MATERIALS TECHNOLOGY FOR ADVANCED COAL POWER PLANTS

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ABSTRACT

The efficiency of conventional boiler/steam turbine fossil power plants is a strong function of steam temperature and pressure. Since the energy crisis of the 1970s, research to increase both has been pursued worldwide. The need to reduce carbon monoxide emissions has provided further incentive to improve efficiency. The main enabling technology is the development of stronger high temperature materials especially for critical pressure parts of the boilers such as piping, headers and superheater tubes. These applications call for not only creep strength but also resistance to fireside and steamside corrosion, weldability, fabricability and the ability to be coated. In spite of these stringent requirements, many new alloys-ferritic, austenitic, and Ni based alloys have been developed that appear capable of operation under severe steam conditions. Worldwide activities have been going on for nearly a decade to develop these materials. This paper is a review of these developments.

KEYWORDS:

Efficiency, Boilers, Ultra Supercritical, Materials, Coal

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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. Table 1 illustrates actual or expected efficiencies corresponding to various steam cycles. The goal for increased efficiencies has acquired special urgency due to environmental and global warming concerns in recent years. The US Department of Energy has identified this as a key component of their clean coal technologies in their Vision 21 plans. A major challenge in constructing ultra-supercritical (USC) plants has been in the area of materials technology. While 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 R&D efforts were carried out in Japan, US and Europe with an intermediate goal of 620-630°C (1150°F-1166°F)/30 MPa (4200 psi). More recently, the Thermie project in Europe has been addressing 700°C (1297°F) 37.5 MPa (5400 psi) main steam conditions[1]. This has been partly made possible by some very exciting progress in developing highly creep resistant 9 to 12%Cr ferritic steels and some Ni base alloys. The objective of this paper is to review developments in materials technology related to boilers and to describe the scope of a new project sponsored by OCDO and the USDOE. Detailed reviews of materials for supercritical boilers may be found in References 2–7.

1.0 Boiler Material Requirements

The key components whose performance is critical for ultra-supercritical (USC) plants are high-pressure steam piping and headers, superheater 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. Since they operate at high temperatures, 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 which 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 oxide spallation. Thermal fatigue resistance as well as cost considerations would dictate the use of ferritic/martensitic steels. Unfortunately, the strongest of these steels which can be used up to metal temperature of 620°C (1150°F)*, purely from a creep strength point of view, are still further limited by fireside corrosion to metal temperature of 593°C (1100°F).

* 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).

This corresponds to a steam temperature of about 565°C (1050°F) since SH/RH metal temperature can exceed the steam temperature by as much as 28°C (50°F) to 39°C (70°F). Excessive corrosion of ferritic steels caused by liquid iron-alkali sulfates in the tube deposits is an acute concern in the US, where high sulfur corrosive coals are used more frequently than elsewhere. Therefore high strength ferritic steels such as T-91 are infrequently used in the US. The standard practice in conventional plants is to use T-22 for the lower temperatures and SS304H or SS347 for the highest temperatures.

Table 1: Estimated Plant Efficiencies for Various Steam Cycles (Ref. P. Weitzel and M. Palkes)*

Efficiency Net HHV			
Description	**Cycle**	**Reported at European Location (LHV/HHV)**	**Converted to US Practice[2] HHV**
Subcritical	16.8 MPa/538°C/538°C[1]		37
Supercritical	24.5 MPa/565°C/565°C/565°C[1]		40.9
ELSAM (Nordjylland 3)	28.9 MPa/580°C/580°C/580°C	47/44	42
State of the Art Supercritical (LEBS)	31.5 MPa/593°C/593°C/593°C[1]		42.3
EPRI/Parson	35 MPa/649°C/649°C/649°C		42.7
Thermie	38 MPa/700°C/720°C/720°C	50.2/47.7	46.43
EPRI/Parson	37.8 MPa/700°C/700°C/700°C		44
DOE/OCDO USC Project	38.5 MPa/760°C/760°C 38.5 MPa/760°C/760°C/760°C		46.5 47.5–48

(1) Eastern bituminous Ohio coal. Lower Heating value, LHV boiler fuel efficiency is approximately 4.2% higher than higher heating value, HHV boiler fuel efficiency. For example, an LHV net plant heat rate at 6205.27 Btu/kWh with the LHV net plant efficiency of 55% compares to the HHV net plant heat rate at 6494.85 Btu/kWh and HHV net plant efficiency of 52.55%.

