Materials for Ultrasupercritical Coal Power Plants—Boiler Materials: Part 1

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The efficiency of conventional boiler/steam turbine fossil power plants is a strong function of the steam temperature and pressure. Research to increase both has been pursued worldwide, since the energy crisis in the 1970s. The need to reduce CO_2 emission has recently provided an additional incentive to increase efficiency. Thus, steam temperatures of the most efficient fossil power plants are now in the 600 °C (1112 °F) range, which represents an increase of about 60 °C (108 °F) in 30 years. It is expected that steam temperatures will rise another 50 to 100 °C (90 to 180 °F) in the next 30 years. The main enabling technology is the development of stronger high-temperature materials, capable of operating under high stresses at ever-increasing temperatures. Recently, the EPRI performed a state-of-the-art review of materials technology for advanced boiler/steam turbine power plants (ultrasupercritical power plants). The results of the review show that with respect to boilers, high-strength ferritic 9-12Cr steels for use in thick section components are now commercially available for temperatures up to 620 °C (1150 °F). Initial data on two experimental 12Cr ferritic steels indicate that they may be capable of long-term service up to 650 °C (1112 °F), but more data are required to confirm this. For higher temperatures, austenitic steels and Ni-based alloys are needed. Advanced austenitic stainless steels for use as super and reheater tubing are available for service temperatures up to 650 °C (1112 °F) and possibly 700 °C (1292 °F). Ni-based superalloys would be needed for higher temperatures. None of these steels have been approved by the ASME Boiler Code Group so far. Higher-strength materials are needed for upper water walls of boilers with steam pressure above 24 MPa (3400 psi). A high-strength 2-1/2%Cr steel recently ASME code approved as T-23 is the preferred candidate material for this application. Field trials are in progress. This paper will present the results of the EPRI review in detail, relating to boiler material. Results relating to turbine materials are presented in a companion paper as Part 2.

Keywords boilers, creep, fatigue, material, oxidation, supercritical

1. Introduction and Background

The goal of improving the efficiency of pulverized coal (PC) power plants, by increasing the temperature and pressure of the working fluid (steam), has been pursued for many decades. Figure 1 illustrates the improvements in heat rate that can be achieved by increasing steam temperature and pressure by use of advanced steam conditions.[1] For example, using a 538 °C/18.5 MPa (1000 °F/2600 psi) steam plant as a base case, an efficiency increase of nearly 6% is achieved by changing the steam conditions to about 593 °C/30 MPa (1100 °F, 4300 psi). At 650 °C (1200 °F), the increase in efficiency is as much as 8%.

The desire for increased efficiency led eventually in the late 1950s and early 1960s to the introduction of numerous supercritical boilers operating at or above 565 °C (1050 °F) and 24 MPa (3400 psi) steam pressure. The more famous ones representing extreme conditions among these include a 375 MW plant Drakelow C in the United Kingdom, a 125 MW plant, Philo 6, owned and operated by Ohio Power Co. since 1957, and the Eddystone 1 plant owned and operated by the Philadelphia Electric Co. since 1959. Philo 6 has been operational under design steam conditions of 31 MPa (4500 psi) and a 610/565/538 °C (1150/1050/1000 °F) double reheat temperature cycle.

Eddystone 1 was designed to operate under steam conditions of 34.5 MPa (5000 psi) and 650/565/565 °C (1200/1050/1050 °F), and has been operational since 1959. The plant has operated under derated conditions of 32.4 MPa (4700 psi) and 605 °C (1125 °F) for most of its service life, because of mechanical and metallurgical problems. Most of the problems were due to the use of austenitic steels for heavy section components operating at high temperatures. These steels have low thermal conductivity and high thermal expansion resulting in high thermal stresses and fatigue cracking. These problems and the general low availability of many supercritical plants due to "teething" problems temporarily dampened utility interest in building super- or ultrasupercritical (USC) plants and, consequently, most utilities reverted back to plants with subcritical conditions of about 525 °C (1000 °F) and 17 MPa (2600 psi).

The energy crisis in the mid-1970s and subsequent sharp increase in fuel prices rekindled interest in the development of more efficient PC power stations. The EPRI initiated a study of the development of more economic coal-fired power plants in 1978.[2,3] This study led to a number of research and development activities involving U.S., Japanese, and European manufacturers. These activities focused on developing further the existing high-temperature-resistant ferritic-martensitic 9%Cr and 12%CrMoV steels for the production of rotors, casings and

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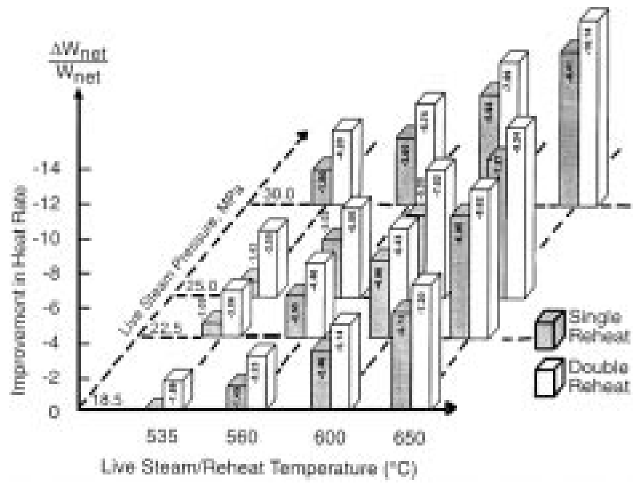

Fig. 1 Improvements in heat rate (efficiency) achieved by increasing steam temperature and pressure using single and double reheat cycles,[1] compared to the base case of 535 °C/18.5 MPa

chests, pipes, and headers capable of operating at inlet steam temperatures of up to 650 °C (1200 °F). One of the early conclusions from this project was that the construction of a plant with a 593 °C (1100 °F)/31 MPa (4500 psi) steam condition would be feasible with only minor evolutionary improvements in materials technology. This has, in fact, proved to be correct, as evidenced by the spate of power plants built in Japan and Europe over the last decade. In Japan, nearly 16 plants, most of them with typical main steam temperature of about 593 °C (1100 °F) and pressure of 24 MPa (3400 psi), are operational. In Europe, nearly a dozen plants are operational with main steam temperature/pressure of 583 °C (1080 °F)/30 MPa (4200 psi).

An improvement in thermal efficiency of the plant not only reduces the fuel costs but also reduces the release of SO_2, NO_x, and CO_2 emissions. The latter is very significant in view of the worldwide agreements to reduce CO_2 emissions by 2010 and the fact that a 1% increase in efficiency of an 800 MW machine would lead to a lifetime reduction in CO_2 approaching one million tonnes.[4] These environmental factors have provided an added incentive to building USC plants in recent years.

Advanced models of combustion turbines being marketed today feature increasingly higher exhaust gas temperatures approaching 593 °C (1100 °F). Harnessing a steam turbine with a combined cycle mode can lead to efficiencies >60%. This is an added incentive for materials development.

A major challenge in constructing USC plants has been in the area of materials technology. Although materials suitable for metal temperatures up to 565 °C (1050 °F) were available, even 20 years ago, further developments were needed to achieve 593 °C (1100 °F) and beyond. Intense research and development efforts were carried out in Japan, the United States, and Europe. In each case, a phased approach was adopted. For instance, in the United States, the phases 0 to 2 were defined as shown in Table 1, where the temperatures given are for the main steam and first and second reheats.

The phase 0 conditions were considered to be achievable with the state-of-the-art technology in 1978 and the phase 1 conditions were considered to be achievable with only minor improvements. The technology needed for phase 2 was considered well beyond reach, and hence, an intermediate goal of 620 to 630 °C (1150 to 1166)/30 MPa (4200 psi) seems to have been established in Europe and Japan. For convenience, this phase will be referred to as 1B in this paper. Although the material developments for phase 2 have not been fully achieved, technology exists today that will enable building plants that can meet phase 1B conditions. This has been made possible by some very exciting progress in developing highly creep resistant 9 to 12%Cr ferritic steels. The objective of this report is to review developments in materials technology related to boilers. A similar review of turbine materials will be presented elsewhere. A complete and more detailed review of materials for all plant components may be found in Ref 5.

Table 1 Steam conditions for coal-fired plants in EPRI program[2]

EPRI program phase	Pressure		Temperature	
	MPa	psig	°C	°F
0	31.0	4500	566/566/566	1050/1050/1050
1	31.0	4500	593/593/593	1100/1100/1100
1B	31.0	4200	620/620/620	1150/1150/1150
2	34.5	5000	649/649/649	1200/1200/1200

2. Boiler Materials Requirements

The key components whose performance is critical for USC plants are high-pressure steam piping and headers, superheater (SH) tubing, and waterwall tubing. Steam pipes carry high-pressure, high-temperature steam from the boiler to the turbine. Headers are also pipes, but contain numerous tube penetrations which either bring in/take out steam to/away from the header. Headers thus serve as receptacle/distribution systems for steam. SH tubes carry steam and waterwalls are tube panels carrying water. All of these components have to meet creep strength requirements. In addition, pipes and headers, being heavy section components, are subject to fatigue induced by thermal stresses. Ferritic/martensitic steels are preferred because of their lower coefficient of thermal expansion and higher thermal conductivity compared to austenitic steels. Many of the early problems in the USC plants were traceable to the use of austenitic steels that were very prone to thermal fatigue. Research during the last decade has, therefore, focused on developing cost-effective, high-strength ferritic steels that could be used in place of austenitic steels. This has resulted in ferritic steels capable of operating at metal temperatures up to 620 °C (1150 °F), with good weldability and fracture toughness.

