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High temperature corrosion of water wall tube in coalfired combustion gases

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Abstract. — The effect of stoichiometry ratio and ash deposits on the corrosion of mild steel and 0.5Cr-0.5Mo steel has been investigated at 450 °C in the simulated combustion gases burning three kinds of coals. Under the assumption that the gas reacts with the metal at the same temperature as the surface and gas has not changed in composition, the corrosion behavior could be estimated from the Fe-S-O phase stability diagram at 450 °C and pseudo equilibrium P_{S_2} and P_{O_2} based on $H_2O : H_2$ at 1200 °C for simulated combustion gases. Ash deposits accelerated the corrosion rates of steels. It is considered that ash deposits act as catalyst and shift the gas composition to the low temperature equilibrium state.

1. Introduction.

Recently substoichiometric combustion has been employed in pulverized coal fired boilers to reduce NO_x concentration [1]. Sulfur is released from coal as H_2S , which sulfidizes boiler tubes at furnace wall temperatures. Sulfide scales are much less protective than oxide scales, and metal sulfidation rates are much higher than oxidation rates. Severe corrosion of furnace wall tubes is expected to take place particularly when firing high sulfur coals.

In a pulverized coal fired boiler a large amount of ash deposits on the water wall tube surfaces. The ash deposition on the tube surface would influence the corrosion behavior. The effect of the ash deposit, however, on the corrosion of water wall tubes has not been well understood.

In this study the effect of stoichiometry ratio and ash deposition on the corrosion behavior of the candidate materials of water wall tubes has been investigated in simulated combustion gases at furnace wall temperature.

2. Experimental procedure.

A mild steel and a 0.5Cr-0.5Mo steel were used in this test. The chemical compositions of materials are given in table I. Corrosion tests were carried out in simulated combustion gases burning Illinois No.6, Daido and Taiheiyo coals at several stoichiometric combustions. The gas temperature during combustion was estimated to be 1200 °C. The chemical compositions

of coals and the thermodynamic equilibrium compositions of combustion gases are presented in tables II and III, respectively. Specimens (7.5 mm × 15 mm × 3 mm) surfaces were ground by # 600 emery papers and degreased by acetone. These specimens were placed in the apparatus and kept at 450 °C for 1000 h max. The gas flow rate during the experiments was 1000 cc/min. The effect of ash deposits on the corrosion behavior of the mild and the low alloy steels was also investigated. The ash was extracted from a water wall tubes of a coal fired boiler. The chemical composition of the ash is shown in table IV.

Table I. — *Chemical compositions of steels used (wt%).*

Material	C	Si	Mn	P	S	Cr	Mo
Mild steel	0.21	0.23	0.75	0.020	0.020	—	—
0.5Cr – 0.5MO steel	0.13	0.34	0.53	0.014	0.011	0.52	0.57

The corrosion resistance was evaluated by the surface recession measured by the microscopic observation of cross sections of specimens or mass increase of the specimens after the test. The scales on the corroded specimen surfaces were analyzed by EPMA. Scale components were also identified by X-ray diffraction.

Table II. — *Chemical compositions of coals (wt%).*

Bland	Illinois No.6	Daido	Taiheiyo
Total Moisture	12.0	10.3	11.0
Ash	16.0	9.2	15.4
C	57.5	76.2	65.7
H	3.7	4.3	5.2
N	0.9	0.87	1.0
S	4.0	0.68	0.3
O	5.8	6.0	11.9

Continuous weight gain measurements of the mild steel were also conducted in simulated combustion gases by using thermogravimetry to investigate the corrosion rate law. Before the start of the experiments the air in the retort was replaced with flowing N₂ gas. The gas flow rate of the gas mixture experiments was 200 cc/min.

