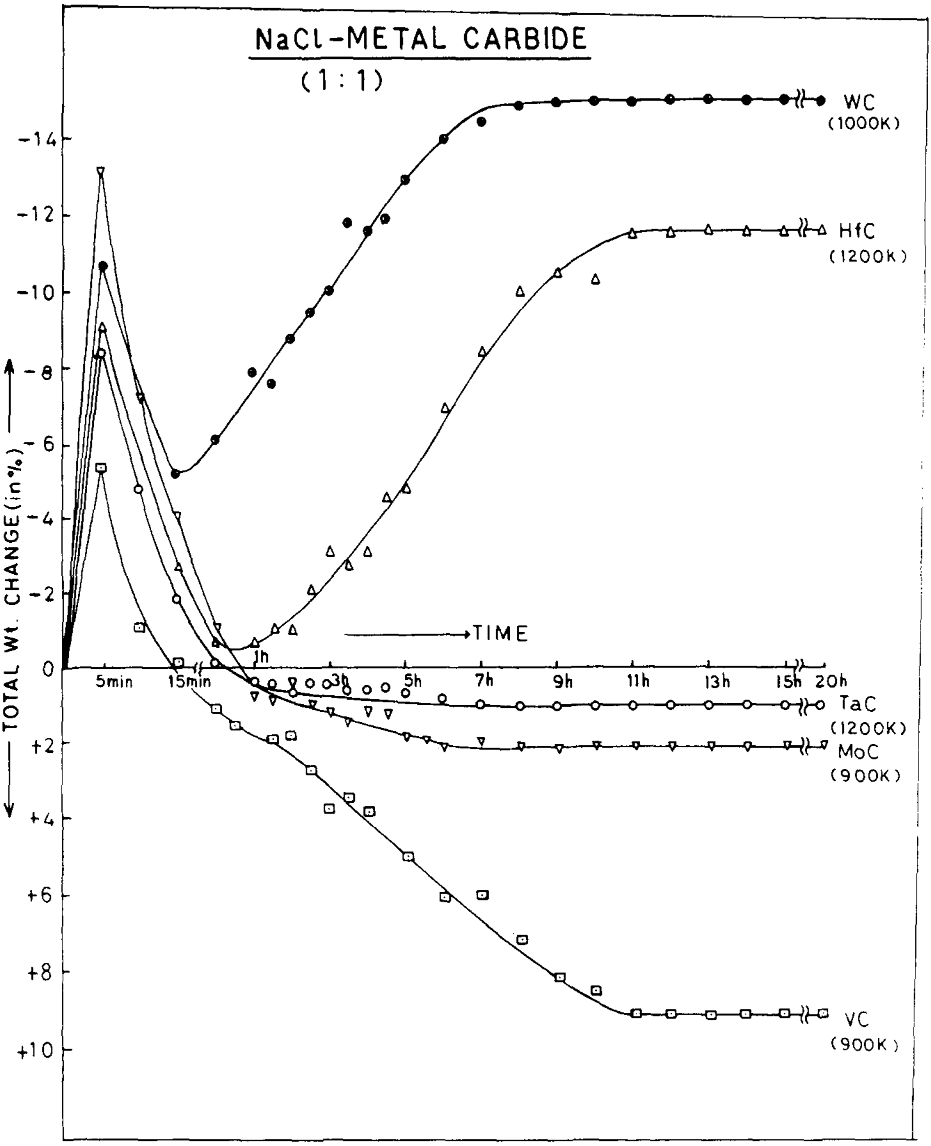
20 h of a mixture of the transition metal carbide and NaCl of known composition at 900, 1000, 1100 and 1200 K in flowing oxygen gas. The weight change incurred during a run of 20 h represents a total change at steady state since no further detectable change in weight was observed after 20 h.

