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THERMOCHEMICAL STUDIES ON HOT ASH CORROSION OF STAINLESS STEEL 304 AND INHIBITION BY MAGNESIUM SULPHATE

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ABSTRACT

The accumulation of mineral ashes from residual fuel oil combustion on stainless steel surfaces causes fouling and corrosion resulting from the formation of low melting aggressive compounds. TG, DTA and weight loss experiments were carried out to study the effect of added $MgSO_4$ in depressing hot ash corrosion on stainless steel 304. Magnesium sulphate raised the melting point of the ash and inhibited the formation of sodium vanadate by formation of the more stable magnesium vanadates. The techniques employed help in determining the optimum amount of the chemical inhibitor to be added. When excesses of $MgSO_4$ were used, the iron was further protected; however, attack by chromium was relatively increased.

INTRODUCTION

Mineral impurities are among the known constituents of crude oils and are often concentrated in the heavy cuts, e.g. residual fuel oils. The use of the residual fuel oils to supply the energy requirements in various industrial heating processes leads to the accumulation of these mineral components as a result of the thermal degradation of the fuel oils. Impurities such as vanadium, sodium and sulphur are of special importance with regard to the formation of aggressive materials towards high temperature heating surfaces [1,2]. The most common deposit found on boiler super-heaters is the sodium vanadyl vanadate, $Na_2O.V_2O_4.5V_2O_5$, which melts at a relatively low temperature, 550 °C, [3,4]. Above the melting point, this ash material corrodes metals by long term contact. Meanwhile, if the molten ash sticks on metal surfaces at lower temperatures it tends to solidify and adhere forming deposits.

Several studies have been conducted to overcome this problem by introducing corrosion resistant alloys [5], removal of sodium and vanadium from

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the fuel [6], applying a corrosion resistant coating on the contact surfaces [7], and trying to develop chemical additives to retard the deposition of mineral ashes and passivate their aggressive activity towards metal surfaces [2]. Magnesium compounds and their mixtures with others are among the recommended additives to fuel oils [2].

We utilize here thermoanalytical techniques to investigate the inhibiting action of magnesium sulphate on hot ash corrosion caused by a sodium sulphate–vanadium pentoxide mixture on 304 stainless steel.

EXPERIMENTAL

All chemicals and solvents were of analytical grade. Weight loss studies were carried out on 304 stainless steel sheet (0.1 cm thick).

Thermogravimetric (TG) and derivative thermogravimetric (DTG) curves were recorded on a Stanton Redcroft model 760 thermobalance equipped with a three-pen recorder. Differential thermal analysis (DTA) was conducted on a Netsch DTA system.

Artificial ash was prepared by mixing and grinding sodium sulphate and vanadium pentoxide in 1 : 3 ratio by weight in an agate mortar for 20 min. Its mixtures with $MgSO_4$ were prepared in a similar manner. For TG measurements, samples weighing 3–5 mg were placed in platinum crucibles and heated at a rate of 20 °C min^{-1} under flowing nitrogen gas (25 ml min^{-1}). The DTA experiments required 15–20 mg samples to be heated in alumina crucibles under static atmosphere at a rate of 10 °C min^{-1}.

A stainless steel 304 sheet was cut into rectangular pieces, 25 × 15 mm. They were degreased with benzene and acetone, annealed at 1100 °C under vacuum for 60 min and then cooled to 25 °C. The specimens were mechanically polished with emery paper grades 120, 320 and 500 under running tap water, rinsed with distilled water, benzene, then dried and left in a desiccator over silica gel for one hour before being weighed accurately. The cleaned specimens were coated uniformly with the artificial ash and its mixtures with $MgSO_4$ to attain a coating of about 20 mg cm^{-2}. The specimens were placed in a muffle furnace with an uncoated specimen to compensate for oxidation, and heated at 600, 700 and 800 °C for 7 h. The furnace was switched off, and the samples were taken out after 18 h to avoid sudden cooling and cracking of the scale material. Finally the specimens were weighed after cleaning (dipping in caustic soda solution containing zinc dust at 60 °C for 5 min, washing with tap water, distilled water, drying and rinsing with benzene [8]) to determine loss in weight. The scale formed was digested with HCl for about 3 h until dissolved completely and analysed on a Pye Unicam SP-9 flame atomic absorption spectrophotometer for Fe, Cr and Ni.