Table III. — *Thermodynamic equilibrium compositions of combustion gases. (vol%).*

coals	Stoichiometric ratio	Gas reference	CO	CO ₂	H ₂ O	H ₂	SO ₂	H ₂ S (ppm)	N ₂
Illinois	0.7	A	11.2	10.1	8.1	2.8	0.1	1690	Bal.
No.6	0.8	B	7.1	12.3	8.5	1.5	0.28	693	Bal.
	0.9	C	3.5	14.3	8.6	0.66	0.44	84	Bal.
	0.7	D	12.2	9.9	7.2	2.8	0.02	360	Bal.
Daido	0.8	E	7.7	12.5	7.7	1.5	0.05	130	Bal.
	0.9	F	3.6	14.9	7.8	0.6	0.06	10	Bal.
	0.7	G	11.5	9.7	9.0	3.3	0.01	200	Bal.
Taiheiyo	0.8	H	7.2	12.1	9.5	1.8	0.02	70	Bal.
	0.9	I	3.4	14.4	9.7	0.7	0.03	6	Bal.

Table IV. — *The chemical composition of ash used (wt%).*

Component	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	ZnO	SO ₃	C
Actual ash	57.3	23.4	4.7	3.2	2.6	2.0	0.5

3. Test results and discussion.

3.1 THERMODYNAMIC CONSIDERATION. — Before the corrosion tests, we try to predict the corrosion behavior of mild steel and 0.5Cr-0.5Mo steel from the Fe-S-O phase diagram and pseudo-equilibrium sulfur and oxygen pressures for simulated combustion gases. The gas temperature at the surface of waterwall tube can approach the metal temperature of 450 °C. The nature of the boundary layer including its thickness, and temperature/composition gradients has not been analyzed. Therefore, some elementary assumptions were made. The first is that the gas reacts with the metal at 450 °C. The second is that the gas composition is not changed. Reaction kinetics in bulk gas seems to be very slow and gas flow velocity is very high [2]. It is considered likely that the gas passes through the waterwall area with a little change in composition. It is necessary to calculate pseudo-equilibrium sulfur and oxygen pressures for the high temperature gas composition at a low gas/surface temperature. As we have estimated that the combustion gas temperature is 1200 °C the P_{O_2} is calculated by using the 1200 °C equilibrium ratios of H₂O : H₂ or CO₂ : CO, and the equilibrium constants at 450 °C. Similarly, P_{S_2} is calculated by using 1200 °C equilibrium ratios of H₂S : H₂. These pseudo equilibrium sulfur and oxygen pressures are shown in table V. The calculated pseudo equilibrium P_{O_2} and P_{S_2} of the gas mixtures used in this study were superimposed on the Fe-S-O phase diagram at 450 °C as shown in figure 1. From this diagram we can predict if Fe tends to form sulfide or oxide in combustion gases under several conditions. Namely, Fe tends to form the sulfide in the range of pseudo equilibrium P_{O_2} and P_{S_2} values based on

Table V. — *Pseudo equilibrium sulfur and oxygen pressures (atm).*

Gas Reference	Equilibrated (450 °C)		Not Equilibrated		
	$\log P_{O_2}$	$\log P_{S_2}$	$\log P_{O_2}$ ($H_2O : H_2$) ⁽¹⁾	$\log P_{O_2}$ ($CO_2 : CO$) ⁽¹⁾	$\log P_{S_2}$ ($H_2S : H_2$) ⁽²⁾
A	-29.37	-9.45	-28.98	-31.83	-10.33
B	-29.36	-9.44	-28.39	-31.26	-10.56
C	-29.04	-9.20	-27.67	-30.52	-11.68
D	-29.37	-11.10	-29.08	-31.92	-11.67
E	-29.36	-11.10	-28.48	-31.32	-12.01
F	-29.35	-11.09	-27.67	-30.51	-13.45
G	-29.39	-11.97	-29.03	-31.89	-12.32
H	-29.38	-11.96	-28.46	-31.29	-12.71
I	-29.30	-11.90	-27.62	-30.49	-14.02

(¹) $\log P_{O_2}$ calculated using the $H_2O : H_2$ or $CO_2 : CO$ ratios of the equilibrium gas composition at 1200 °C and the Gibbs Free Energy at 450 °C.

(²) $\log P_{S_2}$ calculated in a similar manner using $H_2S : H_2$ ratios and free energy data.

Fig. 1. — Fe-S-O Equilibrium phase diagram at 450 °C.

CO₂: CO ratios at 1200 °C. However, the range of those based on H₂O : H₂ ratios at 1200 °C are located at the boundary between FeS and Fe₃O₄.