Superheater and reheater (SH/RH) tubing application calls for high creep strength, thermal fatigue strength, weldability, resistance to fireside corrosion/erosion, and resistance to steamside oxidation and spallation. Thermal fatigue resistance as well as cost considerations would dictate the use of ferritic/martensitic steels. Unfortunately, the strongest of these steels that can be used up to a metal temperature of 620 °C (1150

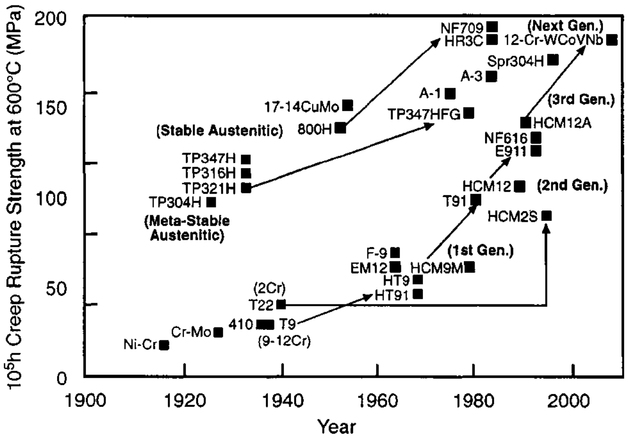

Fig. 2 Historic evolution of materials in terms of increasing creep-rupture strength

°F),[1] purely from a creep strength point of view, are still limited by fireside corrosion to a metal temperature of 593 °C (1100 °F). This corresponds to a steam temperature of about 565 °C, since the SH/RH metal temperature can exceed the steam temperature by as much as 28 °C (50 °F). Excessive corrosion of ferritic steels caused by liquid iron-alkali sulfates in the tube deposits is an acute concern in the United States, where high sulfur corrosive coals are used more frequently than elsewhere. Therefore, high-strength ferritic stainless steels such as T-91 are infrequently used in the United States. The standard practice is to use T-22 for the lower temperatures and SS304H or SS347 for the highest temperatures.

With respect to waterwall tubing, the concern is twofold. High supercritical pressures and the use of high heat release furnaces will increase the waterwall temperatures to the point that easily weldable low alloy steels such as T-11[2] (1.25Cr, 0.5Mo) have insufficient creep strength. Higher-strength steels, such as T-91, are available, but require postweld heat treatments. The second concern is corrosion. Recent results in the United States on boilers retrofitted with low NO_x burner systems, using overfire air, indicate that the present low-alloy steels can suffer from excessive corrosion, as high as 2 mm/year. Weldable high-strength alloys clad or overlaid with high Cr alloys have to be utilized to reduce or eliminate excessive corrosion.[6]

2.1 Historical Evolution of Steels

Masuyama has presented an excellent historical perspective on the development of steels for power plants, as shown in Fig. 2.[7] The figure shows 10^5 h creep-rupture strength at 600 °C (1112 °F) by year of development. They classify the ferritic steel development in terms of four generations, as shown in Table 2.

[1]All temperatures cited in the paper are steam temperatures unless otherwise specified. For header and piping, metal temperature is nearly equal to the steam temperature. For tubing, the metal temperature is generally higher than the steam temperature by up to 28 °C (50 °F).
[2]ASME boiler code steel designation, equivalent pipe steels are designated as P-11, 92, *etc.*, while forgings are designated F-11, 91, *etc.*

In the field of austenitic steels, efforts were made from the 1970s to the early 1980s to improve conventional 18Cr-8Ni series steels originally developed as corrosion-resistant materials for chemical use, mainly with respect to their creep strength. Another goal pursued from the 1980s to the early 1990s was to improve the creep strength of conventional 20-25Cr series steels having superior oxidation and corrosion resistance.

2.1.1 Evolution of Ferritic Steels. Ferritic steel developments are mostly aimed at their use for thick section pipes and headers. Table 3 shows the chemical compositions of ferritic steels for power boilers. The systematic evolution of these steels has been thoroughly reviewed by Masuyama, as shown in Fig. 3.[7] Among the 9%Cr steels fully commercialized, the P91 steel has the highest allowable stress and has been extensively used all over the world as a material for headers and steam pipes in USC plants operating at steam temperatures up to 593 °C (1100 °F). Alloy NF616 (P-92), developed by substituting part of the Mo in P91 by W, has an even higher allowable stress and can be operated up to steam temperatures of 620 °C (1150 °F). Alloy E911 is a European alloy similar in composition to NF616 with similar capabilities. Beyond 620 °C (1150 °F), the 9%Cr steels become limited by oxidation resistance and 12%Cr steel and austenitic steels have to be used.

Among the 12%Cr steels, HT91 has been widely used for tubing, headers, and piping in Europe. Use of the steel in Japan and the United States has been limited due to its poor weldability. Alloy HCM12 is an improved version of HT91 with 1%W and 1%Mo, having a duplex structure of δ-ferrite and tempered martensite with improved weldability and creep strength. Further increases in creep strength by substituting more of the Mo with W and addition of Cu have resulted in alloy HCM12A (P-122), which can be used for header and piping up to 620 °C (1150 °F). Two alloys, NF12 and SAVE12, having an even higher creep strength than HCM12A are in the developmental stage. Alloy NF12 contains 2.5%Co, 2.6%W, and slightly higher B compared to HCM12A. Alloy SAVE12 contains 3%Co, 3%W, and minor amounts of Ta and Nb. These latter elements contribute to strengthening by producing fine and stable nitride precipitates. Alloy HCM2S (T-23), a low carbon 2-1/4Cr-1.6W steel with V and Nb, is a cost-effective steel with higher creep strength than T22. Because of its excellent weldability without pre- or postweld heat treatment, it is a good candidate for waterwall tubing.

The role of alloying elements in development of the ferritic steels has been extensively investigated. Tungsten, molybdenum, and cobalt are primarily solid solution strengtheners. Vanadium and niobium contribute to precipitation strengthening by forming fine and coherent precipitation of M(C, N)x carbonitrides in the ferrite matrix. Vanadium also precipitates as VN during tempering or during creep. The two elements are more effective in combination at levels of about 0.25%V and 0.05%Nb. Chromium contributes to solid solution strength as well as to oxidation and corrosion resistance. Nickel improves the toughness but at the expense of creep strength. Partial replacement of Ni by Cu helps stabilize the creep strength. Carbon is required to form fine carbide precipitates but the amount needs to be optimized for good weldability.

Atom probe results have shown that boron enters the structure of $M_{23}C_6$ and boron segregates to $M_{23}C_6$-matrix interface.[8]

Table 2 Evolution of four generations of ferritic steels (based on Ref 7)

Generation	Years	Alloy modifications	Strength 10^5 h creep rupture achieved, MPa	Example alloys	Maximum metal use temperature, °C
1	1960–1970	Addition of Mo or Nb, V to simple 12Cr and 9Cr Mo steels	60	EM12, HCM9M, HT9, Tempaloy F9, HT91	565
2	1970–1985	Optimization of C, Nb, V	100	HCM12, T91, HCM2S	593
3	1985–1995	Partial substitution of W for Mo	140	P-92, P-122 (NF616, HCM12A)	620
4	Emerging	Increase of W and addition of Co	180	NF12, SAVE12	650

Table 3 Nominal chemical compositions of ferritic steels for boilers

		Specification		Chemical Composition (mass%)												
	Steels	ASME	JIS	C	Si	Mn	Cr	Mo	W	Co	V	Nb	B	N	Others	Manufacturers
1-1/4 Cr	T11	T11	···	0.15	0.5	0.45	1.25	0.5	···	···	···	···	···	···	···	
	NFIH	···	···	0.12	···	···	1.25	1.0	···	···	0.20	0.07	···	···	···	Nippon Steel
2Cr	T22	T22	STBA24	0.12	0.3	0.45	2.25	1.0	···	···	···	···	···	···	···	
	HCM2S	T23	STBA24J1	0.06	0.2	0.45	2.25	0.1	1.6	···	0.25	0.05	0.003	···	···	Sumitomo
	Tempaloy F-2W	···	···	···	···	···	2.0	0.6	1.0	···	0.25	0.05	···	···	···	NKK
9Cr	T9	T9	STBA26	0.12	0.6	0.45	9.0	1.0	···	···	···	···	···	···	···	Vallourec Mannesman
	HCM9M	···	STBA27	0.07	0.3	0.45	9.0	2.0	···	···	···	···	···	···	···	Sumitomo
	T91	T91	STBA28	0.10	0.4	0.45	9.0	1.0	···	···	0.20	0.08	···	0.05	0.8Ni	Vallourec Mannesman
	E911	···	···	0.12	0.2	0.51	9.0	0.94	0.9	···	0.20	0.06	···	0.06	0.25Ni	Sumitomo
	NF616	T92	STBA29	0.07	0.06	0.45	9.0	0.5	1.8	···	0.20	0.05	0.004	0.06	···	Nippon Steel
12Cr	HT91	(DIN × 20CrMoV121)		0.20	0.4	0.60	12.0	1.0	···	···	0.25	···	···	···	0.5Ni	Vallourec Mannesman
	HT9	(DIN × 20CrMoWV121)		0.20	0.4	0.60	12.0	1.0	0.5	···	0.25	···	···	···	0.5Ni	Vallourec Mannesman
	Tempaloy F12M	···	···	···	···	···	12.0	0.7	0.7	···	···	···	···	···	···	NKK
	HCM12	···	SUS410J2TB	0.10	0.3	0.55	12.0	1.0	1.0	···	0.25	0.05	···	0.03	···	
	TB12	···	···	0.08	0.05	0.50	12.0	0.50	1.8	···	0.20	0.05	0.30	0.05	0.1Ni	
	HCM12A	T122	SUS410J3TB	0.11	0.1	0.60	12.0	0.4	2.0	···	0.20	0.05	0.003	0.06	1.0Cu	Sumitomo
	NF12	···	···	0.08	0.2	0.50	11.0	0.2	2.6	2.5	0.20	0.07	0.004	0.05	···	Nippon Steel
	SAVE12	···	···	0.10	0.3	0.20	11.0	···	3.0	3.0	0.20	0.07	···	0.04	0.07Ta, 0.04Nd	Sumitomo

It has also been suggested that boron helps reduce coarsening of $M_{23}C_6$ and that boron also assists in nucleation of VN, the mechanism of "latent creep resistance."[8]

Cobalt is an austenite stabilizer and developers of NF12 suggest that is why they used cobalt additions.[8] Cobalt is known to delay recovery on tempering of martensitic steels. Cobalt also promotes nucleation of finer secondary carbides on tempering. This is attributed both to its effect on recovery and its effect on the activity of carbon.[8] Cobalt also slows coarsening of alloy carbides in secondary hardening steels. This was suggested to be the result of cobalt increasing the activity of carbon and cobalt not being soluble in alloy carbides. Results of Hidaka suggest that Co has a positive effect on creep-rupture stress.

