Studies on the interactions of metal oxides and Na_2SO_4 at 1100 and 1200 K in oxygen

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Abstract. The interaction of different metal oxides such as Co_3O_4 , NiO , Al_2O_3 , Cr_2O_3 , Fe_2O_3 and SiO_2 with Na_2SO_4 at a temperature of 1100 and 1200 K in flowing oxygen has been studied. The thermogravimetric studies for each system were carried out as a function of Na_2SO_4 in the mixture. The presence of different constituents in the reaction products were identified by X-ray diffraction analysis and the morphologies of the reaction products were characterized using metallography and scanning electron microscopy (SEM). The formation of products was also investigated by thermodynamic computation of free energies of the reactions and the study of relevant equilibrium phase diagrams. The soluble species in the aqueous solutions of the reaction products were determined quantitatively using atomic absorption spectrophotometry.

The high temperature interaction products usually contain a 3-phase structure namely, $\text{Na}_2\text{O} \cdot \text{M}_2\text{O}_x$, M_2O_x and metal sulphide and/or metal sulphate. The formation of $\text{Na}_2\text{O} \cdot \text{M}_2\text{O}_x$ depends upon the solid state solubility of metal oxide in the molten salt at high temperatures. Under limited solubility conditions $\text{Na}_2\text{O} \cdot \text{M}_2\text{O}_x$ is invariably formed, but as soon as this condition is relaxed the oxide, M_2O_x , precipitates and forms a separate phase.

Keywords. High temperature interactions; metal oxide solubility; thermogravimetric analysis; morphologies of the reaction products.

1. Introduction

The Fe-, Ni- or Co-base alloys have an excellent high temperature oxidation resistance. This is seriously affected when adhering Cr_2O_3 or Al_2O_3 protective scales are attacked by an electrolytic deposit. This electrolytic deposit (ash or ionic) reacts with normally protective oxide layers on the alloy and gives way to an accelerated corrosion attack, known as hot corrosion. In high temperature applications, based on fossil fuel energy generation or conversion, salt or ash containing environments often exist. The molten salt(s) deposit on the machinery components and initiate hot corrosion (Stringer 1977). During a hot corrosion attack, molten salts react with the metallic material(s) of construction in a processing plant such as fossil fuel power generating units and cause a depletion of the alloying elements required to form a protective oxide film on the surface of machine parts. A large number of publications are available dealing with the phenomenology of Na_2SO_4 -induced hot corrosion attack. But our knowledge regarding actual chemical reactions taking place in the propagation stages of hot corrosion attack, namely, between molten Na_2SO_4 and oxide scales (formed in the initial stages of attack), is rather limited. A review of literature on hot corrosion reveals that only the recent work carried out by Rapp and co-workers on the solubilities of metal oxides in molten Na_2SO_4 provide some information about metal oxide- Na_2SO_4 interaction at high temperatures

(Gupta and Rapp 1980; Misra *et al* 1982; Jose *et al* 1985; Zhang and Rapp 1985; Shi and Rapp 1986; Zhang 1986). The knowledge of the solubility of protective oxide, and its dependence on fused salt chemistry may aid in understanding the occurrence and importance of fluxing (dissolution) and thus in the interpretation of hot corrosion mechanism and in the development of new protective materials. Rapp (1986) presented a compilation of solubility data in fused Na_2SO_4 for the oxides of principal interest to high temperature alloys and coatings and emphasized the importance of local chemistry within a fused salt film. The results of a study of the high temperature interactions of metallic oxides with NaCl have recently been published (Mobin *et al* 1990). It has been found that $\text{Na}_2\text{O} \cdot \text{M}_2\text{O}_x$ and metal chlorides are usual reaction products. Information is also available on the high temperature interactions of metal carbides with Na_2SO_4 and NaCl (Mobin and Malik 1991, 1992). Formation of $\text{Na}_2\text{O} \cdot \text{M}_2\text{O}_x$ and metal sulphide in case of metal carbide- Na_2SO_4 and $\text{Na}_2\text{O} \cdot \text{M}_2\text{O}_x$ and metal chloride in case of metal carbide-NaCl has been confirmed.

The present paper describes the interaction of Na_2SO_4 with a number of metal oxides in oxygen at temperatures relevant to hot corrosion attack. Some of the oxides chosen are formed during the oxidation of industrial heat resistant alloys e.g. steel or Co- or Ni-base super alloys and these oxides are involved in hot corrosion reactions in presence of a salt.