The interactions of transition metal carbides with NaCl result in weight gains or weight losses. Two types of behaviour were observed: (i) weight



(a)

Fig. 1. *(continued)*



(b)

Fig. 1. Plots of % weight change *vs.* time for NaCl–metal carbide systems (1:1 molar ratio): (a) TiC, ZrC, NbC, Fe_3C, Cr_7C_3; (b) WC, HfC, TaC, MoC, VC.

gains at lower concentration of NaCl and weight losses at higher concentration of NaCl in the reaction mixtures, including NaCl–Fe_3C (1100 and 1200 K), NaCl–TaC (1200 K) and NaCl–WC (900 and 1000 K); (ii) an increase in weight loss values with increasing concentration of NaCl in the reaction mixture, including NaCl–TiC (1100 and 1200 K), NaCl–ZrC (1200 K), NaCl–NbC (1200 K), NaCl–MoC (1000 K) and NaCl–HfC (1200 K).

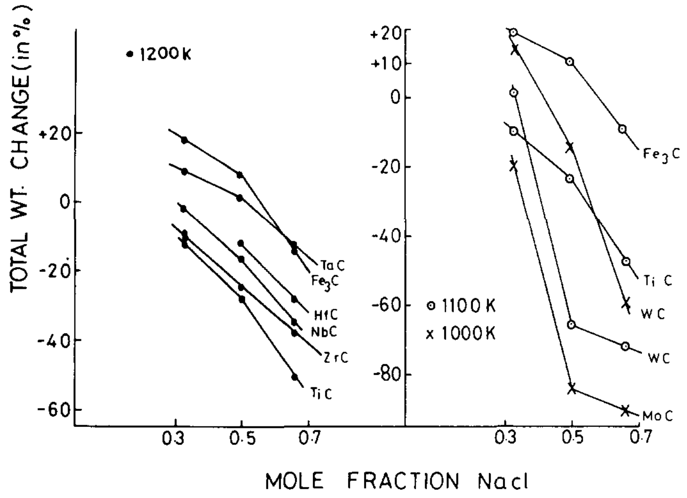


Fig. 2. Plots of % weight change *vs.* mole fraction of NaCl for NaCl–metal carbide systems.

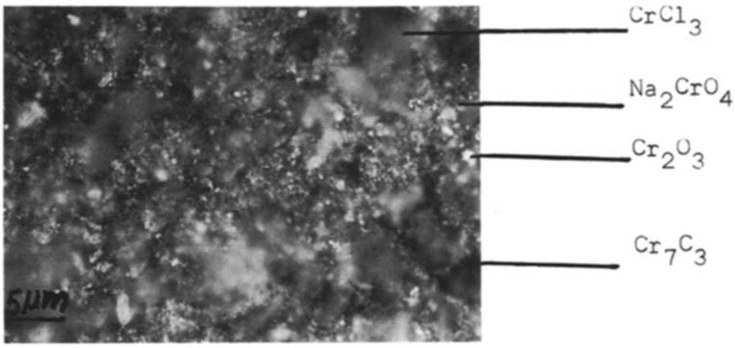


Fig. 3. Photomicrograph of 1:1 NaCl–Cr_7C_3 reaction product oxidized at 1200 K.

3.2. Morphology of the reaction products

Figures 3–9 show some representative photomicrographs and EDAX concentration profiles of the mounted reaction products. The microscopic appearance of the multiphase structure, comprising different shades of grey, shows the presence of different compounds in the reaction products. In general, an oxide alongwith NaCl appears as a whitish grey, flocculent mixed oxide ($Na_2O \cdot M_2O_x$) as grey, and metal chloride/carbide as dark grey. The EDAX concentration profiles show strong evidence of the presence of metal-rich Na- and Cl-containing compounds in most of the reaction products. Table 2 lists the various constituents as identified in the reaction products of 1:1 metal carbide–NaCl systems at 900, 1000 and 1200 K by X-ray diffraction analysis.