RESULTS AND DISCUSSION

Thermal analysis

The TG and DTA curves of magnesium sulphate and its mixtures with vanadium pentoxide are given in Fig. 1. Magnesium sulphate is stable up to 892 ° C, where it decomposes into MgO and SO_3 at increasing rate. In the presence of V_2O_5 the DTA curves indicate the melting endotherm of the V_2O_5, and no influence of $MgSO_4$ can be seen at this temperature range (630–690 ° C) for all the ratios studied. The melting of the V_2O_5 aids the chemical reaction with $MgSO_4$, which is accompanied by weight loss in the range 660–860 ° C. Sulphur trioxide and oxygen are the most likely gaseous species to escape under such an environment. The amount of weight loss in all the ratios corresponds to the formation of the stoichiometric amount of MgO which fulfils the requirements of the equation

$$MgSO_{4(s)} + V_2O_{5(l)} \rightarrow MgV_2O_{6(s)} + SO_{3(g)} \qquad (1)$$

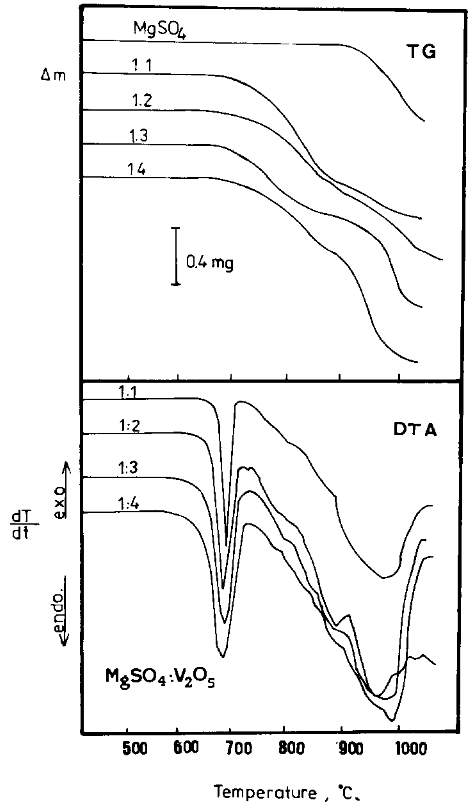

Fig. 1. TG and DTA curves of $MgSO_4$ and $MgSO_4 : V_2O_5$ mixtures.

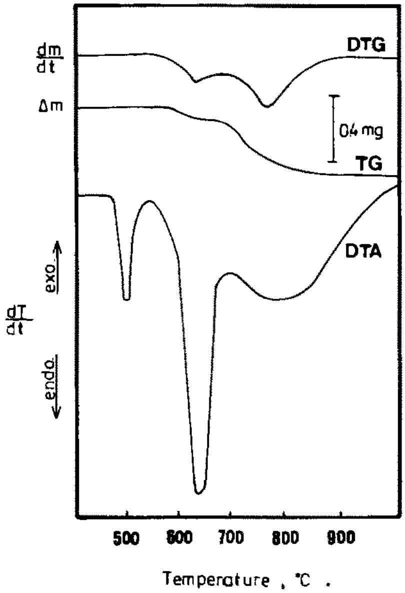

Fig. 2. TG, DTG and DTA curves of $Na_2SO_4 : V_2O_5$ (1 : 3) mixture.

MgV_2O_7 may coexist with MgV_2O_6 as they are predominant products of such a treatment [9]. However, the vanadates exist in the solid state because the possible eutectic melting with V_2O_5 [10] can not be expected here as the material is no longer existing at the reported melting point.

The excess $MgSO_4$, if any, in each sample decomposes in the manner described above ($\geqslant 890\,^\circ C$).

Figure 2 shows the TG, DTG and DTA curves of the 1 : 3 mixture of $Na_2SO_4 : V_2O_5$. An endothermic peak corresponding to the melting of the eutectic mixture is seen between 473 and 530 °C with a peak maximum at 503 °C, in agreement with literature values [1,11]. The TG curve indicates two partially overlapping steps of weight loss after complete melting of the mixture: 580–640 °C, loss of 2.5%; and 645–795 °C, loss of 7.75%. The first step is relatively more endothermic than the second. The total weight loss fulfils the stoichiometric amount of SO_3, necessary for the formation of NaV_3O_8

$$Na_2SO_{4(l)} + V_2O_{5(l)} \rightarrow NaV_3O_8 + SO_{3(g)} \qquad (2)$$

The formation of this vanadate was also possible from the interaction of V_2O_5 with molten sodium pyrosulphate [12].

The addition of $MgSO_4$ to the artificial ash (1 : 3 $Na_2SO_4 : V_2O_5$) significantly alters the thermograms of the ash (Fig. 3). The first melting endotherm shows up between 630 and 680 °C, i.e. the eutectic $Na_2SO_4 : V_2O_5$ melting endotherm disappears. In comparison with Fig. 1, the DTA curves indicate the passivation of the effect of Na_2SO_4 by the existence of $MgSO_4$.

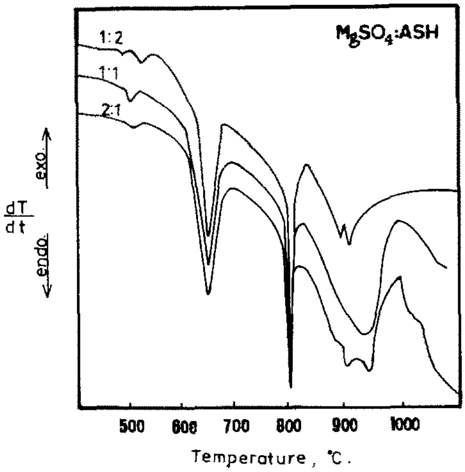

Fig. 3. DTA curves of $MgSO_4$: ash mixtures.