2. Experimental

Co_3O_4 , NiO, Al_2O_3 , Cr_2O_3 , Fe_2O_3 and SiO_2 were all analytical reagent grade products. Analytical grade Na_2SO_4 was dried in an oven at 473 K for about 48 h. Dried and powdered Na_2SO_4 and the oxide (about 80 mesh size) were mixed separately in 1:2, 2:3, 1:1, 3:2, and 2:1 molar ratios and were compacted mechanically into tablets of 1.4 cm at a pressure of 10^7 kg m^{-2} .

The kinetics of reaction between Na_2SO_4 and metal oxide was studied by monitoring weight change as a function of time at 1100 and 1200 K in a stream of dry oxygen gas (purity 99.99%) using a hot stage Sartorius electronic microbalance. A 20 h oxidation run was adequate to provide reaction products under steady state, which was indicated by a 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, 3 silica boats, each containing compacts of the same ratio were placed in

Table 1. Etchants used in metallographic analysis.

System	Etchants
Co_3O_4 - Na_2SO_4	Aqueous sodium thiosulphate solution
NiO- Na_2SO_4	1% Dimethyl glyoxime in alcohol (ammonical solution)
Al_2O_3 - Na_2SO_4	Quinalizarin in pyridine and acetic acid
Cr_2O_3 - Na_2SO_4	Aqueous lead acetate solution
Fe_2O_3 - Na_2SO_4	Aqueous potassium ferrocyanide solution
SiO_2 - Na_2SO_4	Ammonium molybdate and benzidine

a horizontal furnace for oxidation under almost identical conditions. After completion of oxidation, the compacts were taken out and quenched in air and weighed. Out of the three samples, one was mounted for morphological studies (metallography) and scanning electron microscopy (SEM), the second for X-ray diffraction analysis and the third was retained for quantitative determination of soluble species.

Metallographic studies were carried out with a computerized Leitz photomicrographical microscope (Metallux 2). 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 paper followed by polishing with 6μ diamond paste using kerosene as the lapping liquid. Appropriate etchants (table 1) were used to identify the different phases in the microstructures.

The SEM studies were conducted using a JOEL electron microscope JSM 840. The X-ray diffraction studies were carried out using a Philips X-ray diffractometer (Model APD 1700) with Cu K_α or Mo K_α targets and appropriate filters. The concentration of metals in the aqueous solution of the reaction products for the system $\text{Na}_2\text{SO}_4\text{--Co}_3\text{O}_4$, $\text{Na}_2\text{SO}_4\text{--NiO}$, $\text{Na}_2\text{SO}_4\text{--Al}_2\text{O}_3$, $\text{Na}_2\text{SO}_4\text{--Cr}_2\text{O}_3$ and $\text{Na}_2\text{SO}_4\text{--Fe}_2\text{O}_3$ were determined with the help of a Varian atomic absorption spectrophotometer (Model AA 975). 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 Whatman filter paper. The filtrate (with appropriate dilution) was used to determine the concentration of metals in the solution.

Figure 1. Plots of weight loss vs time for 1:1 (molar ratio) Na_2SO_4 metal oxide systems.

3. Results

3.1 Thermogravimetric studies

3.1a *Reaction kinetics:* Weight loss vs time plots obtained during the reaction of 1:1 mixture of metal oxides and Na_2SO_4 in oxygen at 1200 K are shown in figure 1. In general, all systems show an initial weight loss up to a period of about 4 h with no further weight loss on exposure to oxygen.

Figure 2. Plots of total weight loss vs mole fraction of Na_2SO_4 for different Na_2SO_4 -metal oxide systems.

3.1b Influence of salt: Figure 2 shows plots of percent total weight loss at steady state vs mole fraction of Na_2SO_4 in the mixture of Na_2SO_4 and metal oxide. The total weight loss represents the final reading recorded after heating for 20 h, a mixture of Na_2SO_4 and metal oxide of known composition in flowing oxygen at 1100 K and 1200 K. No further change in weight was observed after 20 h.