(2) Reported European efficiencies are generally higher compared US due to differences in reporting practice (LHV vs HHV), coal quality, auxiliary power needs, condenser pressure and ambient temperature and many other variables. Numbers in this column for European project numbers are adjusted for US conditions to facilitate comparison.

* Personal communication from Paul Weitzel, Babcock & Wilcox, Barberton, OH and Mark Palkes, Alstom Power Co., Windsor, CT, May 24, 2002.

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* (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 US 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/yr. Weldable high strength alloys clad or overlaid with high Cr alloys have to be utilized to reduce or eliminate excessive corrosion[2].

* ASME boiler code steel designation, equivalent pipe steels are designated as P-11, 92, etc., while forgings are designated F-11, 91, etc.

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2.0 Historical Evolution of Steels

Masuyama has presented an excellent historical perspective on the development of steels for power plants as shown in Table 2[8]. The table shows 10^{5}h creep rupture strength at 600°C (1112°F) by year of development and classifies the ferritic steel development in terms of 4 generations[8]. His paper serves as a key resource for industry and has been used extensively in preparing this paper.

In the field of austenitic steels, efforts were made from the 1970's to the early 1980's 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 1980's to the early 1990's 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[8]. The systematic evolution of these steels has been thoroughly reviewed by Masuyama, as shown in Figure 1[8]. Among the most recent 9%Cr steels fully commercialized, the P91 steel has been used as a material for headers, steam pipes and superheater tubes in supercritical plants operating 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 temperatures of 620°C (1150°F) purely from creep considerations. E911 is a European alloy similar in composition to NF616 with similar capabilities. Oxidation and fireside corrosion may limit their application still further.

Among the 12%Cr steels, HT91 has been widely used for tubing, headers and piping in Europe. Use of the steel in Japan and US has been limited due to its poor weldability. 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 has resulted in alloy HCM12A (P-122), which can be used for header and piping up to 620°C (1150°F). It has capabilities similar to P92, with slightly increased resistance to steam oxidation due its higher chromium content. Two alloys NF12 and SAVE12 having an even higher creep strength than HCM12A are in the developmental stage. NF12 contains 2.5%Co, 2.6%W and slightly higher B compared to HCM12A. 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. 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 post-weld heat treatment it is a good candidate for waterwall tubing.

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Table 2: Evolution of Four Generations of Ferritic Steels (Based on Reference 8)

Generation	**Years**	**Alloy Modifications**	**Strength 10^5 hr Creep Rupture Achieved MPa at 600°C**	**Example Alloys**	**Maximum Metal Use Temp. °C***
1	1960-70	Addition of Mo or Nb, V to simple 12Cr and 9Cr Mo steels	60	EM12, HCM9M, HT9, Tempaloy F9, HT91	565
2	1970-85	Optimization of C, Nb, V	100	HCM12, T91, HCM2S	593
3	1985-95	Partial substitution of W for Mo	140	P-92, P-122, P-911 (NF616, HCM12A)	620
4	Emerging	Increase of W and addition of Co	180	NF12, SAVE12	650

*Based on 100 MPa/10^5 h

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Table 3: Nominal Chemical Compositions of Ferritic Steels for Boiler (8)