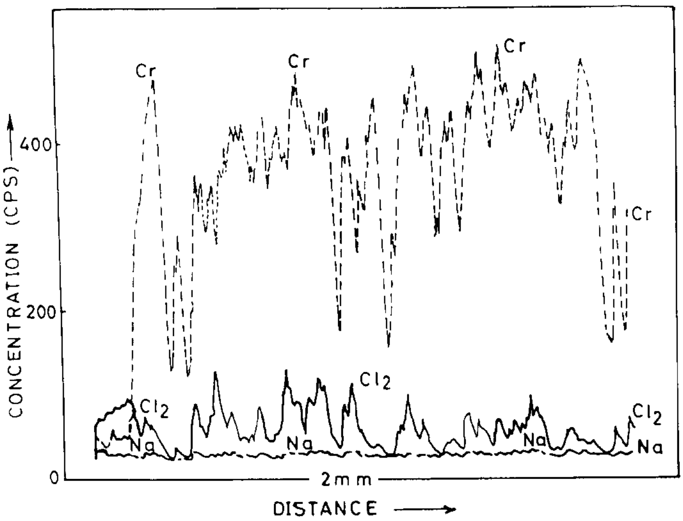


Fig. 4. EDAX concentration profiles of 1:1 NaCl–Cr_7C_3 reaction product oxidized at 1200 K.

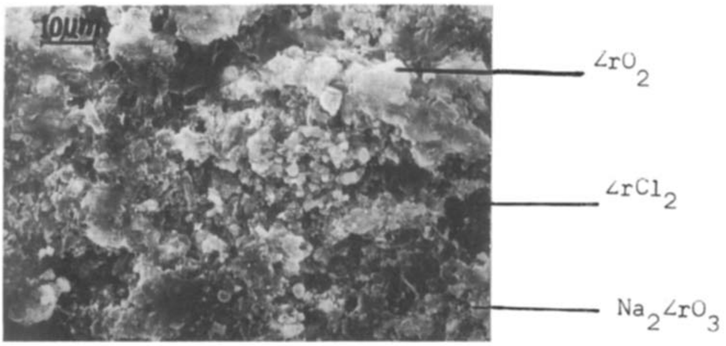


Fig. 5. SEM picture of 1:1 NaCl–ZrC reaction product oxidized at 1200 K.

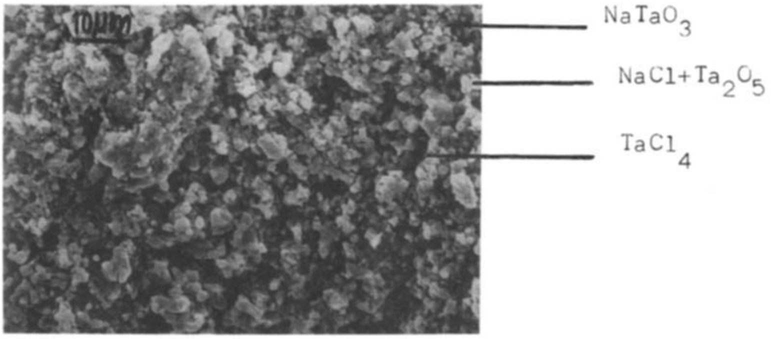


Fig. 6. SEM picture of 1:1 NaCl–TaC reaction product oxidized at 1200 K.

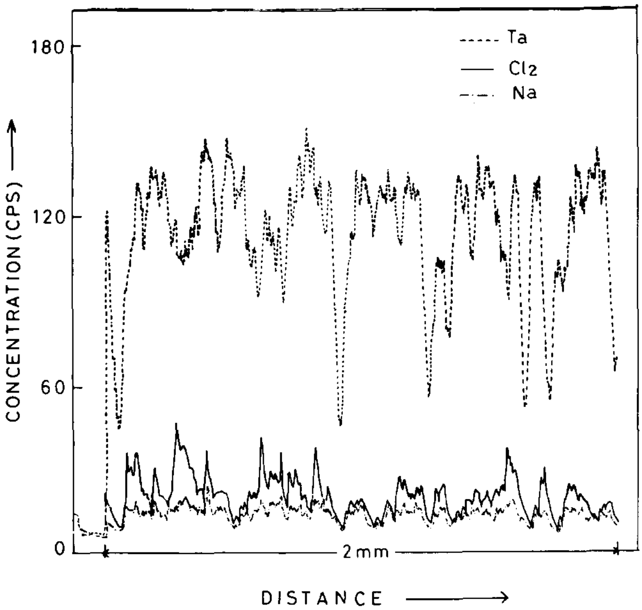


Fig. 7. EDAX concentration profiles of 1:1 NaCl–TaC reaction product oxidized at 1200 K.

