Microstructural Evolution of the Boiler Tubes After Long-Term Service

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Materials applied for boiler tubes are in severe conditions such as high temperature and steam oxidation upon long-term service in fossil power plant system. Generally, there are two fundamental classes of heat-resistant steels used in these power plants, the "ferritic/martensitic" and the "austenitic" steels. Ferritic/martensitic steels can be divided into two classed by microstructure and content of additives, one is low alloy steels with $1\sim3\%$ Cr, the other is $9\sim12\%$ Cr martensitic steels $[1\sim3]$. For the usage at elevated temperature over 600°C, austenitic steels with higher content of Cr and Ni are developed. However, it's clear that the mechanical properties of these heat-resistant steels deteriorate upon long term exposure at elevated temperature and steam, which are due to the degradation of the microstructure. Therefore, the characterization of microstructural evolution are considered fundamental for the assessment and reliability of the boiler tubes.

In this study, we investigated three different classes of materials, i.e., low alloy steel T11/T22, 9% Cr martensitic steel T91 and austenitic steel of S304H. All of these boiler tubes are produced by Nippon Steel & Sumitomo Metal Corporation and then were used in the Boryeong and Samcheonpo coal fired power plants in Korea. The nominal composition and service conditions of these steels are listed in Table 1. Attention is paid to the evolution of precipitates, microstructure stability and oxidation behaviors. The microstructural changes were investigated by using various analytical techniques: optical microscopy (OM), Vickers microhardness test, scanning electron microscopy (SEM), electron backscattered diffraction (EBSD), X-ray diffractometers (XRD) and transmission electron microscopy (TEM).

The microstructural evolutions of the boiler tubes can be summarized as:

For low alloy steel T11/T22, the disappearance of original lamellar pearlite structure and the coarsening of $M_{23}C_6$ precipitates are observed after long-term exposure.

For martensitic steel T91, the coarsening of the main strengthening precipitates $M_{23}C_6$ distributed along grain boundary were observed being influenced by the diffusion of Cr, while the fine MX type precipitates are relatively stable at grain interior after long-term exposed.

For austenitic steel S304H, the formation of coarse Cr-rich and brittle σ phase on grain boundary are the dominant microstructure changes after long-term exposure [4].

References:

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Туре	C	Si	Mn	Ni	Cr	Мо	V	Others	Temp. (°C)	Stress (kg/cm ²)	Times (hrs)
T11	0.05~ 0.15	0.50~ 1.00	0.30~ 0.60	-	1.00~ 1.50	0.44~ 0.65	-	-	400	199	214,362
T22	0.05~	$\left \stackrel{\sim}{_{5}} \right \leq 0.50$	0.30~	-	1.90~	0.87~	-	-	491	176	63,000
	0.15		0.60		2.60	1.13			540	199	214,362
T91	0.08~	0.20~ 0.50	0.30~	-0.40	8.00~	0.85~	0.18~	Nb:	550	176	63,000
	0.12		0.60	≥0.40	9.50	1.05	0.25	0.06~0.10	569	255	77,000
S304H	0.07~ 0.13	≤0.30	≤1.00	7.50~ 10.50	17.00~ 19.00	-	-	Nb:0.30~0.60 Cu:2.50~3.50	596	49	54,750
											68,550
											77,000

Table 1. The nominal composition and service conditions of tested steels.





Figure 1. TEM images of (a) T11 after 214,362h service, (b) T91 after 63,000h service, (c) S304H after 77,000h service.