Steels		**Specification**		**Chemical Composition (mass%)**											
		ASME	JIS	C	Si	Mn	Cr	Mo	W	Co	V	Nb	B	N	Others
2Cr	T22(2.25Cr-1Mo	T22	STBA24	0.12	0.3	0.45	2.25	1.0	-	-	-	-	-	-	-
	HCM2S	T23	STBA24JI	0.03	0.2	0.12	2.25	0.1	1.3	-	0.25	0.05	0.003	-	-
9Cr	T9(9Cr-1Mo)	T9	STBA26	0.12	0.3	0.12	9.0	1.0	-	-	-	-	-	-	-
	HCM9M(9Cr-2Mo)	-	STBA27	0.07	0.3	0.45	9.0	2.0	-	-	-	-	-	-	-
	T91(9Cr—1M)VNb)	T91	STBA28	0.10	0.4	0.45	9.0	1.0	-	-	0.20	0.08	-	0.05	-
	NF616(9Cr-0.5MO-2WVNb)	T92	STBA29	0.07	0.03	0.45	9.0	0.5	1.8	-	0.20	0.05	0.004	0.06	-
	Tempaloy F-9(9Cr-1MoVNb)	-	-	0.06	0.5	0.60	9.0	1.0	-	-	0.25	0.40	0.005	-	-
	EM12 (9Cr-2MoVNb)	(NFA49213)	-	0.10	0.4	0.10	9.0	2.0	-	-	0.30	0.40	-	-	-
12Cr	JT91(12Cr-1MoV)	(DIN X20CrMoV121)	-	0.20	0.4	0.60	12.0	1.0	-	-	0.25	-	-	-	0.5Ni
	HT9(12Cr-1MoWV)	(DIN X20CrMoWV121)	-	0.20	0.4	0.60	12.0	1.0	0.5	-	0.25	-	-	-	0.5Ni
	HCM12(12Cr-1Mo-1WVNb)	-	SUS410J2TB	0.10	0.3	0.55	12.0	1.0	1.0	-	0.25	0.05	-	0.03	-
	HCM12A(12Cr-0.4Mo-2WCuVNb)	T122	SUS410J3TB	0.11	0.1	0.60	12.0	0.4	2.0	-	0.20	0.05	0.003	0.03	1.0Cu
	NF12(11Cr-2.6W-2.5CoVNbB)	-	-	0.08	0.2	0.50	11.0	0.2	2.6	2.5	0.20	0.07	0.004	0.05	-
	SAVE12(11Cr-3W-3CoVNbTaN	-	-	0.10	0.3	0.20	11.0	-	3.0	3.0	0.20	0.07	-	0.04	0.07Ta 0.04Nd

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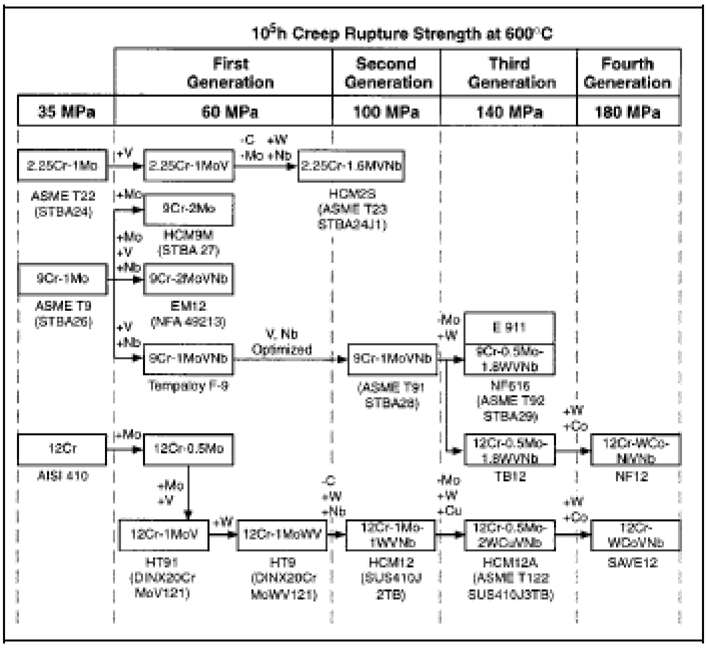

Fig. 1: Evolution of Ferritic Steels for Boilers[8]

2.1.2 Evolution of Austenitic Steels

Austenitic steels have been used primarily in the finishing stages of superheater/reheater 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 (1050°F) steam (metal 593°C [1100°F]) and NF616, HCM12A and E911 are limited to 593°C (1100°F) steam (metal 620°C [1150°F]). Even the strongest ferritic steel today is limited to 593°C (1100°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 conventional plants in the US SS304H and SS347 are widely used instead of T-91 in superheater applications, mainly because they are easier to weld, while the cost difference is relatively small.