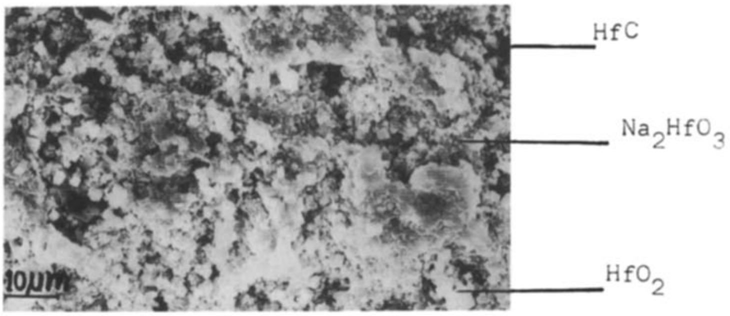


Fig. 8. SEM picture of 1:1 NaCl–HfC reaction product oxidized at 1200 K.

3.3. Estimation of soluble metal

Table 3 lists the molar ratios of the reacting mixture, weight of the reaction product, theoretical weight of the reacting mixture, concentration of the soluble metal and the reaction temperature.

4. Discussion

At high temperatures, the transition metal carbides are readily decomposed in presence of NaCl. During interaction of a carbide and NaCl, the former is invariably converted into an oxide with an appreciable change in weight. The net weight change could be either a weight loss or weight gain. The steady condition during kinetic measurements is indicated by a constant weight with increasing exposure time.

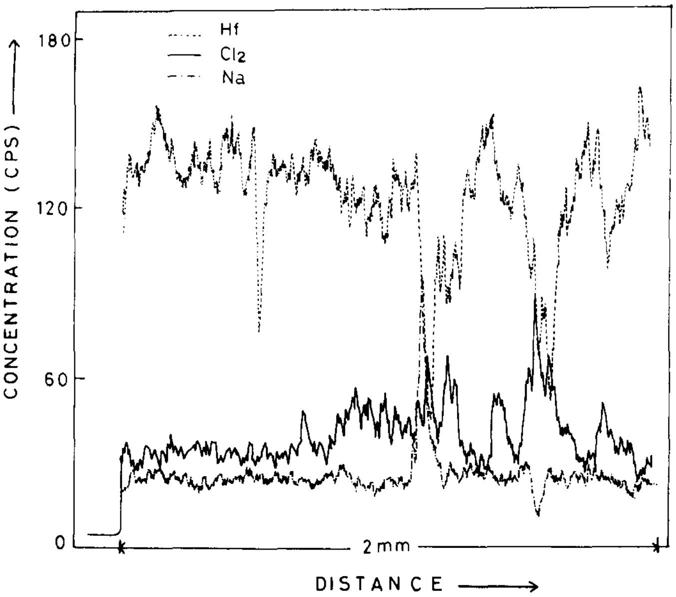


Fig. 9. EDAX concentration profiles of 1:1 NaCl–HfC reaction products oxidized at 1200 K.

TABLE 2

Different constituents identified in the reaction product by X-ray diffraction analysis

System	Molar ratio	Temp. (K)	Constituents identified
NaCl–Cr_7C_3	1:1	1200	Cr_2O_3, Cr_7C_3
NaCl–Fe_3C	1:1	1200	$NaFeO_2$, Fe_2O_3
NaCl–TiC	1:1	1200	TiO_2, $TiCl_2$, TiC
NaCl–ZrC	1:1	1200	ZrO_2, $ZrCl_3$, NaCl
NaCl–NbC	1:1	1200	Nb_2O_5, NaCl, $NaNbO_3$, NbC, $NbCl_2$
NaCl–TaC	1:1	1200	Ta_2O_5, NaCl, TaC, $NaTaO_3$, $TaCl_4$
NaCl–MoC	1:1	900	MoO_3, NaCl, MoC, Na_2MoO_4, $MoCl_2$
NaCl–WC	1:1	1000	WO_3, NaCl, Na_2WO_4, WCl_2
NaCl–VC	1:1	900	NaCl, VC, VCl
NaCl–HfC	1:1	1200	HfO_2, HfC

