



High Temperature Corrosion Behaviour of Steel with a Carbonate Deposit at 1123K

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ABSTRACT

The high temperature corrosion behavior of AISI 304 austenitic stainless steel and S45C carbon steel were studied in presence with CaCO_3 salt at 1123K for 24,48,72, 96 and 120 hour. The studies were carried out to determine the mass change vs times, the morphological structures of deposits on the surface of alloy scales were investigated by scanning electron microscopy (SEM). The results indicated that the initial CaCO_3 coating accelerated oxidation, resulting in the formation of a scales. The mass of metal was related to the consumption of chromium, nickel and iron in the alloy substrate. The characterization of scales were determined by using the EDAX.

Keywords: *austenitic stainless steel, carbon steel, deposit, high temperature corrosion*

Introduction

Steel are widely used in fabrication industries to fabricate boiler part, pressure vessel, steam tube, economizer etc. There are many type of steel in the world market. Austenitic stainless steel, carbon steel and mild steel are commercially grade ferrous base alloy and extensively used in thermal power plant, petroleum refinery plants, chemicals plants, industrial especially used in boiler, pressure vessel, steam tubes, etc. The corrosion of these alloy during operation is not uncommon due to the deposition of metal salts . Gases such as CO_2 , O_2 , SO_2 , H_2S etc or their complex multicomponent mixtures are often presents in such environment and these can attack on the metal parts, leading to failure in service.

Calcium carbonate are the most frequent deposit on alloy surface and may cause severe problem and economics loss (Kjellin, 2002). Many studies have been carried out on steel dealing with deposit.(Misbahul Amin, 1993). However the calcium carbonate deposit at high temperature corrosion has not much studied.

The paper deals on the corrosion behavior of commercial AISI 304 austenitic stainless steel and S45C carbon steel in presence of CaCO_3 deposit at temperature 1123 K for the duration of 24 – 120 hr.

Literature Review

Wehua et al.(2004) reported that the exposure of metal and alloy to high temperatures leads to formation of oxide scales. The deposit can be products of corrosion while accumulation of undesirable deposit on industrial equipment surfaces is a complex phenomenon with severe economic consequences, affecting a wide range of industrial process.

As mentioned by Demadis (2006), deposit cause a reduction in heat transfer rates in equipment such as boiler, steam generators, evaporator, heat exchangers etc. Equipment failure from corrosion as a result under deposit can significantly add to the cost. Cause by deposit the boiler tube will overheating, increased fuel consumption and reduced efficiency of equipment. Equipment failure from corrosion as a result under deposit corrosion can significantly add to this cost. Deposit formed in the pipes can also have significant economic effect on various processes

such as oil production, mining, water supply and disposal pipes.

According Wang & Li (2004) the austenitic stainless steel grade 310SS, 253MA and 353MA coated with NaCl deposit all suffered metal loss and subscale attack during high temperature exposure at 850°C. Both metal loss and total depths of attack of the alloy increased with increasing time exposure. The metal increased slowly after 4 hr exposure.

Tae Hoon Lim et al. (2000) reported that when the material type AISI 316L and 310 stainless steel in presence of molten carbonate salt Li_2CO_3 and Na_2CO_3 at temperature up to 620°C for 100h, the weight loss increases again due to a faster corrosion reaction with increasing temperature.

The mass for AISI 304 coated with Na_2SO_4 for 24 hr at temperature 973 K (700°C) are loss up to 8 hr followed by a relatively small mass gain (Misbahul Amin, 1994).

Perez (2002) reported that a large increase in the oxidation rate at temperature 800°C and after initial period of 20h, the oxidation rate experiences increase but not linear.

Methods and Materials

The chemical composition of the two commercial steels (AISI 304 stainless steel and S45C carbon steel) employed in the study are shown in table 1. Rectangular specimens were cut to dimension 20x10 x 3mm by cutting machine. Specimens were ground sequentially with 180,320 and 600 grades of SiC abrasive paper and cleaned with acetone. Each specimens was weighed and measured the length, width and thickness.