A study of weight loss vs mole fraction of Na_2SO_4 plots indicates three types of behaviour. The first, shows a minima in the weight loss curves. Examples of such behaviour are systems $\text{NiO}-\text{Na}_2\text{SO}_4$ (1200 K), $\text{Al}_2\text{O}_3-\text{Na}_2\text{SO}_4$ (1200 K), $\text{Cr}_2\text{O}_3-\text{Na}_2\text{SO}_4$ (1200 K), $\text{Fe}_2\text{O}_3-\text{Na}_2\text{SO}_4$ (1100 and 1200 K) and $\text{SiO}_2-\text{Na}_2\text{SO}_4$ (1100 and 1200 K). The second, shows a maxima in the weight loss curves: $\text{Co}_3\text{O}_4-\text{Na}_2\text{SO}_4$ (1100 and 1200 K) and $\text{Al}_2\text{O}_3-\text{Na}_2\text{SO}_4$ (1100 K). Lastly, the third type, shows no significant change in total weight loss on varying Na_2SO_4 concentration in the reaction mixture: $\text{NiO}-\text{Na}_2\text{SO}_4$ (1100 K) and $\text{Cr}_2\text{O}_3-\text{Na}_2\text{SO}_4$ (1100 K).

Figure 3. (a) Optical photomicrograph of the reaction product of the 1:2 $\text{Na}_2\text{SO}_4-\text{Co}_3\text{O}_4$ system, oxidized at 1100 K, and (b) scanning electron micrograph of the reaction product of the 2:3 $\text{Na}_2\text{SO}_4-\text{Co}_3\text{O}_4$ system, oxidized at 1100 K.

3.1c Morphology of the reaction products: Figures 3–8 show some representative photomicrographs of mounted reaction products. The microscopic appearance of the multiphase structure, comprising of different shades of grey, shows the presence of different compounds in the reaction products. In general, an oxide or Na_2SO_4 appears as whitish grey, flocculent mixed oxide ($\text{Na}_2\text{O} \cdot \text{M}_2\text{O}_x$) as grey and metal sulphide/sulphate as dark grey. Table 2 lists the various constituents as identified in the reaction products of 2:1 and 1:2 molar ratio of metal oxide and Na_2SO_4 at 1100 and 1200 K by X-ray diffraction analysis.

3.1d Estimation of soluble metal species: The concentration of water-soluble metal species in the reaction products of metal oxide and Na_2SO_4 was determined as a function of Na_2SO_4 in the reaction mixture. Figure 9 shows plots of the concentration of soluble metal vs mole fraction of Na_2SO_4 in the reaction product mixture of

Figure 4. (a) Scanning electron micrograph of the reaction product of the 1:2 Na_2SO_4 –NiO system, oxidized at 1100 K and (b) optical photomicrograph of the reaction product of the 1:1 Na_2SO_4 –NiO system, oxidized at 1200 K.

Figure 5. Scanning electron micrograph of the reaction product of the 2:1 Na_2SO_4 - Al_2O_3 system, oxidized at 1100 K.

Figure 6. Scanning electron micrograph of the reaction product of the 1:1 Na_2SO_4 - Cr_2O_3 system, oxidized at 1200 K.

Na_2SO_4 at 1200 K. Two types of behaviour were noted. The systems Co_3O_4 - Na_2SO_4 , Cr_2O_3 - Na_2SO_4 and Fe_2O_3 - Na_2SO_4 show an increase in the solubility with increasing Na_2SO_4 concentration whereas the systems NiO - Na_2SO_4 and Al_2O_3 - Na_2SO_4 show a maximum at 0.5 mole fraction of Na_2SO_4 .

3.1e Na-M-S-O equilibrium phase diagrams: Since both oxygen and sulphur participate in the reaction between metal oxides and Na_2SO_4 , it is useful to employ Pourbaix type phase stability diagrams using $\log P_{\text{O}_2}$ vs $\log a_{\text{Na}_2\text{O}}$ (or P_{SO_2}) coordinates. The phase stability diagrams are analogous to Pourbaix diagrams of E vs pH for aqueous solutions. The redox potential ($\log P_{\text{O}_2}$ or E_{O_2} ; O^{2-}) can also be plotted against negative of salt basicity ($-\log a_{\text{Na}_2\text{O}}$ or pH) which is shown as a typical example in Na-Al-S-O phase stability diagram (figure 14). The phase stability diagrams

Figure 7. Scanning electron micrograph of the reaction product of the 3:2 $\text{Na}_2\text{SO}_4\text{-Fe}_2\text{O}_3$ system, oxidized at 1100 K.

