

EFFECT OF Na_2SO_4 AND $\text{Fe}_2(\text{SO}_4)_3$ ON THE OXIDATION BEHAVIOUR OF AISI-303 ALLOY AT 900°

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ABSTRACT. The effects of Na_2SO_4 and $\text{Fe}_2(\text{SO}_4)_3$ coatings on the oxidation behaviour of AISI-303 alloy at 900° has been studied in flowing air. The coated samples were oxidised for a period up to 24 hr. The oxidation rate increased with increasing amounts of Na_2SO_4 coatings, but for $\text{Fe}_2(\text{SO}_4)_3$ coatings it decreased with increasing salt deposition. The influence of $\text{Na}_2\text{SO}_4 + \text{Fe}_2(\text{SO}_4)_3$ mixture on the oxidation rates was studied and it was found that the rate increased with increasing the amount of mixture deposition at 900° due to the formation of eutectic i.e. $\text{Na}_3\text{Fe}(\text{SO}_4)_3$. The results indicate the important role played by prior oxide and/or sulphide films, and the need for well-defined surface conditions. The scale morphologies were determined on the basis of X-ray diffraction analysis and scanning electron microscopic studies.

INTRODUCTION

Fe-based alloys with high Cr- and Ni-contents utilised at elevated temperatures are oxidation resistant due to the formation of slowly growing, protective oxide layers. The oxidation of AISI-303 alloy under service conditions is due to deposition of molten salt(s) or ash and/or the attack of gaseous species e.g. O_2 , CO , CO_2 , SO_2 , SO_3 , H_2S , etc. Oxygen active elements improve the oxidation resistance due to formation of Cr_2O_3 on the alloy surface [1-3]. The effects of fuel oil containing chlorides, C, N_2 and H_2 on corrosion resistance of stainless steel have been reported [4].

The effects of $\text{Fe}_2(\text{SO}_4)_3$ or Na_2SO_4 or their mixtures on the alloy surface are responsible for high temperature oxidation. Attack at low temperatures due to formation of eutectics have been investigated [5,6] e.g. $\text{Na}_2\text{SO}_4 + \text{Fe}_2(\text{SO}_4)_3$ (600°); $\text{K}_2\text{SO}_4 + \text{Fe}_2(\text{SO}_4)_3$ (627°); $\text{K}_2\text{SO}_4 + \text{Na}_2\text{SO}_4 + \text{Fe}_2(\text{SO}_4)_3$ (540°). Recently the high temperature oxidation behaviour of austenitic steels and Ni-base alloys have been studied [7,8], in which formation of low melting eutectics e.g. $\text{NiSO}_4 + \text{Na}_2\text{SO}_4$ (667°) and $\text{Na}_2\text{SO}_4 + \text{CoSO}_4$ (655°), respectively, seem to be important factors responsible for inducing high temperature oxidation.

The present study is concerned with the effects of Na_2SO_4 , $\text{Fe}_2(\text{SO}_4)_3$ or $\text{Na}_2\text{SO}_4 + \text{Fe}_2(\text{SO}_4)_3$ coatings on AISI-303 alloy surface at 900° for up to 24 hr.

EXPERIMENTAL

Samples of $1.8 \times 1.2 \times 0.1 \text{ cm}^3$ size were cut from a sheet of a commercial AISI-303 alloy (Cr-18%, Ni-8.5%, Mn-1.5% Si-0.5%, C-0.1% and Fe-balance) were homogenised at 900° for 4 hr in an evacuated quartz tube. The samples were abraded sequentially

with 180, 320 and 600 grades of SiC papers.

The polished samples were uniformly coated with aqueous solutions of Na_2SO_4 or $\text{Fe}_2(\text{SO}_4)_3$ or their mixture by spraying techniques till a nearly uniform coating of the salt (s) was obtained. The salt coated samples were transferred to silica boats and dried in a hot air oven at 110° for 2 hr. The oxidation experiments were carried out in a horizontal tubular furnace in flowing air at 900° for 24 hr. The constituents in the scales of oxidised samples were identified by X-ray diffraction analysis and are listed in Table 1.

Table 1. Constituents in the scales of oxidised AISI-303 alloy as identified by X-ray diffraction analysis (900°).

Coatings on Alloy	Constituents identified
Na_2SO_4	FeS , Cr_2S_3 , FeO , Fe_2O_3 , Na_2FeO_2
$\text{Fe}_2(\text{SO}_4)_3$	FeS , Cr_2S_3 , Fe_2O_3 , FeCr_2O_4 , Fe_3O_4 , NiCrO_4
$\text{Na}_2\text{SO}_4 + \text{Fe}_2(\text{SO}_4)_3$	FeS , $\text{Fe}_3\text{Cr}_2\text{S}_3$, NiCrO_4 , FeCr_2O_4 , Fe_2O_3 , Na_2FeO_2 , Fe_3O_4 , NiS , NiO

The scanning electron microscopic (SEM) studies were carried out using a Cambridge scanning electron microscope S4-10.