Considering the interaction kinetics (1:1 molar ratio), there is a rapid initial weight loss (region I of the kinetic curves) followed invariably by a weight gain in all the systems. The expulsion of $CO_2/Cl_2(g)$ presumably accounts for the initial weight losses incurred during the interaction and is represented by the following general reaction:

$$MC + 2NaCl + 2O_2 \longrightarrow MO + Na_2O + CO_2 + Cl_2 \qquad (1)$$

If thermodynamic conditions permit then the Na_2O formed may dissolve metal oxide to give sodium metal oxide; the Cl_2 evolved may also react with metal oxide to form metal chloride. These reactions, in fact, seemed to be

TABLE 3

Molar ratios, reaction product and reacting mixture weights, soluble metal concentrations and reaction temperatures

System	Molar ratio	Weight of the reaction product (g)	Theoretical wt. of the reaction mixture (g)		Conc. of soluble metal (ppm wt.)	Temperature (K)
			NaCl	Metal carbide		
NaCl–Cr_7C_3	1:2	0.718	0.048	0.670	2049	1200
	1:1	0.362	0.045	0.317	554.7	
	2:1	0.375	0.084	0.291	5840	
NaCl–VC	1:2	0.625	0.198	0.427	15344	900
	1:1	0.431	0.207	0.224	24336	
	2:1	0.729	0.474	0.255	15399	
NaCl–MoC	1:2	0.942	0.200	0.742	104579	900
	1:1	0.440	0.154	0.286	106375	
	2:1	0.715	0.371	0.344	98066	

responsible for the weight gains observed during the course of reaction (region II of the kinetic curves) and are represented in general as follows:

$$MO + Na_2O \longrightarrow Na_2O \cdot MO \tag{2}$$

$$MO + 1/2Cl_2 \longrightarrow MCl + 1/2O_2 \tag{3}$$

The evidence for the formation of the above mentioned reaction products is inferred from the following results: (i) identification of CO_2 and Cl_2 by IR gas analyser; (ii) identification of solid reaction products by X-ray diffraction analysis and energy dispersive X-ray analysis. The metallographic and SEM studies carried out on the mounted reaction products also indicate the presence of multiphase structures.

The weight gain is continuous in some of the systems but some weight loss is also expected due to vaporization of volatile metal chlorides; overall change in total weight is a weight gain.

In some systems there is a sudden interruption in weight gain curves (region II of the kinetic curves) and a continuous weight loss is observed (region III of the kinetic curves) until a steady state is achieved; the vaporization of volatile chlorides undoubtedly seemed the prime cause of weight losses observed in the kinetic curves. High vapour pressure for most of the chlorides formed during the interaction supports the above explanation (Table 4).

In general, the expulsion of CO_2 and Cl_2 gases seems responsible for the initial weight losses as shown by the kinetic curves (region I). The weight gains which are immediately followed by the initial weight losses as shown by the kinetic curves (region II) are due to the formation of sodium metal oxide and metallic chlorides. The weight losses incurred following weight gains in some cases (region III of the kinetic curves) are accounted for by the vaporization of volatile chlorides.

From the total weight change *vs.* mole fraction of NaCl plots it is inferred that all the systems show a decrease in total weight gain values with increasing concentrations of NaCl in NaCl–carbide mixture. Obviously, increasing amount of NaCl in the mixture promotes enhanced formation of CO_2/Cl_2 gases and volatile chlorides, resulting in a net weight loss during the oxidation run.