Figure 8. Optical photomicrograph of the reaction product of the 3:2 $\text{Na}_2\text{SO}_4\text{-SiO}_2$ system, oxidized at 1200 K.

for the systems Na-Co-S-O, Na-Ni-S-O (Gupta and Rapp 1980), Na-Al-S-O (Jose *et al* 1985), Na-Cr-S-O (Zhang 1986), Na-Fe-S-O (Zhang and Rapp 1985) and Na-Si-S-O (Shi and Rapp 1986) were constructed by superimposing Na-S-O diagrams on respective M-S-O diagrams and are reproduced in figures 10–15. Such representation ignores interaction between the two ternary subsystems and is an approximation. The quaternary compounds that may be presented are ignored. The dashed lines in the phase diagram indicate constant activities (10^{-2} , 10^{-4} , 10^{-6}) for the acidic and basic salts in equilibrium with metal oxide and liquid Na_2SO_4 . The solubility of the oxide MO or M_2O_3 as a function of $a_{\text{Na}_2\text{O}}$ can be related to the phase diagram for MO or M_2O_3 (i.e. Na-M-O-S). For example, in Na-Ni-O-S system (figure 10), the vertical line indicates a non dependence of P_{O_2} for the acidic dissolution

Table 2. X-ray identification of the constituents present in the reaction products.

System	Molar ratio	Temperature (°K)	Constituents identified
$\text{Co}_3\text{O}_4\text{--Na}_2\text{SO}_4$	2:1	1100 K	$\text{Co}_3\text{O}_4, \text{Na}_2\text{SO}_4$
	1:2		$\text{Co}_3\text{O}_4, \text{Na}_2\text{SO}_4$
	2:1	1200 K	$\text{Co}_3\text{O}_4, \text{CoS}, \text{Co}_3\text{S}_4, \text{CoSO}_4$
	1:2		$\text{Co}_3\text{O}_4, \text{CoS}, \text{Co}_3\text{S}_4, \text{Na}_2\text{SO}_4$
$\text{NiO--Na}_2\text{SO}_4$	2:1	1100 K	$\text{NiS}, \text{NiO}, \text{NaNiO}_2, \text{Na}_2\text{SO}_4$
	1:2		$\text{NiS}, \text{NiO}, \text{NaNiO}_2, \text{Na}_2\text{SO}_4$
	2:1	1200 K	$\text{NaNiO}_2, \text{Na}_2\text{S}, \text{NiS}, \text{NiSO}_4$
	1:2		$\text{NiS}, \text{NiS}_2, \text{Na}_2\text{SO}_4, \text{NaNiO}_2$
$\text{Al}_2\text{O}_3\text{--Na}_2\text{SO}_4$	2:1	1100 K	$\text{Na}_2\text{SO}_4, \text{NaAlO}_2, \text{Na}_2\text{S}$
	1:2		$\text{Na}_2\text{SO}_4, \text{NaAlO}_2, \text{Na}_2\text{S}$
	2:1	1200 K	$\text{Na}_2\text{SO}_4, \text{NaAlO}_2, \text{Al}_2(\text{SO}_4)_3$
	1:2		$\text{Na}_2\text{SO}_4, \text{NaAlO}_2$
$\text{Cr}_2\text{O}_3\text{--Na}_2\text{SO}_4$	2:1	1100 K	$\text{Cr}_2\text{O}_3, \text{Na}_2\text{CrO}_4$
	1:2		$\text{CrS}, \text{Cr}_2\text{O}_3, \text{Na}_2\text{CrO}_4$
	2:1	1200 K	$\text{Cr}_2\text{O}_3, \text{Na}_2\text{CrO}_4, \text{CrS}$
	1:2		$\text{CrS}, \text{Cr}_2\text{O}_3, \text{Na}_2\text{CrO}_4$
$\text{Fe}_2\text{O}_3\text{--Na}_2\text{SO}_4$	2:1	1100 K	$\text{Na}_2\text{SO}_4, \text{FeS}$
	1:2		$\text{FeS}, \text{Fe}_2\text{O}_3, \text{Na}_2\text{SO}_4$
	2:1	1200 K	$\text{FeS}, \text{NaFeO}_2, \text{Fe}_2\text{O}_3, \text{Fe}_2(\text{SO}_4)_3$
	1:2		$\text{FeS}, \text{NaFeO}_2, \text{Fe}_2(\text{SO}_4)_3$
$\text{SiO}_2\text{--Na}_2\text{SO}_4$	2:1	1100 K	$\text{SiS}_2, \text{Na}_2\text{SO}_4, \text{SiO}_2, \text{Na}_2\text{SiO}_3$
	1:2		$\text{SiS}_2, \text{Na}_2\text{SO}_4, \text{SiO}_2, \text{Na}_2\text{SiO}_3$
	2:1	1200 K	$\text{SiS}_2, \text{Na}_2\text{SO}_4, \text{SiO}_2, \text{Na}_2\text{SiO}_3$
	1:2		$\text{SiS}_2, \text{Na}_2\text{SO}_4, \text{SiO}_2, \text{Na}_2\text{SiO}_3$

