MICROSTRACTURE EVOLUTION OF INTERNAL OXIDATION ZONE FORMED IN THE INITIAL STAGE OF THE STEAM OXIDATION OF Fe-9Cr-0.26Si FERRITIC STEEL AT 973 K

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Introduction- Fe-Cr ferritic steels have been widely used for the superheater and reheater in the fossil fuel fired power plant boiler. Inside the boiler tubes, steam oxidation has been occurred and scale spallation brings the industrial trouble such as the blockage of the tube and the erosion of the turbine components. It is necessary to clarify the steam oxidation behavior and scale formation mechanism. Recently developed ferritic steels contain 9-12 mass%Cr and scales formed inside the boiler tubes exhibit duplex structure consisting of Fe_3O_4 as the outer scale and $(Fe,Cr)_3O_4$ as the inner scale, no protective Cr_2O_3 layer forms under the service conditions. The ferritic steels also contain elements, such as Cr, Si and so on, whose affinity for oxygen is stronger than iron's. These elements will be internally oxidized and form internal oxidation zone (IOZ) beneath the inner scale. The microstructure of the inner scale is strongly dependent on the development of the IOZ between the inner scale and the alloy. In this paper, high temperature steam oxidation of Fe-9Cr-0.26Si ferritic steels are carried out at 973 K in the stream of the Ar-15%H_2O for the initial stage and the formation and disappearance of IOZ will be discussed based on the microstructure observation.

Experiment- Fe-9Cr-0.26Si ferritic steel (ASME T91) was used for steam oxidation. The samples were annealed in vacuum at 1173 K for 43.2 ks and ground with wet abrasive papers up to #2000 and polished with 1 μm-alumina paste. Steam oxidation was carried out at 973 K in the stream of Ar-15%H_2O gas mixture (the dew point : 328 K) up to 626.4 ks. After the oxidation, the cross-section of inner scale and IOZ were observed by optical microscopy (OM). The alloy/IOZ interface of the sample oxidized for 61.2 ks and alloy/inner scale interface of the sample oxidized for 626.4 ks were observed by transmission electron microscopy (TEM) with energy dispersive X-ray spectroscopy (EDS). Samples observed by TEM were prepared by focused ion beam method (FIB).

Results and Discussion- Figure 1 shows optical cross-sectional images of samples oxidized (a) 61.2 ks and (b) 626.4 ks. Outer scale formed on the sample oxidized for (b) 61.2 ks was peeled off by the exfoliation tests to investigate scale adherence[1]. On the sample oxidized for (a) 61.2 ks, IOZ formed continuously and grain boundary preferentially attacked. IOZ was not observed at wide range of the alloy/inner scale interface of the sample oxidized for 626.4 ks and scale exhibited duplex structure. From the measurement of the thickness of IOZ and the inner scale, IOZ formed at the initial stage and disappeared within about 100 ks. Figure 2 shows a bright field image (BFI) of TEM at the alloy/inner scale interface of the sample oxidized for 626.4 ks, EDS spectrum and selected area diffraction (SAD) of point A denoted in BFI. White discontinuous sheet-like oxide was also clearly observed at the alloy/inner scale interface. The EDS analysis and SAD analysis showed that the sheet-like oxide was an amorphous SiO_2. The sheet-like oxide was also observed at the alloy/IOZ interface of the sample oxidized for 61.2 ks. Figure 3 shows a bright field image of TEM at the inner scale in the vicinity of the alloy/inner scale interface of the sample oxidized for 626.4 ks, EDS spectra and SAD of points A and B denoted in BFI. At alloy/inner scale interface, white thin film was observed. From the EDS and SAD analysises, the oxide particle at the point A was Fe-oxide with a rock salt structure. The oxide of point B was a Fe-Cr oxide with a spinel structure. From these results, it is concluded that IOZ disappears due to the oxidation of the matrix in IOZ caused by increasing oxygen potential at the IOZ/SiO_2 interface because of extremely low oxygen permeability in the amorphous SiO_2, which formed at the alloy/IOZ interface.

Reference

[1] M. Ueda, M. Nanko, K. Kawamura and T. Maruyama, Materials at High Temperatures, **18**(S), 37-42(2001).

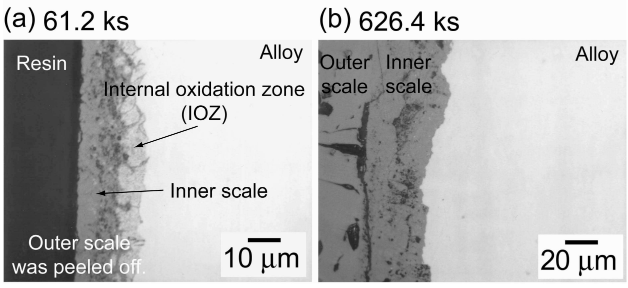

Figure 1 Optical cross-section images of samples oxidized (a) 61.2 ks and (b) 626.4 ks.

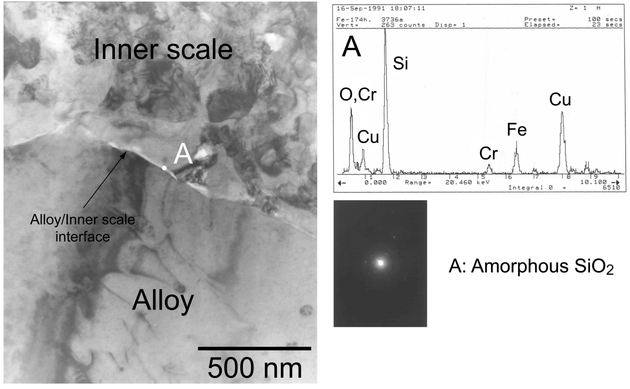

Figure 2 Bright field image of TEM at the alloy/inner scale interface of the sample oxidized for 626.4 ks, EDS spectrum and SAD of point A denoted in BFI.

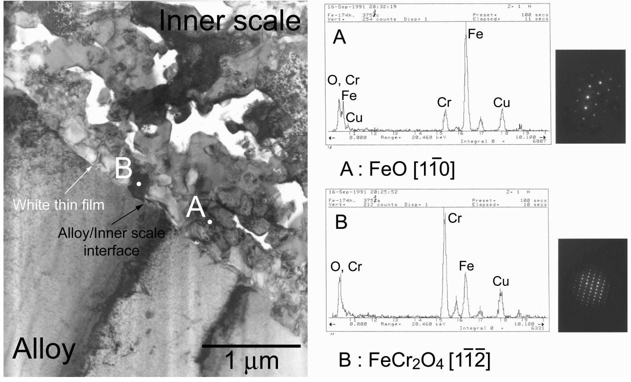

Figure 3 Bright field image of TEM at the inner scale in the vicinity of the alloy/inner scale interface of the sample oxidized for 626.4 ks, EDS spectra and SAD of points A and B denoted in BFI.