2.1.2 Evolution of Austenitic Steels. Austenitic steels are candidates primarily in the finishing stages of SH/RH tubing, where oxidation resistance and fireside corrosion become important in addition to creep strength. From a creep strength point of view, T91 is limited to 565 °C steam (metal 593 °C) and NF616, HCM12A, and E911 are limited to 593 °C steam (metal 620 °C). Even the strongest ferritic steel today is limited to 593 °C (1150 °F) (metal temperature) from an oxidation point of view. At temperatures above these, austenitic steels are required. Hence, there has been considerable development with respect to austenitic stainless steels. In actual practice in the United States, SS304M and SS347 are widely used instead of T-91 in superheater applications, mainly because they are easier to weld, whereas the cost difference is relatively small.

Table 4 lists the compositions of various stainless steels for SH/RH tube applications. The steels fall into four categories: 15Cr, 18Cr, 20-25Cr, and higher Cr stainless steels. The various stages in the evolution of these steels have consisted of initially adding Ti and Nb to stabilize the steels from a corrosion point of view, then reducing the Ti and Nb content (understabilizing) to promote creep strength rather than corrosion, followed by Cu additions for increased precipitation strengthening by fine precipitation of a Cu-rich phase. Further trends have included austenite stabilization using 0.2% nitrogen and W addition for

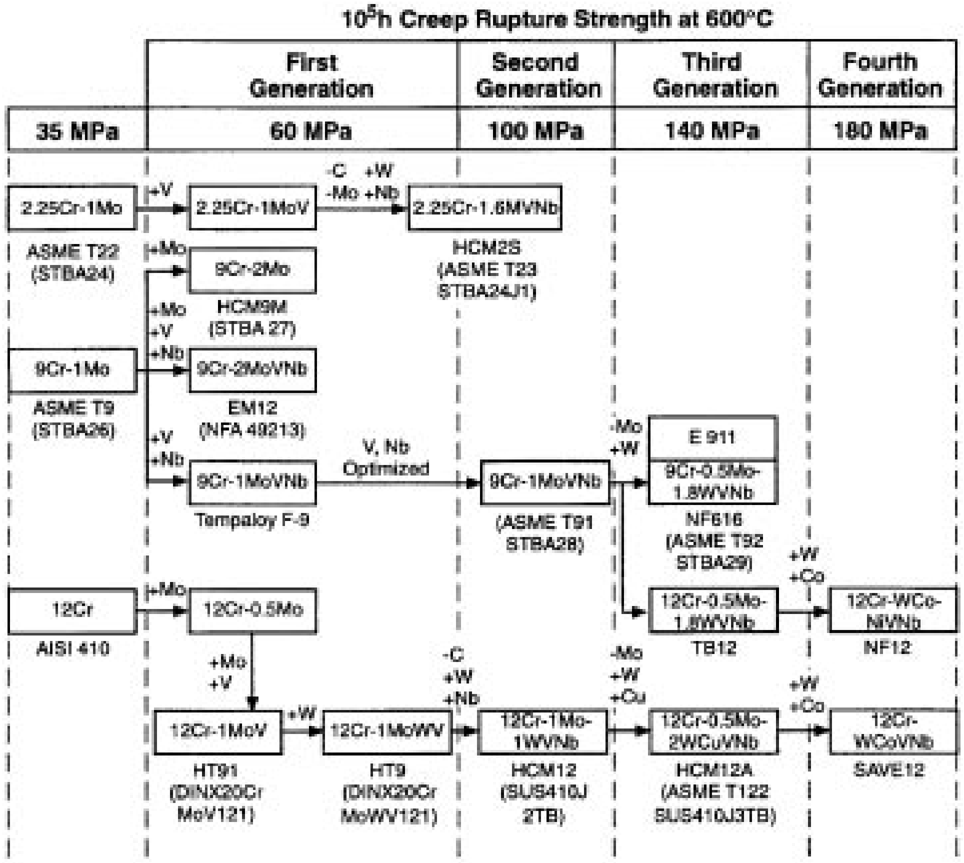

Fig. 3 Evolution of ferritic steels for boilers

Table 4 Nominal chemical compositions of austenitic steels for boiler (wt.%)

	Specifications													
	ASME	JIS	C	Si	Mn	Ni	Cr	Mo	W	V	Nb	Ti	B	Others
18Cr-8Ni	TP304H	SUS304HTB	0.08	0.6	1.6	8.0	18.0	···	···	···	···	···	···	···
	Super 304H	SUS304J1HTB	0.10	0.2	0.8	9.0	18.0	···	···	···	0.40	···	···	3.0Cu, 0.10N
	TP321H	SUS321HTB	0.08	0.6	1.6	10.0	18.0	···	···	···	···	0.5	···	···
	Tempaloy A-1	SUS321J1HTB	0.12	0.6	1.6	10.0	18.0	···	···	···	0.10	0.08	···	···
	TP316H	SUS316HTB	0.08	0.6	1.6	12.0	16.0	2.5	···	···	···	···	···	···
	TP347H	SUSTP347HTB	0.08	0.6	1.6	10.0	18.0	···	···	···	0.8	···	···	···
	TP347 HFG		0.08	0.6	1.6	10.0	18.0	···	···	···	0.8	···	···	···
15Cr-15Ni	17-14CuMo		0.12	0.5	0.7	14.0	16.0	2.0	···	···	0.4	0.3	0.006	3.0Cu
	Esshete 1250		0.12	0.5	6.0	10.0	15.0	1.0	0.2	1.0	···	0.06	···	···
	TempaloyA-2		0.12	0.6	1.6	14.0	18.0	1.6	···	···	0.24	0.10	···	···
20-25Cr	TP310	SUS310TB	0.08	0.6	1.6	20.0	25.0	···	···	···	···	···	···	···
	TP310NbN (HR3C)	SUS310J1TB	0.06	0.4	1.2	20.0	25.0	···	···	···	0.45	···	···	0.2N
	NF707*		0.08	0.5	1.0	35.0	21.0	1.5	···	···	0.2	0.1	···	···
	Alloy 800H	NCF800HTB	0.08	0.5	1.2	32.0	21.0	···	···	···	···	0.5	···	0.4Al
	Tempaloy A-3(a)	SUS309J4HTB	0.05	0.4	1.5	15.0	22.0	···	···	···	0.7	···	0.002	0.15N
	NF709(a)	SUS310J2TB	0.15	0.5	1.0	25.0	20.0	1.5	···	···	0.2	0.1	···	···
			0.10	0.1	1.0	18.0	23.0	···	1.5	···	0.45	···	···	3.0Cu, 0.2N
High Cr-High Ni	SAVE25(a)													
	CR30A(a)		0.06	0.3	0.2	50.0	30.0	2.0	···	···	···	0.2	···	0.03Zr
	HR6W(a)		0.08	0.4	1.2	43.0	23.0	···	6.0	···	0.18	0.08	0.003	···
	Inconel 617		···	0.40	0.4	54.0	22.0	8.5	···	···	···	···	···	12.5Co, 1.2Al
	Inconel 671(b)		0.05	···	···	51.5	48.0	···	···	···	···	···	···	···

(a) Not ASME code approved
(b) Low-strength material for use in coextruded tubing. For weld overlays, IN72 (44%Cr-bal Ni) is the matching weld wire

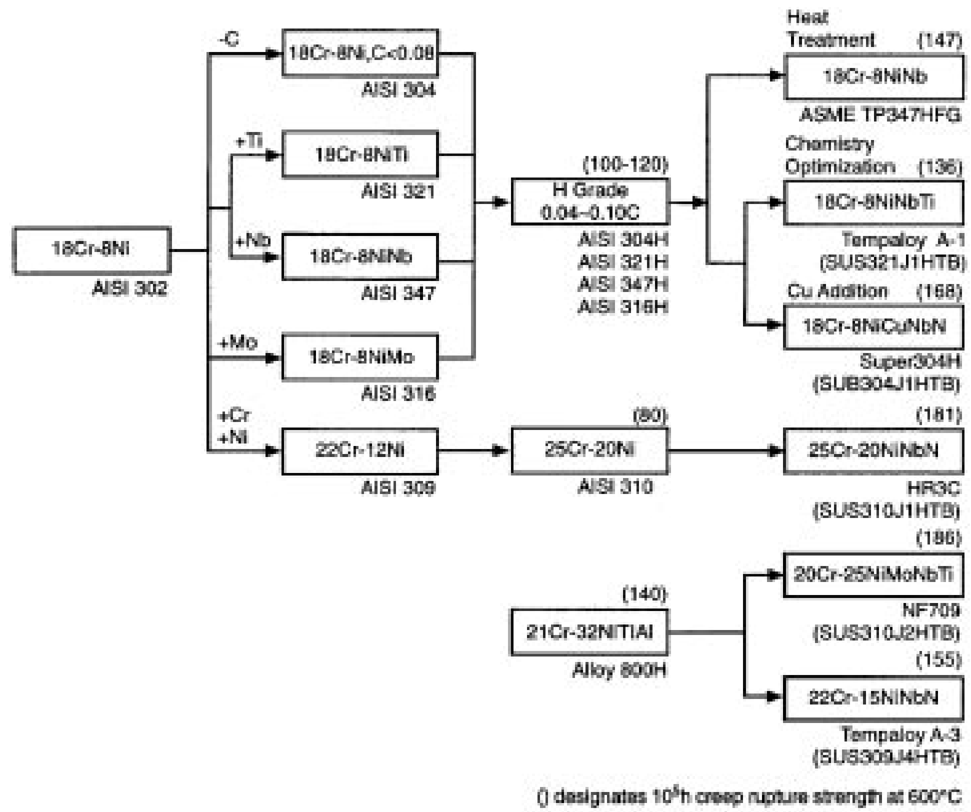

Fig. 4 Evaluation of authentic steels for boilers

solid solution strengthening. This development sequence is illustrated in Fig. 4.[7]

2.2 Choice of Materials for Headers and Steam Pipes

A summary of candidate ferritic steels for thick section applications at various temperatures is shown in Table 5. Material-property requirements for headers and steam pipes are likely to be similar, and hence, they have been grouped together. Some minor differences exist that may affect material selection. The steam temperature is likely to be much more uniform in steam pipes, but subject to time-dependent and location-dependent fluctuations in headers. Hence, the thermal-fatigue-strength requirements are greater for headers than for steam pipes. Self-weight-induced stresses are less important for headers than for steam pipes, permitting heavier-wall construction and an attendant higher temperature/pressure capability for a given material when used in headers. One of the most important differences is that headers have many welded attachments to inlet stub tubes from reheaters and superheaters and intersections of outlet nozzles connecting pipework. Depending on the selection of materials for the SH/RH tubes and the header piping, dissimilar-metal welded joints may be required. The integrity of such austenitic-to-ferritic welds when 9 to 12%Cr steels form the ferritic components needs to be more thoroughly investigated.