Table 1. Chemical Composition (wt.%) of Alloys

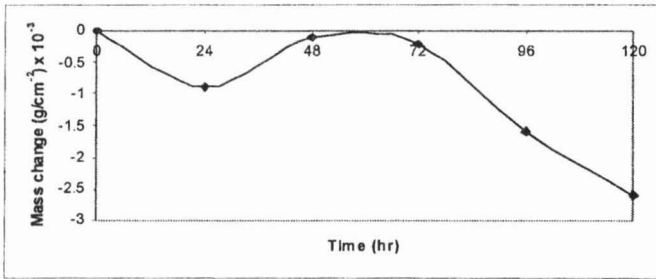
Alloy	C	Cr	Mn	Ni	P	Si	S	Fe
304	0.08	18-20	2	8-10.5	0.05	1	0.03	Bal.
S45C	0.42-0.48	-	0.3-0.9	-	0.03	0.15-0.35	0.035	Bal

The specimens were heated to about 110°C on a hot plate. An air gun was used to spray the saturated CaCO_3 aqueous solution in the air mist until a nearly uniform coating of the salt was obtained. The salt coupon were transferred to crucibles and dried in oven at 110°C for about 1 h, cooled to room temperature and weighed. Oxidation kinetic studies were carried out in a muffle furnace at 1123K for 24 to 120 h duration. After the completion the specimens were taken out, cooled in dessicator and weighed.

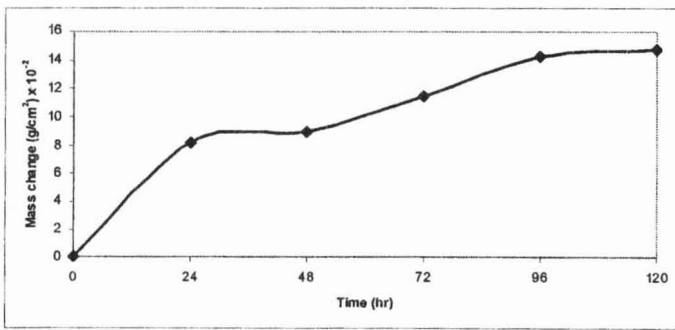
Oxidized specimens were mounted, abraded and polished using SiC paper and diamond pastes of various grades respectively for Scanning electron microscopy (SEM) examination and EDAX.

Results

Figure 1 (a & b) shown oxidation kinetic (mass change vs. time) curves of AISI 304 stainless and S45C carbon steel coated with CaCO_3 oxidized at 1123K for 24 to 120 hr. The curves for AISI 304 shows a mass loss up to 48 h followed by a relatively small gain at 72 h and mass loss up again to 120 h. While for the curves of S45C carbon steel shows mass gain with increasing of time up to 120 h exhibiting approximately parabolic behavior.



(a)



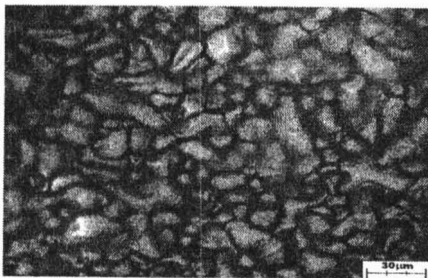
(b)

Figure 1: Oxidation Kinetics (Mass Change vs Time) Curves of Steel Coated with CaCO_3 Oxidized at 1123 K (a) AISI 304 Austenitic Stainless Steel (b) S45C Carbon Steel

The external scale is peel of after cooling for AISI 304 while for S45C is adhere. External morphologies of scale formed on alloys corroded for 48 hr are shown in Figure 2 (a & b).



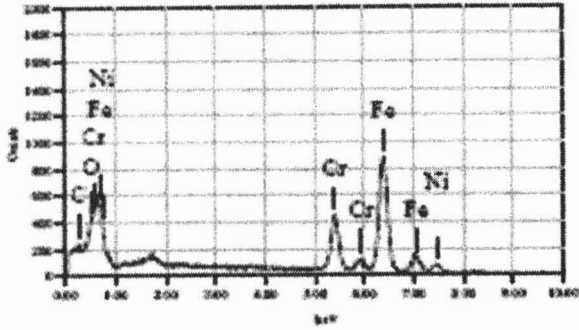
(a)



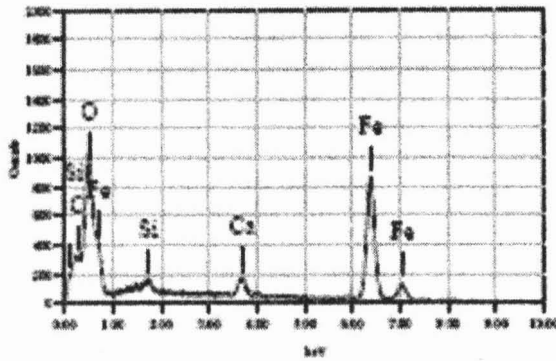
(b)

Figure 2: Surface Morphology of Scale on the Surface Alloy (a) AISI 304 Stainless Steel (b) S45C Carbon Steel Exposed at 1123K for 48 hr.