of NiO since nickel valence is not changed upon dissolution:

$$\left[\frac{\partial(\log a_{\text{NiSO}_4})}{\partial(-\log a_{\text{Na}_2\text{O}})} \right] = 1. \quad (2)$$

However, under conditions of basic dissolution ($-\log a_{\text{Na}_2\text{O}} \leq 10$) of NiO in molten Na_2SO_4 , the solubility can be represented by the following two reactions depending upon P_{O_2} .

(i) $\log P_{\text{O}_2} \leq -6$

The vertical line shows non dependence of oxygen and there is no change in nickel valence.

(ii) $\log P_{\text{O}_2} \geq -6$

Figure 9. Plots of the metal concentration in the aqueous solution of the reaction mixtures vs mole fraction of Na_2SO_4 for the different Na_2SO_4 -metal oxide systems.

where

$$\left[\frac{\partial(\log a_{\text{NaNiO}_2})}{\partial(\log a_{\text{Na}_2\text{O}})} \right]_{\text{O}_2} = -\frac{1}{2}, \quad (5)$$

$$\left[\frac{\partial(\log a_{\text{NaNiO}_2})}{\partial(\log P_{\text{O}_2})} \right]_{a_{\text{Na}_2\text{O}}} = \frac{1}{4}. \quad (6)$$

Thus the change in slope indicates dependence of oxygen upon basic dissolution of NiO , when it dissolves as nicklate ion, NiO_2^- with trivalent nickel.

Using pertinent thermodynamic data available in literature, the behaviour of metal oxide-fused salt systems may be described in terms of the phase stability diagrams.

4. Discussion

The interaction of Na_2SO_4 with metal oxides at higher temperature results in weight losses. The total weight loss at steady state was measured. Steady state is indicated when there is no further loss in weight with increasing exposure time.

Considering the interaction kinetics (1:1 molar ratio), there is initial weight loss up to a period of 2–4 h for all the systems. This is presumably due to the thermal decomposition of salts to Na_2O , and subsequent expulsion of $\text{SO}_2/\text{SO}_3(g)$ and some volatile compounds—in certain cases—formed during the interactions. This is represented by

Figures 10 and 11.

Figures 12 and 13.

Figures 10–15. 10–14. Phase stability diagrams for the systems Na–Ni–S–O, Na–Co–S–O, Na–Cr–S–O, Na–Fe–S–O and Na–Al–S–O, respectively at 1200 K and 15. phase stability diagram for the system Na–Si–S–O at 1173 K.

the following general reactions (Rapp 1986).

If the thermodynamic conditions permit then the Na_2O formed may dissolve metal oxide to give sodium metal oxide, and sulphur oxide gases may react with metal oxide to form metal sulphide and/or metal sulphate. This can be represented by following

general reactions:

The free energy minimization calculations show that in general, reactions (9) and (11) are possible, reaction (10) can undergo under conditions of low P_{O_2} and low basicity in all the systems under study.

The evidence for the formation of the above mentioned reaction products is inferred from the following results: (i) Identification of S-oxide gases by IR gas analyser and (ii) identification of solid reaction products by XRD. The metallographic and SEM studies carried out on the mounted reaction products also indicate the presence of multiphase structure.

From the weight loss vs mole fraction of Na_2SO_4 plots it is inferred that a decrease in the weight loss value with increasing Na_2SO_4 concentration is because of the binding of sulphur in the form of metal sulphide or metal sulphate. Further, an increase in the weight loss value with increasing concentrations of Na_2SO_4 is because of the release of SO_2/SO_3 (g) and volatility of reaction products in certain cases. In the systems where no significant change in weight loss on varying Na_2SO_4 is observed, the absence of complete interaction between Na_2SO_4 and metal oxide at the experimental temperature could be attributed. The initial weight loss in each case is due to the expulsion of SO_2/SO_3 during the overall reaction between Na_2SO_4 and metal oxide. The formation of Na_2SiO_3 , and subsequent evolution of SO_3 has been reported from a reaction between Na_2SO_4 and SiO_2 at 850°C (Halle and Stern 1980).