Headers and pipes have traditionally been made from low alloy steels such as P11 and P22 in the United States. Even in conventional boilers, such headers can fail due to thermal fatigue cracking, caused by cycling. A common failure mode is the cracking of the ligaments between the tube boreholes.[9] The use of higher temperatures and pressures can only increase the problem. Previous attempts to use austenitic steels have not been successful due to high thermal expansion of these steels.

Several candidate ferritic steels have emerged succeeding the P11 and P22 steels that are capable of operation up to 593 °C (1100 °F). These include HT9, HT91, HCM9M, HCM12, and P91. Alloys HT9 and HT91 are well-established steels with an extensive stress-rupture database, which exceeds 10^5 h at temperatures in the range 500 to 600 °C (930 to 1110 °F) for all product forms. There is also extensive operating experience (>20 years) in Germany, Belgium, Holland, South Africa, and Scandinavia for steam temperatures up to 540 °C (1000 °F) and some limited experience on a few small units with steam temperatures from 560 to 580 °C (1040 to 1075 °F). This experience generally has been satisfactory. Difficulties have, however, been reported during fabrication and particularly during welding and postweld heat treatment. This arises because the relatively high carbon content of the steel (0.2%) and the correspondingly low M_s temperature promote the possibility of austenite retention after welding, high residual stresses, and cracking prior to and during stress relief. It is reported that these problems have been overcome by careful control of preheat treatment and postweld heat treatment backed up by vigorous quality control. Difficulties have also been reported when the material has been given inadequate solution heat treatment. Due to these concerns, these alloys have not found much favor in the United States, the United Kingdom, or Japan. Alloys

Table 5 Candidate materials for advanced supercritical plants for various steam conditions

Component	Phase 0 31 MPa (4500 psi) 565/565/565 °C (1050/1050/1050 °F)	Phase 1 31 MPa (4500 psi) 593/593/593 °C (1100/1100/1100 °F)	Phase 1B 31 MPa (4500 psi) 620/620/620 °C (1150/1150/1150 °F)	Phase 2 34.5 MPa (5000 psi) 650/650/650 °C (1200/1200/1200 °F)
Headers/steam pipes	P22, HCM2S (P23), P91, P92, P122	P91, P92, P122, E911	P92, P122 E911, NF12, SAVE12	SAVE12(c) NF12(c)
Finishing noncorrosive SH	T91,304H, 347	TP347 HFG Super 304 H/P-122(a)	NF 709 Super 304 H	NF 709 Inconel 617
Corrosive	310 NbN (HR3C)	310 NbN (HR3C) SS347/IN72(b)	310 NbN (HR3C) Super 304H/IN72(b)	Cr 30A NF 709/IN72(b)
Finishing RH	Same as SH	Same as SH	Same as SH	Same as SH
Waterwall				
Lower wall	C steel	T11, T12, T22	Same as phase 1	
Upper wall	T11, T12, T22	T23, HCM12	Same as phase 1	
For low NO_x boilers + high S coal	Clad with alloy containing >20%Cr or chromized	Same as phase 0	Same as phase 0	Same as phase 0

(a) High strength ferritic alloys with 9%Cr are suitable for steam piping and headers, but may suffer excessive fire side oxidation. 12Cr steels may be suitable, but further testing is needed
(b) IN72 (44Cr, bal Ni) weld overlay for corrosion protection
(c) Developmental alloy

with improved weldability characteristics, such as HCM12M, have been adequately characterized for tubing and large-diameter, thick-wall pipes.

With regard to the 9Cr-2Mo steel (HCM9M), the feasibility of fabrication of large-diameter, thick-wall piping and application to in-plant header and main steam piping was first demonstrated in 1985.[10] The practical use of this material has been easy because its simple composition lends fabricability and weldability comparable to those of low-alloy steels. The toughness of large-diameter pipes has been found to be over 102 J/cm^2 (460 ft lb/in.^{2}) at 0 °C (32 °F). Allowable stresses are comparable to those for the HT9 alloy, but lower than those for P91. Service experience of nearly 25 years has been accumulated since the alloy was developed, with about 2000 tons having been produced specifically for SH/RH tubes and steam pipes.

The modified 9Cr alloy, P91, appears to be quite superior to HT9, HT-91, and HCM9M in terms of creep-rupture strength and is, hence, the most promising candidate for use in header and steam piping for temperatures up to 595 °C (1100 °F). One of the early applications was by the Chubu Electric Power Company (Kawagoe Power Station, units 1 and 2) for 565 °C (1050 °F) steam conditions as headers and steam pipes. A majority of the recent European supercritical plants have utilized P91 as main steam and reheat piping. Numerous retrofit applications have also been carried out for headers/steam pipes. The alloy was approved by the ASME Boiler Code Committee for various uses between 1983 and 1986 as T, P, and F-91.[3] Since that time, the alloy has found applications worldwide and is available from many sources, since the composition is not proprietary. It is especially popular in Europe, where it proved superior in creep strength as well as weldability, compared to the well-known HT91 steel, used in supercritical boilers.

The high creep strength of grade 91 steel is due to small additions of V, Nb, and N, which lead to the precipitation of $M_{23}C_6$ carbides and (Nb, V) carbonitrides, in addition to solution strengthening by Mo. Very extensive studies were made worldwide to evaluate the suitability of P-91 for heavy section components. These included manufacturing studies, welding trials, both similar and dissimilar, bending trials, both hot and cold, and various mechanical tests, on both virgin and aged samples.[11,12] The net result of all these tests is that P-91 is now the preferred heavy-section material for supercritical boilers worldwide. However, most designers feel the use of P-91 will probably be limited to steam conditions of about 593 °C/25 MPa. This is especially the case in Europe, where the allowable creep strength is about 10% lower than in Japan and the United States.

Fortunately, Professor Fujita in Japan discovered that the creep strength of 9-12Cr, Mo, V, and Nb steels can be raised by about 30% through partial substitution of Mo by W.[13] This has spawned another round of intensive alloy development and evaluation worldwide.[14] Two of these steels, a 9Cr steel developed by Nippon Steel NF616 (P-92) and a 12Cr steel HCM12A developed by Sumitomo Metals (P-122), have been approved for use in boiler heavy-section components by ASME. Another W-containing steel, E-911, is in advanced development in Europe. The allowable strength of the new steels at 600 °C is about 25% higher than that of P-91. Thus, these steels should allow steam temperatures up to 620 °C and pressures up to 34 MPa.

Figure 5 shows a plot of the allowable stress at various temperatures for ferritic steels.[7] The figure clearly shows the enormous advances in the materials technology that have been made in the last 20 years. Especially at the higher temperatures, the most advanced steels show allowable stresses that are nearly 2.5 to 3 times that of the workhorse steel in conventional plants, *i.e.*, 2-1/4Cr-1Mo steel (P22). The layering of the alloys into the different generations described earlier is also evident. The alloys HCM12A (P122), NF616 (P92), and E911 emerge as

[3]T = tubing, P = pipe, F = forging.

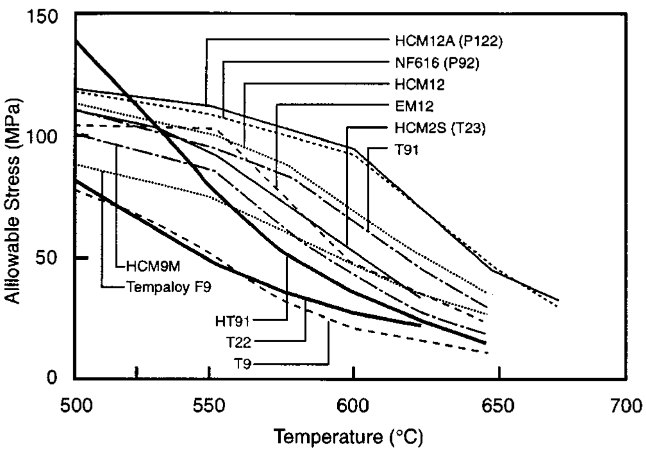

Fig. 5 Comparison of allowable stresses of ferritic steels for boiler

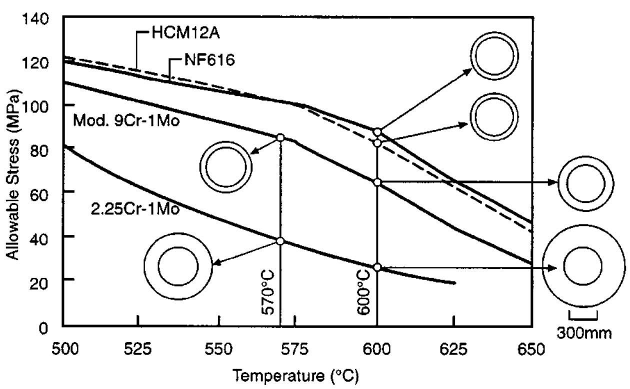

Fig. 6 Comparison of allowable stresses and sectional view of main steam pipes designed at 570 and 600 °C

the three highest strength alloys suitable for USC plants up to 620 °C, followed by T91, HCM12, EM12, HCM9M, and HT91, suitable for intermediate temperatures up to 593 °C, followed by T22 for use up to 565 °C (1050 °F). NF12 and SAVE12 are still developmental, but are expected to meet the phase 2 goals. This rationale has been incorporated in the materials selection shown in Table 5. More recently, Fujita has reported on a modified version of NF12 with aluminum content below 20 ppm and Ni content below 0.1% that has creep properties higher than NF12. This alloy is believed to have adequate strength for 650 °C applications.[15]

