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Chemical Interaction of Ferric Oxide with Sodium Sulfate at High Temperature Relevant to Hot corrosion

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Abstract

The studies include the results and discussion related with reaction of Fe_2O_3 with Na_2SO_4 in presence of SO_2 (g) at 800 and 900 °C. The iron oxides are produced by the oxidation of iron base alloys in many industrial operations. The metal oxide undergoes certain high temperature chemical reactions in presence of a gas (such as SO_2) and molten salts (say Na_2SO_4). The thermo-gravimetric studies had been carried out as a function of variation in Na_2SO_4 concentration in the mixture. The reaction products were identified by XRD analysis. Surface morphologies of the products are discussed on the basis of metallographic and scanning electron microscopic (SEM) studies.

Key Words: High Temperature, hot corrosion, iron oxide, sodium sulfate, XRD, SEM.

1. Introduction

Low-alloy steels are used for non-heated exit areas in super heater tubes and re-heater tubes as part of boiler components. The external surface of these tubes are exposed to air at temperatures between 500°C – 600°C, which leads to a thickness loss of the tubes as a consequence of oxide formation [1-3]. The effect of sodium sulphate coatings on the oxidation behavior of pure iron and iron-5% chromium in oxygen at 1 atm. pressure has been investigated using a conventional thermo-balance technique. The oxidation kinetics and the scale morphology of pure iron were relatively unaffected by the presence of Na_2SO_4, whereas Fe-5Cr was found to undergo an initial enhanced oxidation [4].The high temperature oxidation resistance of alloys depends on the formation of a protective and adherent oxide layer on the metal surface. The oxides are generally formed by oxidation at high temperature of the corresponding elements initially present in the alloy. A wide variety of electrolytic deposits is known to cause hot corrosion, Na_2SO_4 has been found to play a vital role in actual engineering operations. Because of its high thermodynamic stability in the mutual presence of sodium and sulfur impurities in an oxidizing gas, Na_2SO_4 is often found to be dominant salt in the deposit.

Many references are available dealing with the mechanism of Na_2SO_4-iduced hot corrosion attack [5-8]. The work related to the chemical reactions taking place between molten Na_2SO_4 and the oxide scales, which are usually present in the outer surface of metal, is reported very few. One of the factors that affect the oxidation resistance of protective oxide scales is their solubility in molten Na_2SO_4 [9,10]. The dissolution behavior of metal oxide is important in explaining the electro-chemical mechanism of hot corrosion in which soluble metal species are involved. The results of study of the high temperature interaction of some transition and non-transition metal oxides with Na_2SO_4 in oxygen have been published [11-13]. The work was carried out in pure O_2 (g) atmosphere and the influence of SO_2/SO_3 partial pressure on the reaction product was not considered.

The paper contains the results of the studies concerning with reaction of iron oxide and Na_2SO_4 in flowing SO_2(g) in the temperature range of 800 and 900 °C where hot corrosion reactions usually show optimization. In the present investigation, studies have been carried out taking into consideration the effect of SO_2 gas partial pressure.

2. Experimental

2.1. Chemicals used

Fe_2O_3 was analytical reagent grade BDH products. Analytical grade Na_2SO_4 and iron oxide of about 80 mesh size were dried in an oven at 200ºC for about 48 hours.

2.2. Preparation of the specimens

Dried and powdered Na_2SO_4 and iron oxide were mixed in 1:2, 2:3, 1:1, 3:2 and 2:1 molar ratios of Na_2SO_4 and oxide and were put in a die (diameter 1.4 cm) and pressed into compact tablets using a hydraulic press.

2.3. Solid State Reaction Kinetics

The kinetics of the reaction between Na_2SO_4 and metal oxide was studied by monitoring weight change as a function of time at 800 and 900 °C in SO_2 gas environment using 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 negligible change in weight for a considerable period of exposure time.

