2. State of the art

2.1. Applications

Figure 2-1 shows the various boiler components such as the water wall, superheater, reheater, header and main steam pipe and their typical materials used in a recent fossil fired power plant. The water wall tubes are welded in a panel structure to achieve effective heat exchange in order to produce pressurized steam from water under the super critical conditions in a furnace.
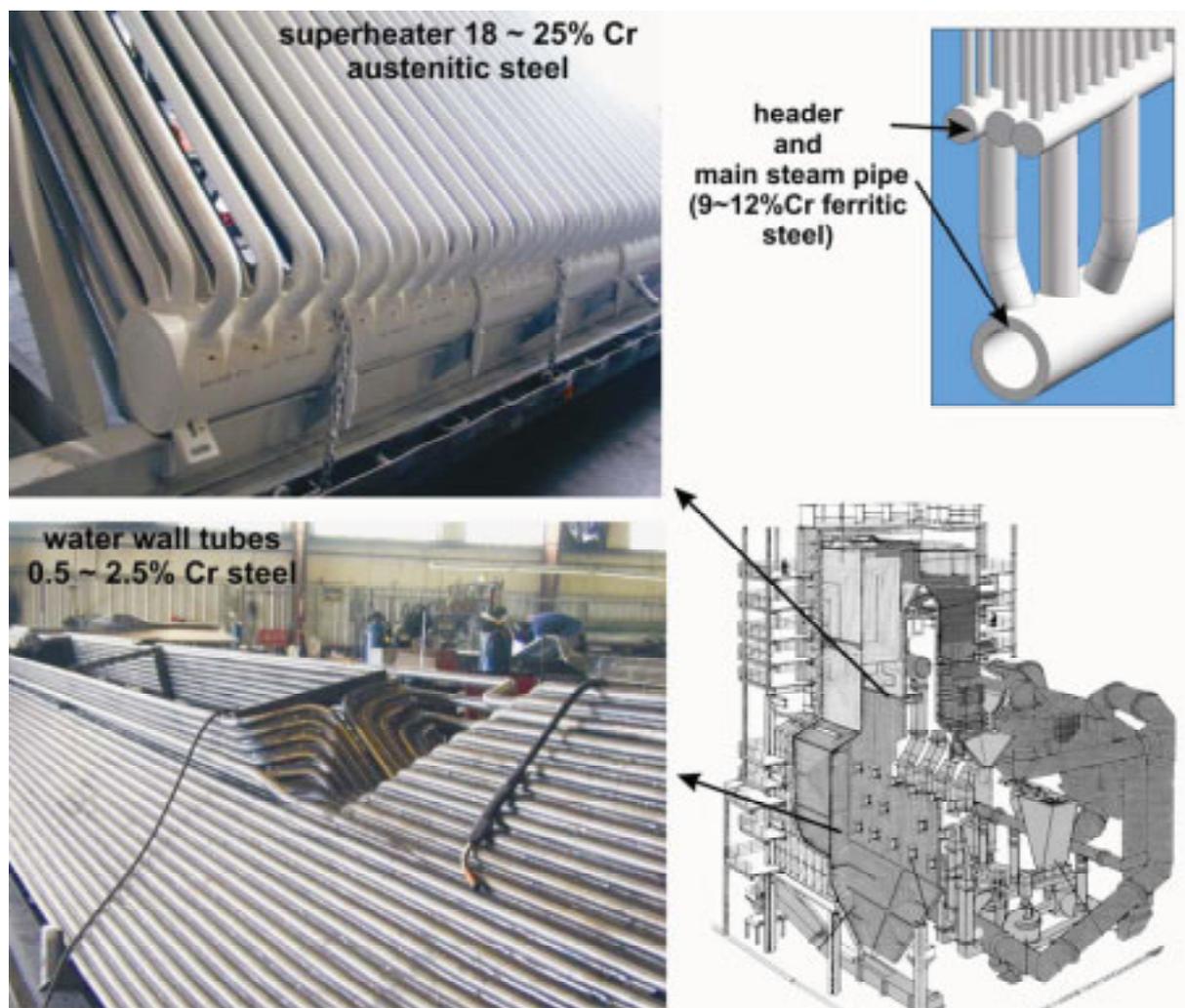

Figure 2-1: Schematic illustration and photographs of a fossil fired boiler and their typical materials.

Conventional steels and Cr-Mo steels are used for the water wall tubes according to the operating temperatures and pressures, which are usually heated up to 500°C in the latest ultra supercritical pressure plants. The steams are superheated in a superheater up to the highest pressure at a designed temperature and reheated in reheater up to the highest temperature that will achieve the designed thermal efficiency. The superheated steams are gathered into a header pipe and transferred to a turbine system through main steam piping. The header and main steam piping should, therefore, be a heavy wall thickness pipe with a large diameter to keep huge amounts of steam pressurized. It is suggested that 9-12% Chromium creep-resistant steels are suitable materials to fulfill mentioned requirements in header and main steam pipes [16, 17].