Series of endothermic processes are seen in Fig. 3 above 700 °C. Sharp endotherms characterize all three mixtures studied, and decrease in relative intensity as the amount of the ash is reduced in the mixtures. This can be related to the melting process of the eutectic mixture of Na_2SO_4 and excess $MgSO_4$ [2] within the mixtures. Magnesium sulphate, therefore, inhibits the interaction of Na_2SO_4 with V_2O_5 and hence the aggressive sodium vanadate was not formed to any significant extent.

Weight loss studies

Heating of the 304 stainless steel specimens at 600 and 700 °C resulted in almost identical rates of corrosion. The specimen corroded at a faster rate by heating at 800 °C and a red oxide layer was formed on the surface. The initiation and propagation of corrosion in chromium rich alloys are usually related to the formation and growth of Cr_2O_3 due to the expected stress build up which eventually causes rupture of the film at 800 °C and above [13]. Stress in the oxide layer is an effective factor in determining the service life in oxidizing atmosphere, because it influences adherence and resistance to cracking.

The application of artificial ash on the specimen surface resulted in increased corrosion rates with increasing temperature (600–800 °C). The scale formed after the thermal treatment is sticky and metallic in colour. The TG and DTA results presented above indicate that the formation of sodium vanadate, the most important aggressive species in the Na–V–O system, became appreciable after the melting of the eutectic mixture (Na_2SO_4–V_2O_5) and increased with temperature. Therefore Na_2SO_4, which has no individual aggressive behaviour towards metals [14], facilitates the low temperature

TABLE 1

Corrosion rates and inhibition efficiency in the presence of magnesium sulphate

$MgSO_4$:ash	Corrosion rate ($10^7 \times$ kg m^{-2} s^{-1})			Inhibition efficiency [a] (%)		
	600 °C	700 °C	800 °C	600 °	700 °C	800 °C
Nil [b]	1.279	1.676	7.650	–	–	–
0:1	5.808	73.670	312.90	–	–	–
1:2	2.516	32.960	131.60	57	55	58
1:1	1.271	17.120	56.12	78	77	82
2:1	1.111	4.816	15.35	81	84	95

[a] Inhibition efficiency $= [(W_0 - W_i)/W_0] \times 100\%$ where W_0 = weight loss in the presence of ash; and W_i = weight loss in the presence of ash + $MgSO_4$. [b] Uncoated specimen.

melting of the ash and initiates the formation of sodium vanadate, which attacks the metal surfaces.

Inhibition of the corrosive behaviour of the ash may be achieved by one of two means or both; raising of the melting point of the ash or the involvement of one of the components (mostly V_2O_5) in a chemical reaction that is prefered to sodium vanadate formation.

The addition of $MgSO_4$ raises the melting point of the ash (Fig. 3); the ash then reacts preferentially with $MgSO_4$ over Na_2SO_4.

Weight loss experiments on specimens treated with the artificial ash and $MgSO_4$, with $MgSO_4$: ash ratios of 1 : 2, 1 : 1 and 2 : 1, respectively, indicated reduction in corrosion rates with increasing $MgSO_4$ content (Table 1). The colour of the scale changed from brown–yellow to red. However, Nishikawa et al. [2] reported that $MgSO_4$ is ineffective at temperatures above 700 °C, and even becomes corrosive beyond 750 °C for carbon steel. In this work, where SS 304 was used, the results (Table 1) indicated that inhibition efficiency is a function of the $MgSO_4$ content of the ash. At high $MgSO_4$: ash ratios (2 : 1), the inhibition efficiency improved with temperature. Such behaviour may be related to decomposition of the excess $MgSO_4$ to give MgO which is effective in hot ash corrosion inhibition [15]. Furthermore, the high temperature is important in driving the $MgSO_4$ reaction to give magnesium vanadate which seems a rather good inhibitor for high temperature applications. The last finding contradicts the conclusion of Nishikawa et al. [2]. Table 2 shows the metal analysis of the scale materials formed on the specimens at 800 °C. It is clear that, although the total weight loss of the specimen decreases by the addition of $MgSO_4$ (Table 1), the composition of the scale was different for different $MgSO_4$: ash ratios. The Cr to Fe ratio increases as the $MgSO_4$ content increases. Therefore $MgSO_4$ is effective in reducing the total weight loss but not in diminishing the growth of Cr_2O_3 within the scale layer, and consequently is ineffective to stop the propagation of hot ash corrosion.

TABLE 2

Elemental analysis of the scale in the presence of $MgSO_4$, at 800 °C. Values given in $\mu g\ g^{-1}$

$MgSO_4$:ash	Iron	Nickel	Chromium	Ni:Fe	Cr:Fe
1:2	163,809	13,285	19,500	12.33	0.119
1:1	58,181	5,192	7,406	11.20	0.120
2:1	39,292	3,665	8,604	10.70	0.218

The optimum $MgSO_4$: ash ratio was 1 : 1, where the scale analysis showed Cr : Fe values of 0.12, which corresponded to a range of 77–82% inhibition efficiency at temperatures ranging between 600 and 800 °C.

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