A very interesting fact is that application of the new steels may actually result in a capital cost reduction. Figure 6 shows the allowable design stresses and a comparison of the relative wall thicknesses at various temperatures.[16] At any given temperature, higher allowable stresses for a material permits design of thinner wall headers/pipes. This not only reduces thermal stresses, but also reduces cost. From Fig. 6, section thicknesses and materials costs can be calculated as a function of temperature and pressure. Figure 7 shows the results for a pressure of 31 MPa (4500 psi). The cost of using high-strength steel becomes lower than that of P-22 steel at about 520 °C. The cost of using the W-containing steel is lower than that of P-91 above about 550 °C. These relations do not change very much

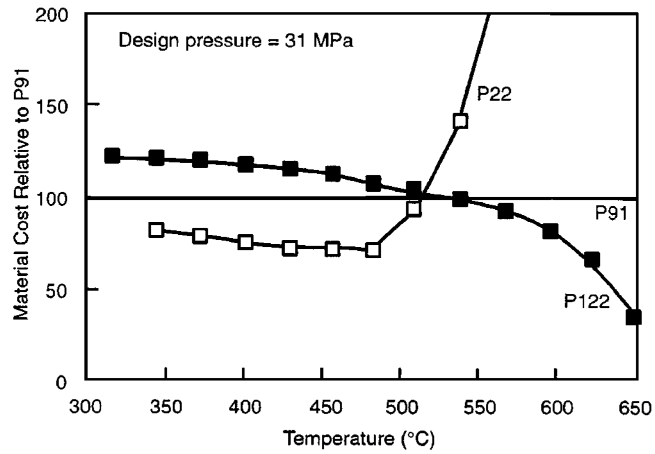

Fig. 7 Cost of P-22, P-91, and P-122 steels header materials as a function of temperature at 31 MPa steam pressure

with decreasing pressure down to 20 MPa (3000 psi). Actual fabricated and installed cost differences should be even larger as the thinner pipes need less welding and are easier to install. Fewer supports are needed, thus reducing costs further.

A sample list of European installations using the most advanced steels, NF616 (P92), HCM12A (P122), and E911, is shown in Table 6.[17] There is considerable interest in using these alloys for outlet headers and main steam and reheat pipe work. Full-scale headers have been installed in a 415 MW supercritical plant under consideration by the Danish utility, ELSAM. Headers using P92 and P122 have been constructed and installed. Two of the headers will be tested under accelerated high-temperature conditions in a high-pressure cell operated by Mitsubishi Heavy Industries.

Some additional design considerations in applying the advanced ferritic steels are as follows.

- The high-temperature strength of the advanced alloys, *e.g.*, NF616, HCM12A, and E911 (P-92, P-122, and E911), is essentially the same as that of austenitic alloys. But oxidation resistance is less than that of austenitic alloys. This parameter of advanced 9 to 12Cr alloys must be more fully evaluated prior to application to high-temperature parts.
- Postweld heat treatment is always required for welded joints of advanced 9 to 12Cr alloys to ensure minimal stress and optimal ductility. Design must be made to reduce field heat treatment as much as possible to keep production and postweld heat treatment costs minimal.
- In the weldment of dissimilar alloys, material selection must be based on consideration of postweld heat treatment temperature. For example, the 9Cr-1Mo alloy and 1Cr-0.5Mo steel would not be acceptable materials for the case of joints in a longitudinal direction; measures must be taken to consider the behavior of welded joint creep-rupture strength.
- Last, but not least, is the apparent susceptibility of ferritic steel welds to type IV cracking, which occurs at the edges of fine-grained HAZ material adjacent to unaffected parent material. Susceptibility to this has been clearly demonstrated for 1/2CrMoV, 2-1/4Cr-1Mo, and 9Cr-1Mo (T91)

Table 6 Application of new tungsten-bearing steels in European power stations[17]

Power station	Material grade	Size	Component	Steam conditions °C/MPa	Installation
Vestkraft unit 3	P92 (NF616)	ID 240 × 39	Straight pipe steam main	560/25	1992
Nordjyllands-vaerket	P92 (NF616) P122 (HCM12A)	ID 160 × 45	Header	582/29	1996
Schkopau unit B	E911	ID 550 × 24	Induction hot reheat bend	560/7	1996
Staudinger unit 1	E911	ID 201 × 22	Induction main steam bend	540/21.3	1996
Skaerbaek unit 3	E911	ID 230 × 60	Induction main steam bend	582/29	1996
GK Kiel	P92	ID 480 × 28	Header	545/5.3	1997
VEW	E911	OD 31.8 × 4	Superheater	650	1998
Westfalen	E911	ID 159 × 27	Steam loop	650/18	1998
Westfalen	P92	ID 159 × 27	Steam loop	650/18	1998

steels. Safety margins of 10 to 20% are sometimes adopted to provide for this mechanism. Since the problem in girth welds is primarily associated with bending stresses, the problem can be overcome by proper plant design and maintenance. This issue has, therefore, been generally glossed over.

2.3 Choice of Materials for Superheater/Reheater Tubes

The superheater tubes in the boiler are likely to undergo the most severe service conditions and must meet stringent requirements with respect to fireside corrosion, steamside oxidation, creep-rupture strength, and fabricability. In addition, they must be cost effective. Based on these issues, candidate materials for various steam conditions have been summarized in Table 5. The rationale for these selections is discussed in the following sections.

2.3.1 Creep-Rupture Strength. In terms of creep-rupture strength, application of ferritic steels for tubes follows the same logic as for the headers/pipes discussed earlier. Thus, tubes made of T22 should be limited to a steam temperature of 538 °C (1000 °F); alloys T91, HCM12, EM12, HCM9M, and HT91 limited to a steam temperature of 565 °C (1050 °F); and alloys T-92, P-122, and E911 limited to a steam temperature of 593 °C (1100 °F). Under corrosive conditions, however, even the best ferritic steel may be limited to 563 °C (1050 °F) and austenitic steels are needed. Although the creep resistance of 9Cr steels is adequate for use at 593 °C, there is considerable doubt about their fireside oxidation resistance. Thus, 12Cr steels, such as P122, are preferred.

In practice, the high-Cr, high-strength ferritics have found little use in the United States because of perceived welding problems. Alloys T-22, SS304H, and SS347 are the steels most commonly used in supercritical boilers (3500 psi) in the United States.

For convenience, austenitic steels can be classified as those containing less than 20%Cr and those containing more than 20%Cr. Alloy modifications based on the 18Cr-8Ni steels, such as TP304H, 316H, 347H, and Tempaloy A-1, and alloys with lower chromium and higher nickel contents, such as 17-14CuMo steel, Esshete 1250, and Tempaloy A2, fall into the classification of steels with less than 20%Cr. The allowable tensile stresses for steels in this class are compared in Fig. 8. Tempaloy A1, Esshete 1250, and 17-14CuMo steel are found to offer major improvements over the 300 series stainless steels. It has been reported that grain-size modifications of AISI type 347H stainless steel can, in some instances, lead to rupture properties somewhat better than those of Tempaloy A-1.[18]

Several high-creep-strength alloys containing more than 20%Cr, such as NF707, NF709, and HR3C, have been developed, and offer low-cost alternatives to Incoloy 800 for use in the temperature range from 650 to 700 °C (1200 to 1290 °F). A comparison of the ASME code allowable stresses for the high-chromium alloys is shown in Fig. 9. Clearly, NF709 and HR3C are leading candidates for use in the highest-temperature applications. The latter steel was approved for use in boilers by ASME as SS310NbN. The highest creep strength is achieved in Inconel 617, which contains 22%Cr, but it is also likely to be the most expensive alloy to use, due to its high Ni content.

A comparison of allowable temperatures at a constant allowable stress of 49 MPa (7 ksi), as a function of chromium content, is shown in Fig. 10. With increasing chromium, a discontinuity is seen in the allowable metal temperatures of austenitic steels, rising about 50 °C (90 °F) above those of ferritic steels.[19] In terms of increasing temperature capability, stable austenitic alloys offer the highest capability, followed by metastable austenitic steels, and then by ferritic steels. The fully enhanced, stable austenitic alloys are clearly capable of operating under phase 2 steam conditions (650 °C, or 1200 °F).

2.3.2 Fireside Corrosion. Fireside corrosion results from the presence of molten sodium-potassium-iron trisulfates. Because resistance to fireside corrosion increases with chromium content, the 9 to 12%Cr ferritic steels are more resistant than the 2-1/4Cr-1Mo steels currently used. The 12%Cr steel, in turn, shows better corrosion resistance than 2-1/4%Cr steel and 9%Cr steel, as shown in Fig. 11.[20] Stainless steels and other superalloys containing up to 30%Cr represent a further improvement. Increasing the chromium content beyond 30% results in a saturation effect on the corrosion resistance, at least in the laboratory, as shown in Fig. 12.[21] For practical purposes, when corrosive conditions are present, fine distinctions between ferritic steels may be academic, and it is usually necessary to use austenitic steels containing chromium in excess of 20%.