From the available solubility data there is ample evidence of the formation of water soluble metal-containing species in the solid reaction products. The metal species present in the solution are either in the form of metal chloride and/or in the form of MO_2^{2-}, MO_2^{-} or MO_4^{2-}.

On interaction with molten NaCl the transition metal carbides are decomposed into respective metal oxides with simultaneous evolution of CO_2 and Cl_2. The surface of the reaction mixture is the region of high oxygen activity and formation of sodium metal oxide is therefore the predominant reaction. The regions beneath the surface layers have relatively low oxygen activity or higher chlorine activity, thus favouring the formation of chloride(s).

In regions where the formation of metal chlorides is favoured, two cases are to be considered: (i) due to the high vapour pressure of volatile metal chloride the chloride vapours exert sufficient pressure in the outer layer and

TABLE 4

Thermodynamic data (K) for the chlorides [12–13][a]

Chloride	Temp. at which vapour pressure is 760 mm	M.p.	B.p.
$CrCl_2$	–	1088	1577
$CrCl_3$	–	1220 S	–
$FeCl_2$	1299	950	1285
$FeCl_3$	592	576	592
$TiCl_2$	–	1290 S	–
$TiCl_3$	–	1200 D	–
$TiCl_4$	409	249	410
$ZrCl_2$	–	1000	–
$ZrCl_3$	–	900	1000 D
$ZrCl_4$	604 S	710	–
$NbCl_5$	–	483	519
$TaCl_2$	–	1210	1650
$TaCl_3$	–	1300	1620
$TaCl_4$	–	570	1050
$TaCl_5$	–	494	507
$MoCl_2$	–	1000	1700
$MoCl_3$	–	1300 S	–
$MoCl_4$	–	595 S	–
$MoCl_5$	–	467	540
$MoCl_6$	–	630 S	–
WCl_2	–	900 D	–
WCl_4	–	600	606
WCl_5	–	509	549
WCl_6	–	548	610
VCl_2	–	1300	–
VCl_3	–	1000 D	–
VCl_4	–	–	437
$HfCl_4$	–	590 S	–
NaCl	1338	1073	1659

[a] S = sublimes; D = decomposes.

are deposited or condensed at the surface. The deposited chloride at the surface–O_2 interface is either volatilized off or oxidized, forming oxide and Cl_2(g). The O_2(g)/and or Cl_2(g) from the surface may penetrate into the underneath layers producing oxidation or chlorination reactions. This provides a porous structure in which the outer surface layer should contain oxide and Na–metal oxide in predominant concentrations and the underneath layers are relatively rich in chloride(s). Any residual chloride and/or carbide also forms the part of the multiphase structure. (ii) In the case of non-volatile chlorides, the metal chlorides have relatively low vapour pressures and are therefore mostly retained in the lower layers.

The microstructural features of the reaction products containing non-volatile chlorides are expected to be slightly different from those containing volatile chlorides. In the former the multiphase structure should be relatively non-porous, with a much higher chloride content in the lower layers. A schematic diagram representing the formation of different constituents in the NaCl-metal carbide reaction products is given in Fig. 10.

The optical and scanning photomicrographs show the presence of a multiphase structure in which each constituent, *e.g.* metal oxide, metal chloride, sodium metal oxide, NaCl or metal carbide, forms a separate phase.