Two silica boats, each containing compacts of the same ratio were placed in a horizontal tubular furnace for oxidation under almost identical conditions. After completion of the oxidation, the compacts were taken out and quenched in air and weighed. One sample was mounted for morphological studies (XRD, metallographic and SEM) and the second for qualitative chemical and oxidation analysis.

2.4. X-ray diffraction studies

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

2.5. Metallographic studies

Metallographic studies were carried out on a computerized Leitz photometallurgical 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 specimens were ground on 600 grit Silicon Carbide paper followed by polishing with 6μ diamond paste using kerosene as the lapping liquid. Appropriate etchant aqueous ferro-cyanide solution was used to identify the different phases in the microstructures in the metallographic studies.

2.6. 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.

3. Results and discussion

3.1. Thermo gravimetric studies

3.1.1. Reaction kinetics

Figure 1 represents the total percent weight change versus time plots obtained during the reaction of 1:1 mixture of iron oxide and Na_2SO_4 at 800 and 900 °C. The salient features of the results from reaction kinetics for the metal oxide-Na_2SO_4 system are given as follows.

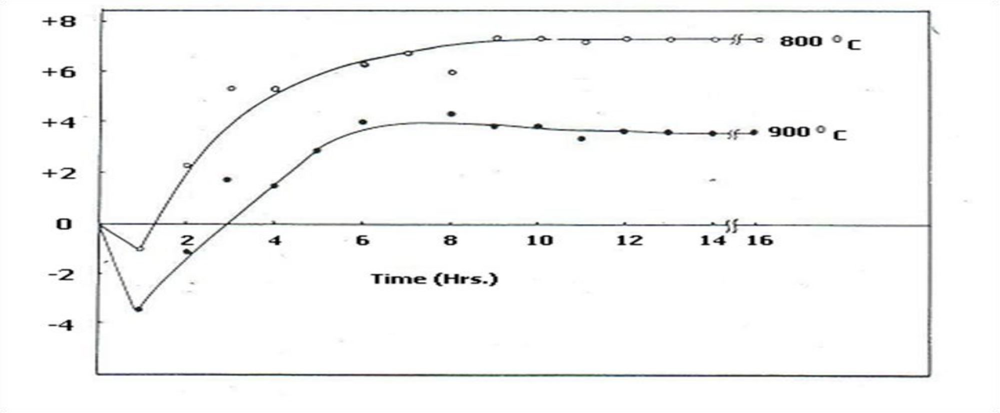

Figure – 1: Plots of total percent weight change vs time for Fe_2O_3-Na_2SO_4 system (molar ratio 1:1) at 800 and 900 °C.

At 800 °C, after an initial weight loss, the system shows a rapid gain in weight up to 9 hours. No further change in weight was observed after time period extending 9 hours. At 900 °C, after an initial weight loss during the early period of interaction, there was an increase in weight gain values up to 8 hours with no further change in weight up to 20 hours. The net weight change was weight gain at both 800 and 900 °C.

3.1.2. Influence of salt

Figure 2 shows plots of percent total weight change at steady state versus mole fraction of Na_2SO_4 in the mixture of Na_2SO_4: iron oxide. The total weight change represents the final reading recorded after heating for 20 hours, a mixture of Na_2SO_4 and iron oxide of known composition in SO_2 (g) at 800 and 900 °C. No further change in weight was observed after 20 hours. The results of the study of weight change versus mole fraction of Na_2SO_4 for metal oxide- Na_2SO_4 system can be generalized as follows.

The reaction of Fe_2O_3 with Na_2SO_4 at 800 and 900°C resulted in net weight loss at lower concentration of Na_2SO_4. There was a decrease in weight loss (or increase in weight gain) values with increasing Na_2SO_4 till a maximum was noticed followed by a decrease in the weight gain values on further addition of Na_2SO_4.