2.2. 9-12% Cr steels

The development of creep-resistant 9-12%Cr steels was strongly motivated by two major events: (1) the development of thermal power plants for public power supply operating at steam temperatures ranging from 538-566°C during the 1950s and (2) the target to develop low-pollution power plants operating at steam admission temperatures of 600-650°C with supercritical pressures up to 350 bar during the 1980s [40-44]. The steel X20CrMoV12-1 was developed in the 1950s for thin- and thick-walled power station components. The creep strength of X20CrMoV12-1 is based on solid solution hardening and on the precipitation of $M_{23}C_6$ carbides. This steel has been used successfully in power plants over several decades up to temperatures of about 566°C. A newer generation steel, referred to in the literature as modified 9Cr-1Mo or P91 [15], was developed under a USA project in the late 1970s for the manufacture of pipes and vessels for a fast breeder. This steel has been widely used for pipes and small forgings in all new Japanese and European power plants with steam temperatures up to 600°C. The increase of creep strength in comparison to the X20CrMoV12-1 steel is caused by forming thermal stable VN and Nb(C, N) precipitates. A lower Cr content of about 9% also contributes to the higher

creep strength. Similar creep strengths are exhibited by new steels developed for rotors, castings and pipes which are in addition alloyed with Tungsten (W). A further increase in creep strength reveals the steel type P92 which, in addition to the other alloying elements, is alloyed with Boron and has an increased W content. The addition of boron gives thermally stable $M_{23}(C,B)_6$ precipitates whereas the higher W content leads to a higher amount of the Laves phase. Steels for rotors, casings and pipes with higher B contents can be used up to temperatures of about 630°C. Further ferritic 9-12%Cr steels are under development for steam temperatures up to 650°C [45-50]. An overview of the historical development of creep-resistant ferritic 9-12%Cr steels from the 1950s to the 1990s is given in Table 2-1 [17].

2.3. Metallurgy

The standard heat treatment of martensitic-ferritic steels consists of austenitizing and tempering. In austenitizing at temperatures above Ac_1, ferrite (bcc) transforms to austenite (fcc). During cooling from the austenitizing temperature to room temperature, a martensitic structure forms. Tempering results in a ferritic subgrain microstructure with carbides and carbonitrides forming at former austenite boundaries, subgrain boundaries and dislocations within the grains (Figure 2-2).
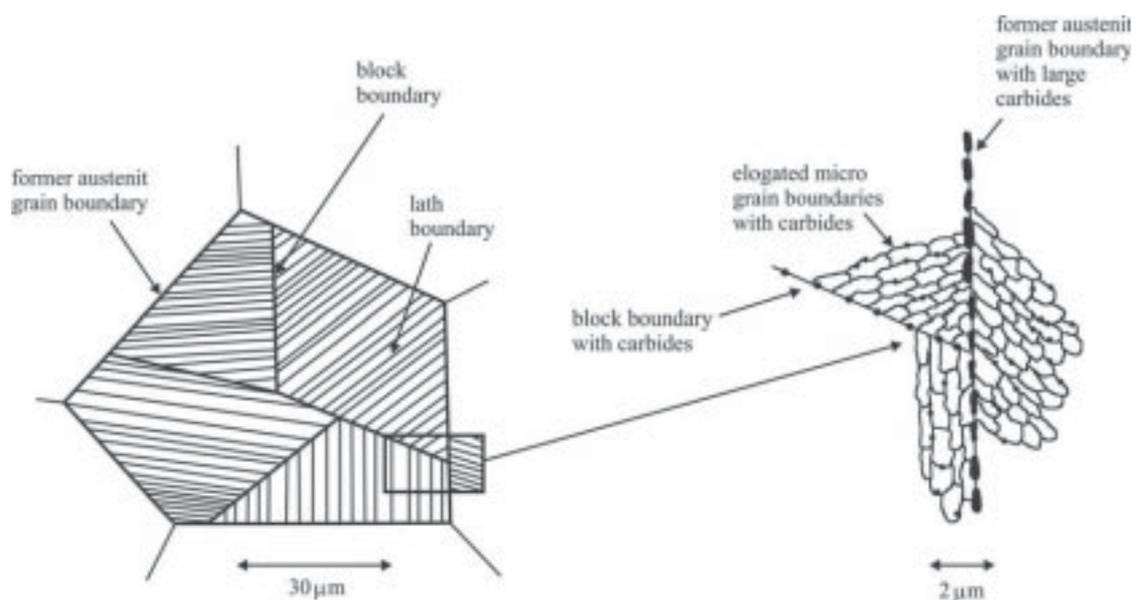

Figure 2-2: Schematic illustration of microstructure of tempered martensite 9-12%Cr creep-resistant steel contains precipitates on the internal interfaces.