A ranking of the performance of various austenitic alloys in the presence of trisulfates has been provided by Ohtomo *et al.*[22] on the basis of short-term laboratory tests (Fig. 13). The plots of weight loss versus temperature exhibit a bell-shape curve. At temperatures below 600 °C (1110 °F), corrosion is

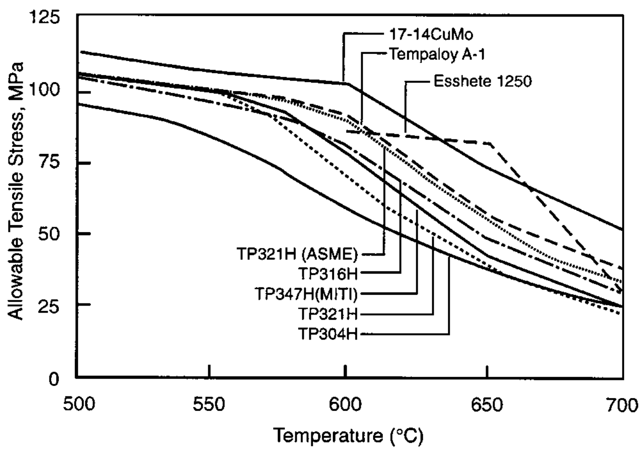

Fig. 8 Comparison of allowable stresses for 18Cr-8Ni and 15Cr steels

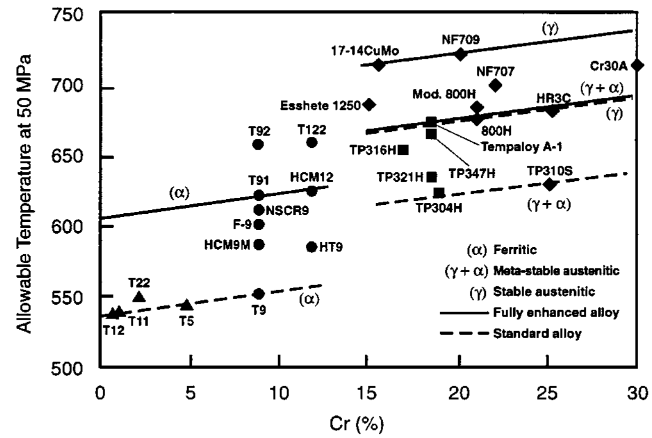

Fig. 10 Allowable metal temperatures at constant allowable stress of 49 MPa (7 ksi) as a function of chromium content for various alloys

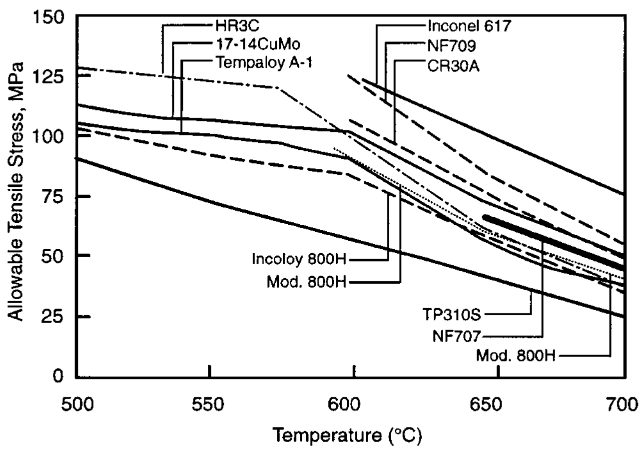

Fig. 9 Comparison of allowable stresses for austenitic alloys containing more than 20%Cr

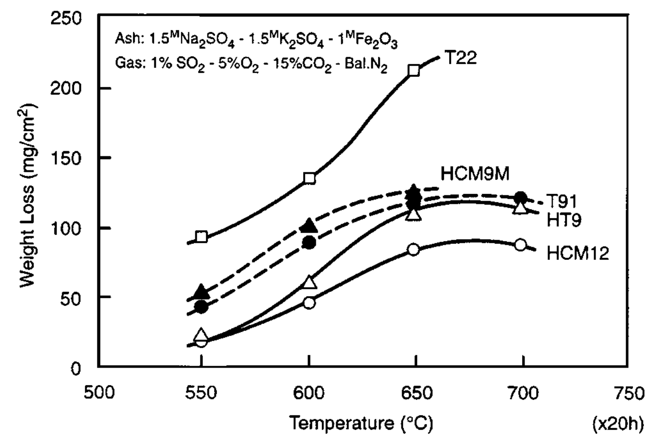

Fig. 11 Relationship between hot-corrosion weight loss and temperature for ferritic steels

believed to be low because the trisulfate exists in solid form. Above 750 °C (1380 °F), corrosion rates are once again low, as the trisulfates vaporize. The worst corrosion problem is in the range 600 to 750 °C (1110 to 1380 °F). The data indicate that the high-chromium alloys such as type 310 stainless steel and Incoloy 800H are superior to the other alloys tested, and that Inconel 671 (Ni-50Cr) or its matching weld metal IN72 is virtually immune to attack. Lower-chromium stainless steels, such as type 316H, type 321H, and Esshete 1250, show considerable susceptibility to attack. The alloy most susceptible to attack seems to be the 17-14CuMo alloy used in the Eddystone 1 plant. Results of field probe studies confirm the following ranking of alloys in increasing order of corrosion resistance: T91, HCM12, type 347 stainless steel, Incoloy 800, and Inconel 671.[23] In addition to alloy selection, other “fixes” to minimize fireside corrosion, such as shielding of the tubes, may also be applied, if economical.[24]

Results of extensive field tests have also been reported by Blough.[25] This was based on a collaborative study by EPRI, IHI, and F-W, who carried out extensive laboratory and field tests in three boilers, two of them fueled with somewhat corrosive Eastern bituminous U.S. coal and one fueled with a supposedly noncorrosive Western low sulfur subbituminous coal. The experiments were carried out using air-cooled, retractable probes, inserted in finishing superheater or reheater areas. Metal temperatures were maintained in the 600 to 690 °C range (1250 to 1300 °F). Exposure time was 16,000 h with samples removed after 4000, 12,000, and 16,000 h. Figure 14 shows metal losses observed in one of the boilers, using an Eastern bituminous coal and Fig. 15 those observed in the boiler using subbituminous Western coal. The losses observed were about the same, but the corrosion mechanisms were different. Tubes from the boilers using Eastern bituminous coals showed the classic liquid ash corrosion in the 10 and 2 o’clock positions of the tube, where sulfur-rich fly ash impacts on the tube. Potassium-rich sulfate was found in the ash deposits, and metal wastage was caused by internal oxidation and sulfidation, because a fully protective Cr_2O_3 scale could not form in the presence of sulfur-rich deposits. With increasing Cr content in the alloy, the Cr_2O_3 scale became more protective, but in all alloys, internal oxidation and sulfidation occurred in Cr-depleted zones below the scale.

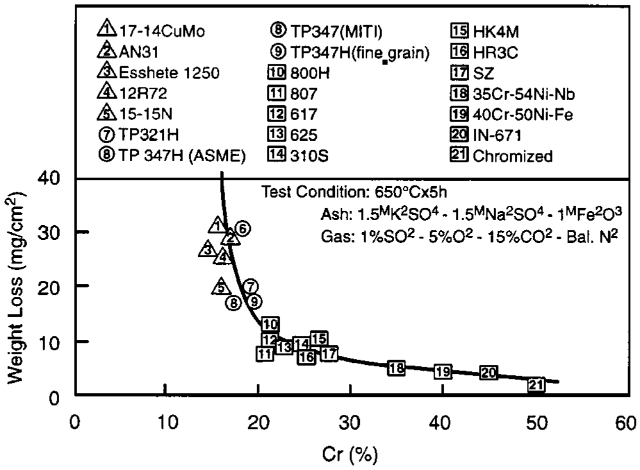

Fig. 12 Relationship between hot-corrosion weight loss and chromium content for various alloys

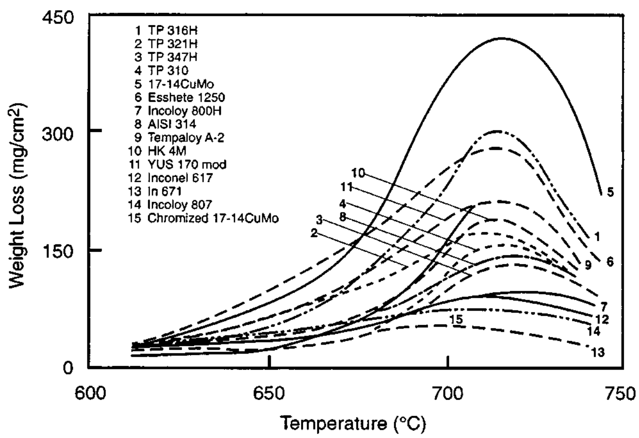

Fig. 13 Comparison of fireside corrosion resistance of various alloys

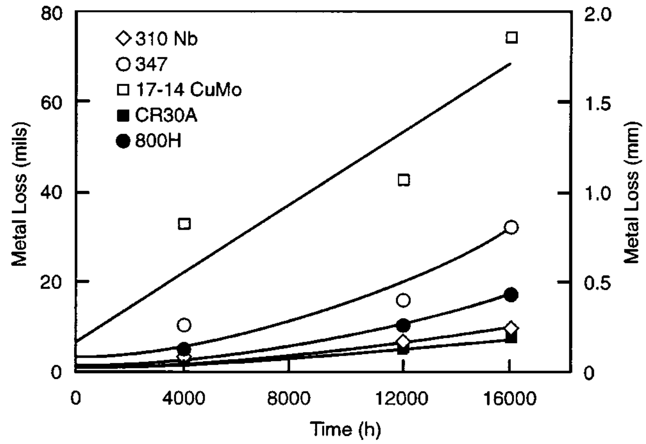

Fig. 14 Metal losses of various superheater steels in a boiler using bituminous Eastern U.S. coals

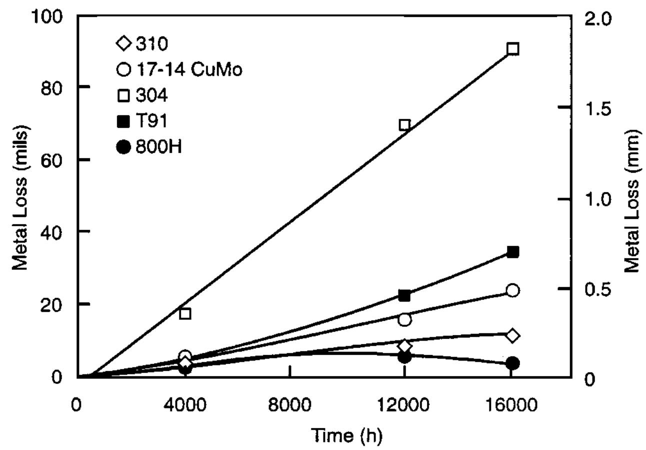

Fig. 15 Metal losses of various superheater steels in a boiler subbituminous Western U.S. coals

The corrosion morphology of the tubes from the boiler using Western subbituminous coal was similar, but the area of major attack was on the side of the tube facing away from the flue gas stream, where deposits rich in very fine $CaSO_4$ were found.