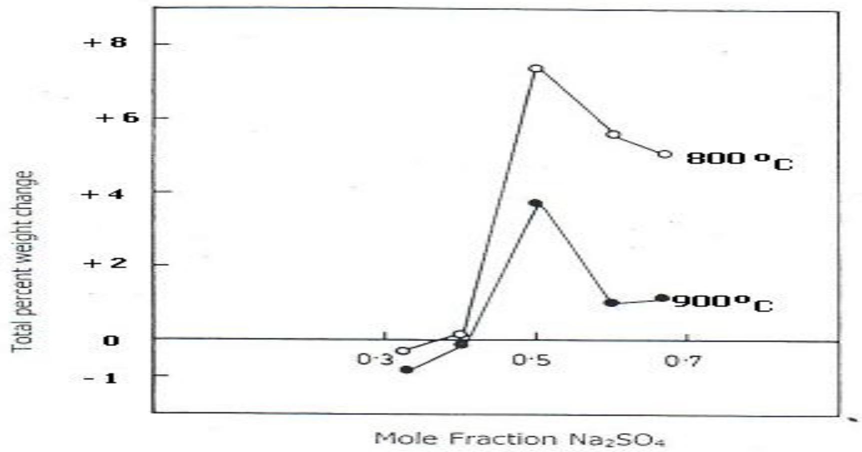

Figure-2: Plots of total percent weight change vs mole fraction of Na_2SO_4 for Fe_2O_3-Na_2SO_4 system at 800 and 900 °C.

3.1.3. X-ray Diffraction Analysis

Table 1 lists the different constituents as identified in the reaction products of metal oxides and Na_2SO_4 at 800 and 900 °C by X-ray diffraction analysis.

3.1.4. Metallographic and SEM Studies

Figure 3 shows some photomicrographs of mounted reaction products. The salient features of the results from metallographic studies for the iron oxide- Na_2SO_4 systems are generalized as follows:

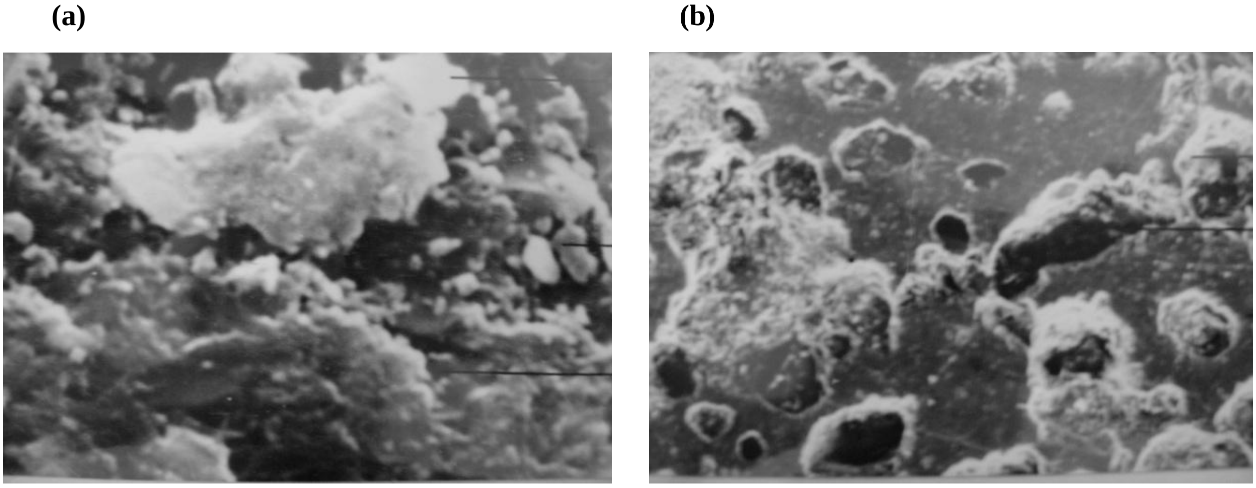

Figure 3- SEM picture of the reaction products of Fe_2O_3-Na_2SO_4 system (molar ratio 1:1), oxidized at (a) 800 °C (1000x) (b) 900 °C (1000x)

At 800 and 900 °C, the presence of multiphase structure comprising of FeS (dark grey), Na_2SO_4 (whitish grey) and $NaFeO_2$ (light grey) was indicate by the photomicrographs. A very dark grey presumably represented $Fe_2(SO_4)_3$ which was admixed with light grey constituent $NaFeO_2$ (Figure 3a). The micrograph also showed dispersion of white phase, which was presumably, Fe_2O_3 precipitated from $NaFeO_2$ during cooling.(Figure 3b).