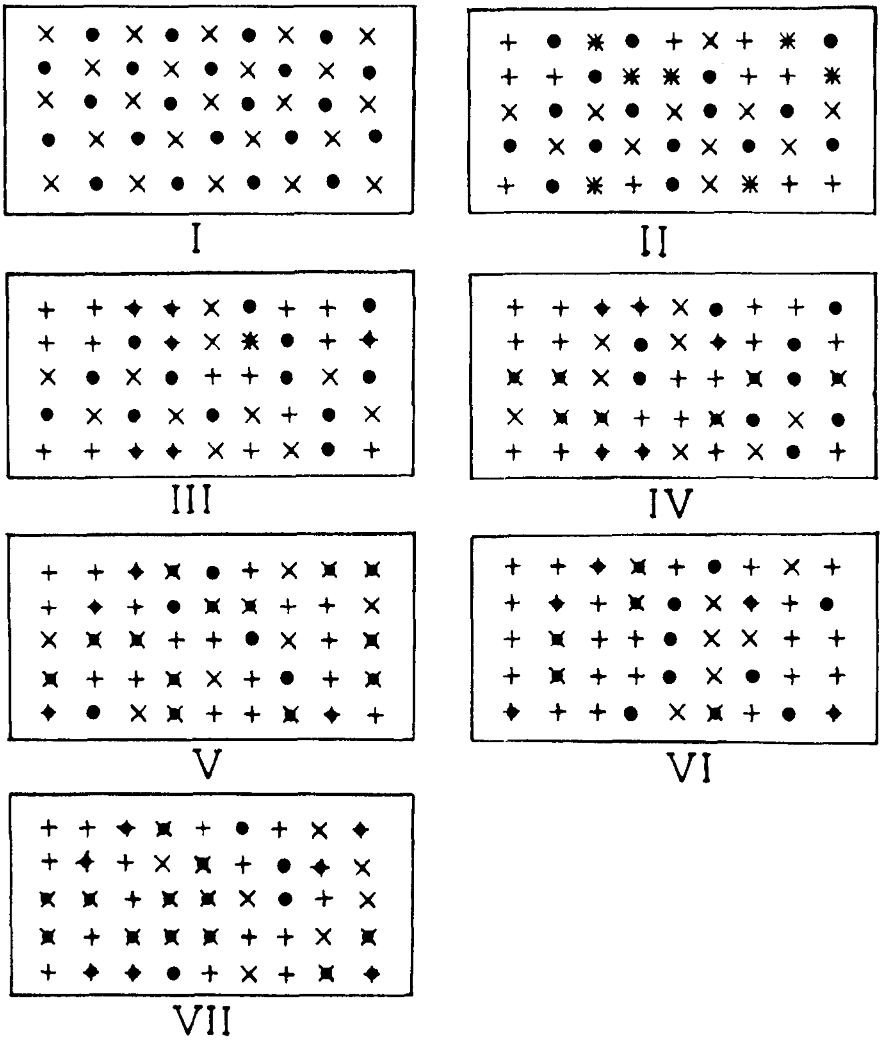


Fig. 10. Schematic diagram showing different species formed during the interaction of NaCl with metal carbide. I, NaCl-carbide composite; II, formation of metal oxide and Na_2O; III, formation of Na_2O M_2O_x; IV, formation of MCl_x in the underneath layers; V, accumulation of MCl_x at the surface/oxygen interface (if chloride is volatile); VI, conversion of chlorides into oxides (if chloride is volatile); VII, chloride enriched underneath layers (if chloride is non volatile). ●, carbide; ×, NaCl; *, Na_2O; +, metal oxide; ✦, Na_2O M_2O_x; ✖, MCl_x.

The EDAX concentration profiles of the reaction products support the existence of metal chloride and sodium metal oxide.

5. Conclusions

(i) With a few exceptions, the high temperature interaction of transition metal carbide and NaCl in $O_2(g)$ results in a rapid initial weight loss followed by gradual weight gain.

(ii) On interaction with NaCl the transition metal carbides are decomposed into their respective metal oxides, with simultaneous evolution of CO_2 and Cl_2. The surface of the reaction mixture is the region of high oxygen activity and formation of sodium metal oxide is therefore the predominant reaction. The regions beneath the surface layers have relatively low oxygen activity or high chlorine activity and thus favour the formation of chloride(s).

(iii) The microstructural features of the reaction product containing volatile chloride are different from that containing non-volatile chloride. In the latter, the multiphase structure is relatively non-porous, with much higher chloride contents in the lower layers, whereas in the former, a porous structure is present in which outer layers contain oxide and sodium metal oxide in predominant concentrations.

Acknowledgment

The financial assistance from Council for Scientific and Industrial Research, New Delhi is gratefully acknowledged by the authors.

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