RESULTS AND DISCUSSION

Figure 1 represents plots of mass gain or loss *versus* amount of salts deposited (Na_2SO_4 , $\text{Fe}_2(\text{SO}_4)_3$ or 1:1 equimolar mixture of $\text{Na}_2\text{SO}_4 + \text{Fe}_2(\text{SO}_4)_3$) for AISI-303 alloy, oxidised at 900° for 24 hr. The oxidation rate of Na_2SO_4 -coated alloy increases with increasing amount of salt deposition up to 4 mg/cm^2 while for $\text{Fe}_2(\text{SO}_4)_3$ -coated AISI-303 alloy the mass loss decreases with increasing salt deposition. The oxidation rate of AISI-303 alloy coated with $\text{Na}_2\text{SO}_4 + \text{Fe}_2(\text{SO}_4)_3$ shows higher increase in mass gain than that coated with either Na_2SO_4 or $\text{Fe}_2(\text{SO}_4)_3$. This could be attributed to the formation of an eutectic which could facilitate oxidation.

Fig. 2 (a & b) shows scanning electron photo-micrographs of $\text{Na}_2\text{SO}_4 + \text{Fe}_2(\text{SO}_4)_3$ -coated alloy corroded at 900° for 24 hr. There is greater perturbation of the scale layers which is evident by the presence of voids and cavities in the scales. The inner layers are richer in Cr_2S_3 incorporated with FeS . The middle and outer layers contain Fe_3O_4 combined with NiCrO_4 . The outermost layers of the scales predominantly constitute Fe_2O_3 with NiO inclusions. The perturbation of the scales is presumably due to evolution of SO_2 and reactions of the decomposition product of $\text{Fe}_2(\text{SO}_4)_3$ with Cr_2O_3 and NiO .

The Na_2SO_4 -coated AISI-303 alloy shows increasing oxidation rate with increasing salt deposition up to a deposition of about 4 mg/cm^2 while the rate of the $\text{Fe}_2(\text{SO}_4)_3$ -coated alloy decreases with increase of salt deposition. A sample coated with a 1:1 equimolar mixture of $\text{Na}_2\text{SO}_4 + \text{Fe}_2(\text{SO}_4)_3$ shows maximum mass gain due to formation of eutectic i.e. $\text{Na}_3\text{Fe}(\text{SO}_4)_3$ at 900° .

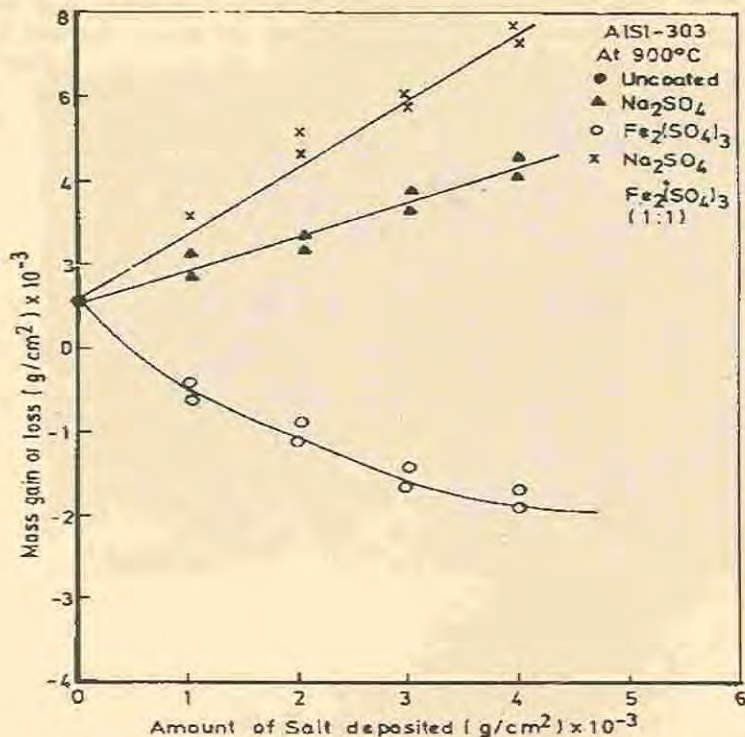
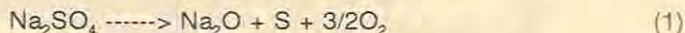


Fig.1. Amount of Na_2SO_4 , $\text{Fe}_2(\text{SO}_4)_3$ and $\text{Na}_2\text{SO}_4 \cdot \text{Fe}_2(\text{SO}_4)_3$ deposited versus mass gain or loss plots of AISI-303 alloy, oxidised at 900°C for 24 hours.