From the results presented above, it may be concluded that substantial superheater corrosion can occur, especially in high-strength austenitic alloys with a low chromium content. For most coals, high-strength modified alloy 800 type alloys, such as NF709, will probably have sufficient corrosion resistance, whereas for more corrosive coals, modified SS 310 type alloys, *e.g.*, HR3C, should give an extra margin of safety. It is of interest to note here that the T-91 sample exposed in the low-sulfur-coal-fueled boiler had a corrosion loss similar to SS 347, which is considerably less than that of SS 304 and 17-14CuMo. A probable reason is that scales and deposits usually adhere tightly to ferritic/martensitic steels, but spall readily from all austenitic steels.

Based on the favorable results from the air-cooled probes in one of the plants, the SS304M reheater, which suffered from severe alkali sulfate corrosion, was replaced by one made from SS310 NbN (HR3C).[26] Test sections of other alloys were built into the reheater and carefully monitored. It was found that 310NbN (HR3C) was a satisfactory material for 90% of the reheater, with less than 0.25 mm/year (10 mils/year) corrosion.

However, in one area, about 10 tubes wide and 10 feet (3 m) high, corrosion rates ranged from 0.5 to 1.25 mm/year (20 to 50 mils/year). Here, the corrosion resistance of SS310 was about the same as that of SS347 and alloy 800H. Only a Cr-Ni steel (Cr30A) with 30%Cr had significantly lower corrosion rates, ranging from 0.125 to 0.5 mm/year (5 to 20 mils/year). It is concluded that increasing the Cr content of the alloy from 18 to 20% to 23 to 25% will only significantly increase corrosion resistance when the corrosivity of the deposits is moderate, *i.e.*, ≤0.5 mm/year (20 mils/year for 18-8 stainless steels). For more corrosive conditions, coextruded tubes or weld overlay claddings containing at least 40%Cr are strongly recommended.

2.3.3 Steamside oxidation. Steamside oxidation of tubes and exfoliation of the oxide scale and its consequence in terms of solid-particle erosion damage to the turbine are well known. This problem is expected to be more severe in advanced steam plants, because the much higher steam temperatures employed are likely to cause more rapid formation of oxide scale.

Very limited data are available regarding the steamside scale-growth characteristics of the ferritic tubing alloys. In a study by Sumitomo Metal Industries,[27] the oxide growth in steam for alloys T22 (2-1/4Cr-1Mo), T9, HCM9M, and the modified 9Cr-1Mo (T91) were compared based on 500 h tests. Results showed the superiority of the T91 alloy over the other alloys. Masuyama *et al.* compared alloys HCM12, HCM9M, 321H, and 347H in field tests in the temperature range 550 to 625 °C (1020 to 1155 °F) over a period of one year.[28] Samples were inserted in the tertiary and secondary superheaters and reheaters. From the results, they concluded that the resistance to steam oxidation of HCM12 is superior to those of 321H and HCM9M and comparable to that of fine-grained 347H for exposure to the high-temperature region of the reheater. Subsequent monitoring over a period of three years has borne out their earlier conclusions.[29] In addition to the inherent resistance of HCM12M steel to steamside oxidation, Masuyama *et al.* suggest that the tendency toward exfoliation of oxide scale would also be less for this alloy than for austenitic steels.[28,29] Additional improvements in 9 to 12%Cr steels may be possible by extending the chromizing[30,31] and chromate conversion treatments[32] that currently are applied to lower-alloy steels; grain refinement during heat treatment has been shown to be clearly beneficial as well. Internal shot blasting is also known to improve the steam oxidation resistance of 300 series stainless steels by enhancing chromium diffusion. It is therefore anticipated that these steels would be used in the fine-grain and shot-peened conditions. Results of steam oxidation tests at 650 °C (1200 °F) for times up to 2000 h have been reported for several austenitic steels.[33]

2.3.4 Summary of SH/RH Tube-Material Status. Based on the discussion thus far, recommendations for materials selection have been made in Table 5. For phase 0 steam conditions, alloys T91, HCM12M, and AISI type 304 stainless steel are viable candidates for SH/RH tubing, provided that fireside corrosion is not a major problem. Under mildly corrosive conditions, 310NbN stainless steel may be the most cost-effective option. For severe corrosion cladding, SS304 with IN72 (44%Cr) is recommended.

For intermediate-temperature applications corresponding to phase 1 steam conditions (595 °C, or 1100 °F), Tempaloy A-I and type 347 fine-grained stainless steel are deemed to be adequate in the absence of corrosive conditions. Under mildly corrosive conditions, 310NbN stainless steel may offer the best combinations of creep strength and corrosion resistance. For severe corrosion, cladding with IN72 is recommended.

For phase 1B, *i.e.*, 620 °C conditions, Super 304H, Tempaloy AA1, Esshete 1250, and 17-14CuMo may be acceptable under noncorrosive conditions. For mildly corrosive conditions, alloys with 20 to 25%Cr, such as HR3C and NF709, will have the best combination of creep strength and corrosion resistance. For severe corrosion, cladding with IN72 is again recommended.

For the highest-temperature application corresponding to phase 2 steam conditions (650/650 °C, or 1200/1200 °F), the creep strength requirements are met by Inconel 617, 17-14CuMo steel, Esshete 1250, and NF709. Among these alloys, 17-14CuMo steel and Esshete 1250 have inadequate corrosion resistance and will have to be clad with corrosion-resistant claddings of Inconel 671 if corrosive conditions are present. NF709 and CR30A may be used without any corrosion protection for mildly corrosive conditions, but will require cladding with IN72 for severely corrosive conditions.

2.4 Choice of Materials for Waterwalls

2.4.1 Metal Temperature Concerns. This issue has been discussed recently by Blum.[34] In boilers operating at 625 °C/32 MPa, maximum midwall temperatures can be as high as 500 to 525 °C, depending on magnetite deposits at the inside of the tube. This means that the creep resistance of standard low alloy ferritic steels such as T-11 is not adequate. Originally, T-91 steel was the only suitable substitute. Under the COST program,[35] it was demonstrated that this material can be fabricated into waterwalls. However, a postweld heat treatment is required, which is difficult to do in the field. Two steels containing 2.5 and 12%Cr, respectively, developed by Sumitomo and MHI are more promising in that they do not require preheat or postweld heat treatment.[34,36] Both steels have creep strength in the same range as T-91 and use similar precipitation strengthening mechanisms. Especially, the 2.5%Cr steel appears promising for this application. This steel also has recently been approved by the ASME boiler code committee as T-23. Test panels are now in service in various boilers.

2.4.2 Waterwall Corrosion Concerns. Recent reductions in NO_x emissions, mandated by the Environmental Protection Agency in the United States, have led to the introduction of deeply staged combustion systems, in which the air/fuel ratio is significantly less than 1, and additional combustion air is added above the burners *via* overfire air ports. Several boilers in the United States retrofitted with such systems have reported severe corrosion of low alloy steel waterwalls, with metal losses in the 1 to 3 mm/year (40 to 120 mil/year) range. Supercritical units are generally more severely affected than subcritical units, and severe corrosion is generally limited to coals with more than 1%S. However, above 1%S, there is no strict correlation between S and corrosion rate. The highest corrosion losses are found in regions where H_2S-rich substiochiometric flue gas mixes with air from the overfire air ports. Laboratory studies indicate that the high corrosion rates cannot be explained by the presence of H_2S and CO in the flue gas alone. Work by Kung[37] has shown that corrosion rates in gas mixtures, actually found in boilers, containing 500 to 1500 pm H_2S and 5 to 10%CO, are generally less than 0.5 mm/year (20 mils/year) at 450 °C. More recently, it was shown that the presence of FeS deposits can greatly increase the corrosion rate, but only under alternating oxidizing/reducing conditions or oxidizing conditions alone. Figure 16 shows corrosion losses of a low-alloy steel, T-91, and SS-304 in the presence of FeS containing deposits and a gas mixture containing 1% oxygen. Although the corrosion rates are probably artificially high, because of the short duration of the test, it is clearly demonstrated that low-alloy steels will corrode quite rapidly in the presence of FeS deposits and an oxidizing gas. The tests further show that claddings or weld overlays containing at least 18 and preferably more than 20%Cr are needed to assure acceptably low corrosion rates.

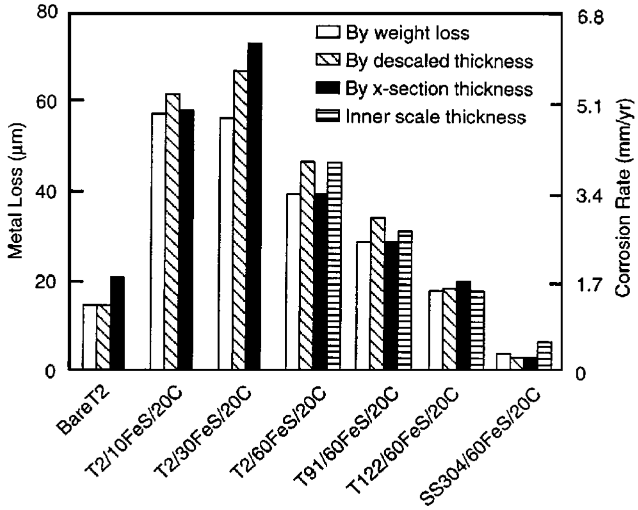

Fig. 16 Corrosion of steels containing 0.5 to 18%Cr under FeS containing deposits in oxidizing flue gas

3. Futuristic Programs for 700 °C (1300 °F) and Beyond

Until now, worldwide efforts have concentrated materials development along the following lines.