The standard free energy values for some of the reactions at 1200 K, as computed from the available data, indicate that most of the proposed reactions are thermodynamically feasible at this temperature (table 3) (Kubaschewski *et al* 1967; JANAF Thermochemical tables 1971; Knacke 1973).

From the available solubility data there is ample evidence of the formation of water soluble metal containing species in the reaction products. The metal species present in the solutions are in the form of MO_2^- or MO_4^{2-} . In case of CO_3O_4 , Cr_2O_3 and Fe_2O_3 , fluxing reaction continue with increasing Na_2SO_4 concentration. However, in case of NiO and Al_2O_3 fluxing reaction terminates at ~ 0.5 mole fraction of Na_2SO_4 in the

Table 3. Standard free energy of the reaction, G° at 1200 K*.

Reaction	$G^\circ(\text{Kcal mol}^{-1})$
$\text{Na}_2\text{O}(\text{s}) + 2\text{NiO}(\text{s}) + \frac{1}{2}\text{O}_2 \rightarrow 2\text{NaNiO}_2$	-1.14
$3\text{Na}_2\text{O}(\text{s}) + 2\text{Co}_3\text{O}_4(\text{s}) + \frac{1}{2}\text{O}_2 \rightarrow 6\text{NaCoO}_2$	-7.59
$2\text{Na}_2\text{O}(\text{s}) + \text{Cr}_2\text{O}_3(\text{s}) + \frac{3}{2}\text{O}_2 \rightarrow 2\text{Na}_2\text{CrO}_4$	-4.52
$\text{Na}_2\text{O}(\text{s}) + \text{Al}_2\text{O}_3(\text{s}) \rightarrow 2\text{NaAlO}_2$	-1.84
$\text{Na}_2\text{O}(\text{s}) + \text{Fe}_2\text{O}_3(\text{s}) \rightarrow 2\text{NaFeO}_2$	-5.37
$\text{NiO} + \text{SO}_3 \rightarrow \text{NiSO}_4$	-0.10
$\text{Co}_3\text{O}_4 + 3\text{SO}_3 \rightarrow 3\text{CoSO}_4 + \frac{1}{2}\text{O}_2$	-1.18
$\text{Fe}_2\text{O}_3 + 3\text{SO}_3 \rightarrow \text{Fe}_2(\text{SO}_4)_3$	-21.1

*Values calculated from the thermodynamic data available from JANAF Thermochemical Tables (1971), Knacke (1973) and Kubaschewski *et al* (1967).

mixture, this may be attributed to the precipitation of oxide on enhancing the amount of Na_2SO_4 . Referring to phase stability diagrams in pure oxygen atmosphere ($\log P_{\text{O}_2} = 0$): NaCoO_2 , NaNiO_2 , NaAlO_2 , Na_2CrO_4 , NaFeO_2 and Na_2SiO_3 are the predominant stable species at higher Na_2SO_4 concentrations; and CoSO_4 , NiSO_4 , $\text{Al}_2(\text{SO}_4)_3$, $\text{Cr}_2(\text{SO}_4)_3$ and $\text{Fe}_2(\text{SO}_4)_3$ are the predominant stable species at lower Na_2SO_4 concentration. In the present studies, evidence of the formation of most of these species, as indicated by phase stability diagrams, has been obtained by XRD.

The optical and scanning micrographs show the presence of a multiphase structure in which each constituent, e.g. metal oxide, sodium metal oxide, Na_2SO_4 , metal sulphide or metal sulphate, forms a separate phase.

5. Conclusion

(I) The high temperature interactions of metal oxide and Na_2SO_4 in $\text{O}_2(g)$ result in weight losses indicating the expulsion of S-oxide gases and/or vapourization of some volatile compounds.

(II) During the interaction, sodium metal oxide ($\text{Na}_2\text{O} \cdot \text{MO}$) and metal sulphide and/or metal sulphate are usual reaction products.

(III) Determination of soluble metal species in the reaction product indicates the presence of water soluble species CoO_2^- , NiO_2^- , CrO_4^{--} , AlO_2^- , and FeO_2^- in the respective metal oxide– Na_2SO_4 systems.

(IV) The constituents in the reaction products appear in the form of discrete and distinct phases in the optical and scanning micrographs.

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