Na_2SO_4 (m.p. 884°) decomposes according to the following reaction:



In such a situation there would be sufficient activity of sulphur to form FeS and Cr_2O_3 at the oxide/salt interface. The formation of sulphide will result in a decrease in the sulphur activity and consequently an increase in the oxygen activity. The increased oxygen activity at oxide/salt interface results in the oxidation of some of the sulphides, and sulphur thus released is available for internal sulphidation. FeO and Cr_2O_3 formed as a result of oxidation of sulphides would mix with Na_2O (melt) to form Na_2FeO_2 and $\text{Na}_2\text{CrO}_4/\text{NaCrO}_2$ according to the following reactions:

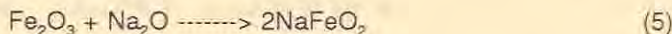
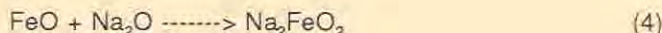
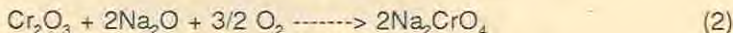
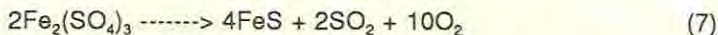
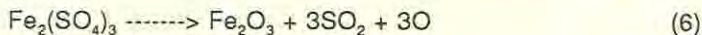




Fig. 2 Scanning electron micrographs of AISI-303 alloy coated with Na_2SO_4 + $\text{Fe}_2(\text{SO}_4)_3$ (1:1), oxidised at 900° for 24 hrs. (a) 1000 X and (b) 1500 X

The reactions (2) to (5) are thermodynamically feasible at 900°. The reactions are likely to continue until all the Na_2O is consumed. At the salt/air interface the activity of Na_2O is very low, and NaCrO_2 and Na_2CrO_4 would dissociate to precipitate Cr_2O_3 . Similarly, FeO may be precipitated as a result of the dissociation of Na_2FeO_2 .

$\text{Fe}_2(\text{SO}_4)_3$ decomposes as follows:



At 900°, reaction (6) is feasible at the salt/air interface whereas reaction (7) is favourable at the oxide/salt interface. Conversion of $\text{Fe}_2(\text{SO}_4)_3$ into FeS will increase the activity of oxygen at the oxide/salt interface, resulting in the conversion of FeS into Cr_2O_3 and iron into FeO . Thus the scales should comprise inner scale containing pockets of $\text{FeS}/\text{FeCr}_2\text{S}_4$ followed by thicker layers of Cr_2O_3 and Fe_2O_3 .

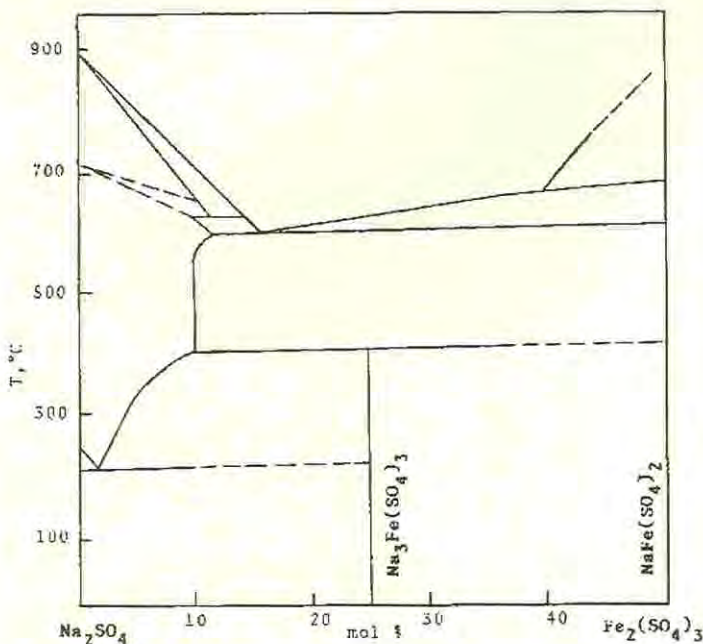
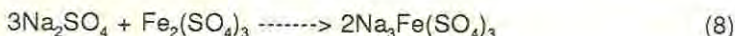
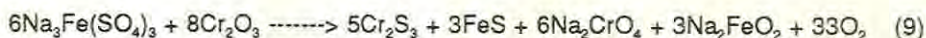


Fig. 3. Phase equilibrium diagram for the $\text{Na}_2\text{SO}_4 + \text{Fe}_2(\text{SO}_4)_3$ system [5].

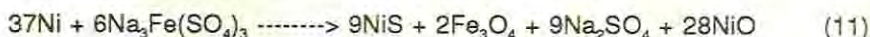
The phase equilibrium diagram of the mixture, according to Bol'shakov *et al.* [5], giving a liquid phase at high temperature, is shown in Fig. 3:



This liquid phase, when in contact with AISI-303 alloy, attacks the Cr_2O_3 film on the alloy surface:



This will result in complete destruction of the oxide scale and formation of sulphides and molten products as indicated by reaction (9). The liquid phase further attacks the alloy:



The Na_2SO_4 which is released by the reactions (10) and (11) is further available to attack the alloy provided the conditions are favourable. The scales formed on the AISI-303 alloy corroded at 900° contain thicker oxide layers in comparison to low temperature scales which are primarily sulphide dominant. The Fe_2O_3 , Fe_3O_4 , Cr_2O_3 , NiO are formed by the precipitation of molten species at salt/air interface due to the activity of O^{2-} ions.

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