The inner layer of scales of AISI 304 steel and S45C carbon steel corroded at 1123K for 72 hr in the presence of CaCO_3 contain Cr_2O_3 , FeO , SiO , NiO are shown in Fig.3 (a) and (b) and Table (2 & 3)



(a)



(b)

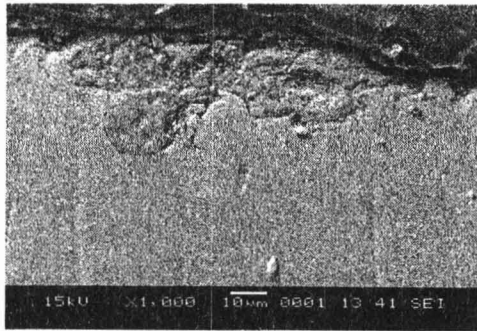
Figure 3: EDAX Analysis Result of the Scale on the Alloy Surface Oxidized at 1123 K for 72hr

Table 2: Deposit Composition (wt %) of AISI 304 Austenitic Stainless Steel

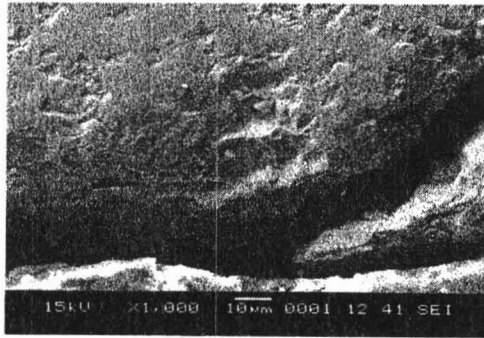
Element	Mass (%)	Compound	Mass (%)
C	0.90	C	0.90
Cr	13.91	Cr_2O_3	20.33
Fe	54.41	FeO	69.99
Ni	6.89	NiO	8.77
O			
Total	100	Total	100

Table 3: Deposit Composition (wt %) of S45C Carbon Steel

Element	Mass (%)	Compound	Mass (%)
C	0.277	C	1.67
Si	0.39	SiO ₂	0.82
Fe	73.36	FeO	94.38
Ca	2.24	CaO	3.13
O	22.35		
Total	100	Total	100



(a)



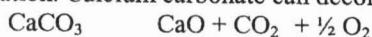
(b)

Figure 4: SEM of CaCO₃ Deposit on Steel (a) AISI 304 Austenitic Stainless Steel (b) S45C carbon Steel Oxidized at 1123K for 72 hr

Discussion

Formation of oxide layer by CaCO₃ deposit on the metal surfaces cause mass change of the steel. There is evidence for AISI 304 stainless steel showed mass loss due evolution of CO₂, resulting cracks and voids. While S45C Carbon steel coated with CaCO₃, oxidized at 1123 K showing mass gain due to alloy is soft and malleable, exhibiting formation of ferrous oxides. It is because chromium containing on iron AISI 304 as a major element for corrosion resistance at high temperature. Meanwhile the carbon steel not contain these element as a corrosion resistance. With the lack of compact scale formed on the carbon steel surface and not be used for oxidation resistance application, especially in oxidizing environment at elevated temperatures.

The oxidation behavior of steel in presence of salt calcium carbonate salt would be explained on the basis of the following equation. Calcium carbonate can decompose as follow :



For these study the scale consist of inner oxide layers of Cr_2O_3 , NiO , SiO_2 and CaO while external layer of FeO .

Conclusion

- i. Corrosion of stainless steel and carbon steel with CaCO_3 deposit at 1123K causes mass change. The AISI 304 coated with CaCO_3 showed weight loss while the carbon steel exhibiting weight gain with increasing time exposure.
- ii. Exposed to high temperature cause the formation of oxide layer scale on the surface of alloys exhibiting Cr_2O_3 , NiO and SiO_2 and carbon steel FeO , CaO and SiO_2 respectively.
- iii. Oxidation of carbon steel is generally slower than stainless steel. The scale remains adherent to the surface of carbon steel and spalling for the stainless steel.

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