- Use of high-strength ferritic stainless steels for heavy section components to avoid thermal fatigue related failures.
- Use of relatively high chromium creep resistant stainless steel for SH/RH tubing to provide fireside corrosion resistance and adequate creep life.
- The use of higher-strength, low-alloy steels for waterwalls.

This development path has now largely run its course. Research activities by EPRI and its international partners have resulted in ASME code approved ferritic stainless steels (P9l, 92, and P122) capable of long-term service up to 630 °C and 35 MPa (5000 psi). Developments in Japan and elsewhere have resulted in ASME code approved stainless steels, such as 310 CbN, capable of service up to 650 °C. Superheater boilers with steam temperatures up to 620 °C are now under construction in Japan.

The question is, where do we go from here? Evolution of the present technology may make it possible to increase steam temperatures up to 650 °C if improved versions of P122, such as NF12 and SAVEI2, under development in Japan, prove to possess long-term structural stability at 650 °C. This is by no means certain at this time. In any case, increasing the superheat temperature to 650 °C would only marginally increase efficiency.

Based on these considerations, a European consortium, partially funded by the European Economic Community under the Thermie program, has made a bold leap and decided to develop boiler technology allowing steam temperatures up to 700 °C. This will require higher-strength stainless steels and nickel-based superalloys for critical high-temperature components. However, for the U.S. market, 700 °C is not an optimum choice, since at this temperature, fireside corrosion is still very severe. Fireside corrosion is very dependent on coal properties and is specifically severe for some bituminous U.S. coals. Extensive laboratory experiments indicate that the temperature at which fireside corrosion caused by liquid iron alkali sulfates occurs is somewhat alloy dependent. It ranges from 600 to 650 °C for more corrosion-resistant alloys (>25%Cr) and to 650 to 700 °C for less corrosion-resistant alloys (<20%Cr). However, all laboratory corrosion tests agree that fireside corrosion is greatly diminished at 750 °C or above. These laboratory data have recently been confirmed by a seven-year field exposure project carried out by EPRI and TVA on a boiler experiencing serve superheater corrosion, up to one month per year in the most corrosive areas. This study showed that the most severe corrosion occurred at nominal temperatures of 600 to 675 °C and greatly decreased above 725 °C.

It seems desirable therefore that development of a revolutionary boiler design for U.S. markets should be based on super/reheater temperatures above the temperature range at which fireside corrosion is the most severe. A design goal of 760 °C (1400 °C) appears appropriate. Such a boiler would have considerable advantages over designs pursued elsewhere, both in general and specifically for the U.S. market, as follows.

The higher steam temperature will result in another 2 to 3% efficiency increase over a 700 °C design, thus improving fuel usage and CO_2 emissions.

A wider range of Ni-based superalloy compositions can be explored for application in boilers, when the risk of fireside corrosion is low, as the strength of Ni-based superalloys is generally inversely related to chromium content of the alloy. This will decrease alloy development cost, as it requires less modification and testing of existing, proven superalloy compositions.

A comparison of potential materials for heavy-section pipes and headers is shown in Table 7. Since thermal fatigue due to cyclic operation will be a main design criterion, in addition to adequate creep strength, a nickel-based alloy is the preferred choice. These alloys have a relatively low thermal expansion coefficient, comparable to that of 9-12Cr ferritic steel, with proven fatigue resistance. Since fireside corrosion is not a problem here, the alloy composition can be optimized for strength, although resistance to steam oxidation should be further investigated by appropriate testing. The only ASME approved Ni alloy is In625, with an allowable strength of 52 MPa at 760 °C. This is generally considered too low for large utility borders, where an allowable stress of >75 MPa would be desirable. Other superalloys of similar strength level include Incone1617, Nimomic263, and NimomicPK-33. These alloys are expected to be extrudable and weldable. They are currently used in combustion turbine systems as combustor cans and transition pieces. Nickel- based bar product alloys Nimonic105, Nimonic115, and Waspoloy, which are estimated to have 100,000 h rupture strength at 760 °C (1400 °F) in excess of 16 ksi (112 MPa), are very desirable, but their extrudability into headers and pipes and weldability may be less than the sheet alloys and need to be investigated. Other high-strength superalloys such as the Udimet series alloys are expected to have very little fabricability. Thus, there is an excellent chance that an alloy suitable for boiler use can be developed. However, considerable development is anticipated because of the much

Table 7 Candidate alloys for heavy-section application at $T > 650$ °C (1200 °F)

650 °C (1200 °F)		700 °C (1300 °F)		760 °C (1400 °F)
Ferritics		Autenitics 1		*Ni-based alloys*
Mod NF 12		Eshete 1250	15 Ni 15Cr alloys	Inconel 617/625(a) Nimonic 263
NF 12		Tempaloy A1		Nimonic Pk-33 (sheet alloys)
Save 12		17-14 CuMo		Nimonic 105
Austenitics				Nimonic 115, Waspaloy (bar alloys)
TP 304H		Incoloy 800 H		
321H	8Ni 18Cr Alloys	Mod 800H	20–35 Ni alloys	
316H		NF 707		
347FG		NF 709	20–25Cr alloys	
310CbN	25Cr - 20Ni	Save 25		
Eshete 1250		Cr 30 A		
Tempaloy A1	15 Ni 15 Cr Alloys	Inconel 617	50 Ni-22 to 30 Cr	
17-14 CuMo		HR 6W		

Notes
- Ferritics are pushing the limit at 650 °C. May also be limited by oxidation. Austenitic alloys of the 18Cr-8Ni type can be the most cost effective at 650 °C
- At 700 °C 15Ni-15Cr alloys may meet creep strength, but Cr may be too low for oxidation resistance. Higher Cr austenitics or Ni-based alloys are needed
- At 760 °C, only a Ni-based alloy can meet the requirements. Expected 100,000 h rupture strength $>$7 ksi (50 MPa) for sheet and $>$10 ksi (112 MPa) for bar products

(a) Allowable strength low ~50 MPa at 760 °C

larger component sizes involved, which will require a greatly improved hot workability and fabricability.

With respect to SH/RH tubes, for the lower temperature parts, existing alloys, such as 319CbN, NF709, and SAVE25, or minor modifications thereof should be usable for temperatures up to 700 °C. If more attractive alloys are developed under the Thermie program, these could be used as well. For the higher-temperature sections, any new programs will need to concentrate on superalloys for use at 760 to 800 °C. Alloy design considerations are somewhat different than for heavy-section materials, as fireside corrosion is still an important consideration, although it is expected to be considerably less than at temperatures in the 600 to 700 °C range. To minimize fireside corrosion, it is necessary to start with Ni-based superalloy compositions with a relatively high Cr content ($>$20%) and relatively low Mo content. Since In617 and 625 contain 9%Mo, they may be marginal. A more detailed search is needed to identify potential candidates.

Extensive field experience at EPRI and TVA has shown that fireside corrosion is very local, even with very corrosive coals. Thus, 20%Cr alloys are generally suitable as the main material of construction. Local areas where severe corrosion is predicted by combustion modeling or found after initial operation can then be made more corrosive resistant by high chromium weld overlays. These overlays, using weld metal In72 (44Cr and balNi), are commercially available, although improved application methods and reduced costs are desirable.

The temperature of waterwalls is driven by the steam pressure. Present maximum waterwall temperatures are in the 470 °C range for steam pressures of 3500 psi. If this is increased to 5000 psi, the expected maximum waterwall temperature will increase by 50 to 75 °C to 500 to 525 °C. Alloy T23 is deemed sufficient for this application from a creep standpoint. Qualification and field trials of this alloy are needed to allow routine commercial application.

4. Summary and Conclusions

Literature pertaining to materials technology for boilers in USC PC power plants has been reviewed. Extensive development in strengthening of 9 to 12% ferritic steels has resulted in temperature/pressure capabilities well over the conventional framework of 538 °C/17 MPa (1000 °F/2400 psi) for the steam. Nearly two dozen plants have been commissioned worldwide with main steam temperatures of 585 to 600 °C (1080 to 1112 °F) and pressures of 24 to 30 MPa (3400 to 4200 psi). Specific materials developments with respect to key components are as follows.

For heavy-section components such as pipes and headers, minimizing thermal fatigue has been a major driver in addition to achieving high creep strength. For this reason, alloy development has focused on ferritic steels containing 9-12%Cr. Optimization of C, Nb, Mo, and V and partial substitution of W for Nb in the 9-12%Cr ferritic steels has resulted in three new alloys HCM12A, NF616, and E911 (P122, P92, and E911), capable of operating up to 620 °C (1150 °F) at steam pressures up to 34 MPa (4800 psi). Beyond 620 °C, oxidation resistance may become an additional limiting factor, especially for the 9% containing steels. A newer class of 12%Cr alloys, NF12 and SAVE12, containing cobalt and additional W, is being evaluated for possible 650 °C (1200 °F) application. It appears from preliminary results that austenitic steels or nickel alloys would be needed for temperatures exceeding 650 °C.

For SH/RH tubes, steamside oxidation resistance and fireside corrosion resistance are major drivers in addition to creep resistance. Furthermore, tube metal temperatures often exceed the steam temperature by as much as 28 °C (50 °F). It is unlikely that any ferritic steels can be used in the finishing stages of SH/RH circuits at steam temperatures exceeding 565 °C (1050 °F). Austenitic steels need to be used at these higher temperatures. Depending on the corrosivity of the coal used, higher Cr steels or clad steels may be required. For 620 °C application, Super 304H, Tempalloy AA1, Eshete 1250, and 17Cu-Mo are acceptable under noncorrosive conditions, whereas 20-25%Cr alloys such as HR3C, NF709, and cladding with IN72 are recommended for more corrosive conditions. Several candidate alloys, Inconel 617, NF709, and Cr30A, and alloys clad with Inconel 671 (50%Cr) are available for use at 650 °C.

For upper waterwall sections, two new steels containing 2.5 and 12%Cr known as HCM2(T23) and HCM 12, respectively, are very promising in terms of creep strength and weldability. They are suitable for use in the range of 595 to 650 °C steam conditions purely from a creep-strength point of view. When fireside corrosion in low NO_x boilers is an issue, these alloys will have to be clad or weld overlaid with alloys containing more than 18 to 20%Cr.

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