3.2 CORROSION TEST RESULTS. — Table VI shows the corrosion test results of the mild steel and 0.5Cr-0.5Mo steel in simulated combustion gases. The corrosion rates of the both steels were almost the same. Severe corrosion was observed on the steels in simulated combustion gases under stoichiometry ratio of 0.7 (gases A, D, G). Figure 2a shows the cross sectional photomicrograph of 0.5Cr-0.5Mo steels after exposure in gas A for 500 h. The X-ray diffraction and EPMA analysis showed that the outer layer scales consisted of FeS, and the inner scales consisted of a mixtures of FeS and Fe₃O₄. The corrosion rates of the steels were high in gas B simulating the combustion environment burning the high sulfur Illinois No. 6 coal under stoichiometry ratio of 0.8. However, the corrosion rates were small in gases E, H simulating the combustion environments burning Daido and Taiheiyo coals, respectively under the same stoichiometry ratio. The corrosion rates were also very small in gases C, F, I simulating the combustion environments under stoichiometry ratio of 0.9. The scales formed on 0.5Cr-0.5Mo steel in gas I were very thin and adherent as shown in figure 2b, which were identified as Fe₃O₄.

Table VI. — *Max-surface recessions of steels in simulated combustion gases at 450 °C.*

		Max. Surface Recession (μm)					
		100 h		500 h		1000 h	
Material	Gas reference	No deposit	with deposit	No deposit	with deposit	No deposit	with deposit
0.5Cr – 0.5Mo Steel	A	26.3	33.8	88.0	130.0	—	—
	B	27.5	52.5	—	—	—	—
	C	5.0	5.5	7.0	40.0	—	—
	D	22.5	27.5	75.0	155.0	110.0	160.0
	E	10.0	17.5	50.0	80.0	—	—
	F	3.3	6.3	—	—	—	—
	G	30.0	20.0	—	—	—	—
	H	7.0	7.5	—	—	—	—
	I	5.0	5.0	6.8	7.0	8.5	8.0
Mild steel	A	25.0	32.5	100.0	120.0	—	—
	B	20.0	25.0	—	—	—	—
	C	5.0	5.0	7.0	20.5	—	—
	D	17.5	22.5	—	—	—	—
	E	3.8	12.5	70.0	150.0	100.0	140.0
	F	3.8	3.8	75.0	90.0	—	—
	G	22.5	17.5	—	—	—	—
	H	7.5	5.0	—	—	—	—
	I	5.0	5.0	7.0	7.0	8.75	7.5

Pseudo equilibrium P_{S_2} and P_{O_2} based on CO₂: CO ratios predicted sulfide formations in all atmosphere tested. Low temperature equilibrium P_{S_2} and P_{O_2} also predicted sulfide formations in all cases. However, the results were quite contrary. The corrosion rates of 0.5Cr-0.5Mo steel were superimposed on the applicable gas equilibrium based on H₂O : H₂ ratios

Fig. 2. — Scales formed on 0.5Cr-0.5Mo in gas A and gas H at 450 °C for 500 h: a) in gas A; b) in gas H.

Fig. 3. — Max-surface recessions of 0.5Cr-0.5Mo steel in simulated combustion gases at 450 °C for 100 h.

at 1200 °C in the Fe-S-O phase diagram as shown in figure 3. Where the pseudo equilibrium positions of simulated combustion gases were in the FeS stable field the corrosion rates of 0.5Cr-0.5Mo steel were high. However, the corrosion rates were very low in the atmospheres where Fe_3O_4 was expected to form. Thus the estimation using pseudo equilibrium P_{S_2} and P_{O_2} based on $\text{H}_2\text{O} : \text{H}_2$ ratios were well consistent with test results. It seemed therefore that the gas composition has not drastically changed in the corrosion apparatus. These data

Fig. 4. — Effect of deposition of ash components on the corrosion rates of 0.5Cr-0.5Mo steels.

suggest that it may be possible to predict the corrosion behavior of waterwall tubes from the Fe-S-O phase diagram and pseudo-equilibrium P_{S_2} and P_{O_2} based on $H_2O : H_2$ and $H_2S : H_2$ ratios at 1200 °C for a simulated combustion gas.