Table 2-1: Chemical composition and creep rupture strength at 600°C of basic and advanced creep-resistant steels used in power plants (mass %) [17].

	country	steel	Chemical composition (weight %)									Rupture strength at 600°C (MPa)	
			C	Cr	Mo	Ni	W	V	Nb	N	B	10^4h	10^5h
		Basic steels											
1	Germany	X20CrMoV12-1	0.22	12.0	1.0	0.50	-	0.30	-	-	-	103	59
2	UK	H 46	0.16	11.5	0.65	0.70	-	0.30	0.30	0.05	-	118	62
		FV448	0.13	10.5	0.75	0.70	-	0.15	0.45	0.05	-	139	64
3	France	54T5	0.19	11.0	0.80	0.40	-	0.20	0.45	0.05	-	144	64
4	Japan	TAF	0.18	10.5	1.5	0.05	-	0.20	0.15	0.01	0.035	216	150
5	USA	11%CrMoVNbN	0.18	10.5	1.0	0.70	-	0.20	0.08	0.06	-	165	85
		Advanced steels											
6	USA	P 91	0.10	9.0	1.0	<0.40	-	0.22	0.08	0.05	-	124	94
7	Japan	HCM 12	0.10	12.0	1.0	-	1.0	0.25	0.05	0.03	-		75
8	Japan	TMK 1	0.14	10.3	1.5	0.60	-	0.17	0.05	0.04	-	170	90
		TMK 2	0.14	10.5	0.5	0.50	1.8	0.17	0.05	0.04	-	185	90
9	Europe	X18CrMoVNbB 91	0.18	9.5	1.5	0.05	-	0.25	0.05	0.01	0.01	170	122
10	Europe	X12CrMoWVNbN	0.12	10.3	1.0	0.80	0.80	0.18	0.05	0.06	-	165	90
		E911	0.11	9.0	0.95	0.20	1.0	0.20	0.08	0.06	-	139	98
11	Japan	P92	0.07	9.0	0.50	0.06	1.8	0.20	0.05	0.06	0.003	153	113
12	Japan	P122	0.10	11.0	0.40 1Cu	<0.40	2.0	0.22	0.06	0.06	0.003	156	101
13	Japan	HCM 2S	0.06	2.25	0.20	-	1.6	0.25	0.05	0.02	0.003		80
14	Germany	7CrMoTiB	0.07	2.40	1.0	-	-	0.25	-	0.01	0.004 0.07Ti		60

In order to reach the optimum strength, it is essential to obtain a fully martensitic transformation by cooling to room temperature. Because of the Cr level, carbon diffusion in austenite is slowed down; consequently, the ferrite nose in the CCT (continues cooling transformation) diagram shifts to longer cooling times [51-53]. If the martensitic transformation does not proceed to the end, the so-called retained austenite remaining in the microstructure decreases the strength before tempering. For 9-12%Cr steels, the martensite start (M_s) temperature is about 400°C and M_f is in the range 100-150°C [17].

The composition of the steel controls the M_s and M_f temperatures. A rough estimate of the M_s temperature can be determined by the following empirical equation (2.1):

$$M_s = 550°C - 450C - 33Mn - 20Cr - 17Ni - 10W - 20V - 10Cu - 11Nb - 11Si + 15Co \qquad (2.1)$$

It is essential to have a fine distribution and high thermal stability of the precipitates to obtain a high creep strength in 9-12%Cr steels. The tempering temperature is chosen with respect to properties required for the component. Higher tempering temperatures are used for components like steam pipes, where high ductility during post weld treatment is important [23, 54]. For large components like turbine rotors, lower tempering temperatures are used to take advantage of the resulting high tensile strength [55-57].

Elemental effects

Classification of alloying elements according to their effect in the steel is difficult, because the influence varies so widely with each element addition, depending on the quantity used and other elements present. A useful approach to grouping, however, is based upon the effect of the element on the stability of carbides and the stability of austenite [10, 17, 23, 54]. With this approach, alloying elements are classified as follows:

- Elements that tend to form carbides: Chromium, tungsten, titanium, vanadium, molybdenum, and manganese.

- Elements that tend to graphitize the carbide: silicon, cobalt, aluminum, and nickel. Only a small proportion of these elements can be added to the steel before graphite (which degrade the mechanical properties of the steel) starts forming instead of carbide during processing, unless elements from group 1 are added to counteract the effect.

- Elements that tend to stabilize austenite: manganese, nickel, cobalt, and copper. These elements tend to retard the separation of carbides. They have a crystal lattice (fcc) similar to that of γ-iron, in which they are more soluble than they are in α-iron.

- Elements that tend to stabilize ferrite: Chromium, tungsten, molybdenum, vanadium, and silicon. These elements are more soluble in α-iron than in γ-iron. They diminish the amount of carbon soluble in the austenite and thus tend to increase the volume of free carbide in the steel for a given carbon content. With a certain amount of each of these elements, the austenite phase disappears and ferrite exists from the melting-point down to room temperature.