Table 1: Different constituents identified in the reaction product by X-ray diffraction analysis.

System	Temperature (°C)	Constituents identified
Na_2SO_4-Fe_2O_3	800	Na_2SO_4, Fe_2O_3, $NaFeO_2$, $Fe_2(SO_4)_3$
	900	Na_2SO_4, Fe_2O_3, $NaFeO_2$, $Fe_2(SO_4)_3$

Further the Na_2O formed may dissolve metal oxide to give sodium metal oxide. This can be represented by following reactions:

$$Na_2O + Fe_2O_3 \rightarrow 2NaFeO_2 \qquad ......3$$

The sulfur oxide gases may also react with metal oxide to form metal sulfide and / or metal sulfate. This is represented by the following reactions:

$$Fe_2O_3 + 3SO_3 \rightarrow Fe_2(SO_4)_3 \qquad ....4$$

The weight gain after initial weight loss in the kinetic curves for the systems was due to the formation of sodium metal oxide and metal sulfide and / or metal sulfate. Identification of reaction products by X-ray diffraction analysis, standard free energy calculations were favorable for the proposed reactions (Table 2) and weight gain after initial weight loss in the kinetic curves for the systems. The reactions 4 can undergo at experimental conditions of lower SO_2 pressure in the systems under study. The metallographic and SEM studies carried out on the mounted reaction products also indicate the presence of multiphase structure.

Table 2: Standard free energy of the reaction, ΔG^0 at 900 °C [14, 15]

Reaction	ΔG^0 (Kcal/mol)
$Na_2O(s) + Fe_2O_3(s) \rightarrow 2NaFeO_2(s)$	− 44.591
$Fe_2O_3(s) + 3SO_3(g) \rightarrow Fe_2(SO_4)_3(s)$	−170.773

In some systems, there was a sudden interruption in weight gain curves and a decrease in weight gain was observed till net weight change is weight loss. The release of SO_2/SO_3 (g) and the vaporization of some reaction products undoubtedly seemed to be the prime cause of the decrease in weight gain values in the kinetic curves.

Studying the total weight change as a function of mole fraction of Na_2SO_4 in the reaction mixture, for the system Fe_2O_3-Na_2SO_4, there was an increase in weight gain (or decrease in weight loss) values with increasing concentration of Na_2SO_4. This is followed by a decrease in weight gain (or increase in weight loss) values. An increase in the weight gain values with increasing Na_2SO_4 concentration is because of the formation of $Na_2O.Fe_2O_3$ ($NaFeO_2$) and binding of S in the form of metal sulfate and / or metal sulfide. A decrease in the weight gain values with increasing Na_2SO_4 concentration is because of release of SO_2/SO_3(g).

The photomicrographs of the reaction products show the presence of multi phase structures. Each phase represents a constituent usually identified by XRD and predicted by proposed reactions. In general, an oxide phase or Na_2SO_4 appear as whitish grey, sulfide or sulphate as dark grey, and $NaFeO_2$ as light grey.

Conclusion

Initially there were weight losses followed by weight gains in high temperature reactions of iron oxides and Na_2SO_4. The weight losses were due to the thermal decomposition of Na_2SO_4 and subsequent expulsion of SO_2/SO_3 (g). The weight gains were due to formation of sodium metal oxide ($Na_2O.Fe_2O_3$ or $NaFeO_2$), metal sulfate and/or metal sulfide. Optical and scanning micrographs showed the constituents in the reaction products were present as distinct phases.

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