Ash deposit slightly accelerated the corrosion rates. Ash deposition on the tube surface may influence the gas phase reactions. Also, ash deposits prevent from forming uniform outer scales and may make it easy to transport sulfur containing species to the metallic surface. However, the mechanism is not clear as yet. As shown in table IV ash contains various components such as SiO_2 , Al_2O_3 , Fe_2O_3 , FeS and unburned coal *et al.* The effect of these ash components on the corrosion of 0.5Cr-0.5Mo steel was investigated. Figure 4 shows the corrosion rates of 0.5Cr-0.5Mo steel covered with various ash components. Fe_2O_3 and FeS remarkably increase the corrosion rates. Activated carbon also increased the corrosion rates but the influence was not remarkable like that of Fe_2O_3 and FeS. Al_2O_3 and SiO_2 did not appreciably change the corrosion rates. Fe_2O_3 and FeS also increased the corrosion rates even in oxide stable atmosphere. As shown in figure 5, EPMA maps of the scales indicate that sulfide increased in the inner scales. These results suggest that Fe_2O_3 and FeS act as catalyst and the gas composition has changed to its low temperature equilibrium. Thus, the P_{S_2} near the metal surface and consequently the corrosion rates would increase. The acceleration mechanism of the activated carbon seems rather different. Carbon may serve as a buffer to maintain low oxygen concentration as reported by Harb *et al.* [3]. From these investigations, it became clear that the effect of ash deposit highly depends on its composition. Therefore the increase of the corrosion rate can not be determined quantitatively at present.

It is well known that the corrosivity of reducing gas depends on its H_2S concentration [4]. Figure 6 shows the effect of H_2S content on the corrosion rates of the mild steel and 0.5Cr-0.5Mo steel in simulated combustion gases at 450 °C for 100 h. The corrosion rates increased with increasing H_2S content in a low H_2S range. However, the corrosion rates tend

Fig. 5. — Scales formed on 0.5Cr-0.5Mo covered with Fe_2O_3 in gas F at 450 °C for 200 h: a) B.S.E.; b) iron; c) oxygen; d) sulfur.

to saturate in high H_2S content region. Also, the corrosion rates remained low with levels up to 100 ppm H_2S . In this case, oxide scales tend to form. It is, therefore, considered that the corrosivity of simulated combustion gas depends not only on H_2S content but also on the oxygen pressure.

3.3 CORROSION KINETICS. — It is necessary to know the corrosion rate law in order to estimate long term behavior from short time data. For this purpose, mass increases of the mild steel were continuously measured in the simulated combustion gas atmosphere at 450 °C by using thermogravimetry. Figure 7 shows the continuous weight gain curves of mild steel in gas A and gas H at 450 °C. In gas H the corrosion progressed approximately following parabolic rate law. On the other hand, the corrosion rate law in gas A was more complex than in gas H. The corrosion rate followed a linear rate law at the first stage of corrosion, but the gradient tend to decline with time. It is highly probable that more than one factor is determining the corrosion rate in this atmosphere at each stage. Namely, the reaction between metal and gas species determined the corrosion rate at the beginning of corrosion, but later, when the metal surface was covered with the protective scales, the outward cationic diffusion determined the corrosion rate.

Fig. 6. — Effect of H_2S content on the corrosion rates of steels.

Fig. 7. — Continuous weight gains of mild steel in gases A and H at 450 °C.

4. Conclusion.

The corrosion resistance of a mild steel and 0.5Cr-0.5Mo steel has been evaluated in simulated combustion gases at 450 °C. The results are summarized as follows:

1) The corrosion behavior can be predicted by the Fe-S-O phase diagram at tube surface temperature and pseudo-equilibrium P_{S_2} and P_{O_2} based on $H_2O : H_2$ at 1200 °C for simu-

lated combustion gases.

2) Ash deposit increases the corrosion rates slightly. It is considered that ash deposit acts as catalyst and alters the gas composition to the low temperature equilibrium state.

3) The corrosion rates increase with H_2S content in a certain range, but tend to saturate in a high H_2S level region.

4) The corrosion rate of mild steel follows the parabolic rate law in an oxidizing atmosphere. In a reducing atmosphere it follows a periodically linear or a parabolic rate law.

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