Table 4 includes a list of the compositions of various high strength 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, and heat treatment modifications. Further trends have included austenite stabilization using 0.2% nitrogen and W addition for solid solution strengthening. This development sequence is illustrated in Figure 2[8]. The highest creep strength is achieved in SAVE 25, but the fireside corrosion resistance of the alloy is controversial.

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2.2 Choice of Materials for Headers and Steam Pipes

Material-property requirements for headers and steam pipes are likely to be similar, and hence they have been grouped together. Some minor differences exist which 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 superheater/reheater 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 US. 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.

As shown in Table 2, ferritic steels can be used up to the temperature limits indicated. The most creep resistant steels, P92, P122 and P911 can be used for heavy section applications up to 620°C (1150°F), although steamside oxidation may lower their applicability to lower temperatures. At temperatures exceeding 620°C (1150°F) and up to about 675°C (1250°F) austenitic steels may be needed. Beyond 675°C (1250°F) up to 788°C (1450°F) nickel base alloys may be used.

Figure 3 shows a plot of the allowable stress at various temperatures for ferritic steels[8]. The figure clearly shows the enormous advances in the materials technology which 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. HCM12A (P122), NF616 (P92) and E911 emerge as the three highest strength alloys suitable for ultra supercritical plants up to 620°C, followed by T91, HCM12, EM12 and HT91 suitable for intermediate temperatures up to 593°C (1100°F) followed by T22 for use up to 565°C (1050°F). NF12 and SAVE12 are still developmental. Alloy HCM2S has much higher strength than P22, is weldable and therefore suitable for application as a replacement for P22. More recently, Fujita has reported on a modified version of NF12 with aluminum content below 20 ppm and Ni content below 0.1%, which has creep properties higher than NF12. This alloy is believed to have adequate strength for 650°C applications[10].

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Table 4: Nominal Chemical Compositions of Austenitic Steels for Boiler (mass%)(8)

	Steels (JIS)	C	Si	Mn	Ni	Cr	Mo	W	V	Nb	Ti	B	Others
18Cr–8Ni	ASME 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
	ASME 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	–	–
	ASME TP316H (SUS316HTB)	0.08	0.6	1.6	12.0	16.0	2.5	–	–	–	–	–	–
	ASME TP347H (SUSTP347HTB)	0.08	0.6	1.6	10.0	18.0	–	–	–	0.8	–	–	–
	ASME 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	–	–
20–25Cr	ASME TP310 (SUS310TB)	0.08	0.6	1.6	20.0	25.0	–	–	–	–	–	–	–
	HR3C (SUS310J1TB)	0.06	0.4	1.2	20.0	25.0	–	–	–	0.45	–	–	0.2N
	Alloy 800H (NCF800HTB)	0.08	0.5	1.2	32.0	21.0	–	–	–	–	0.5	–	0.4Al
	Tempaloy A–3 (SUS309J4HTB)	0.05	0.4	1.5	15.0	22.0	–	–	–	0.7	–	0.002	0.15N
	NF709 (SUS310J2TB)	0.15	0.5	1.0	25.0	20.0	1.5	–	–	0.2	0.1	–	–
	SAVE25	0.10	0.1	1.0	18.0	23.0	–	1.5	–	0.45	–	–	3.0Cu, 0.2N
High Cr–High Ni	CR30A	0.06	0.3	0.2	50.0	30.0	2.0	–	–	–	0.2	–	0.03Zr
	HR6W	0.008	0.4	1.2	43.0	23.0	–	6.0	–	0.18	0.08	0.003	–

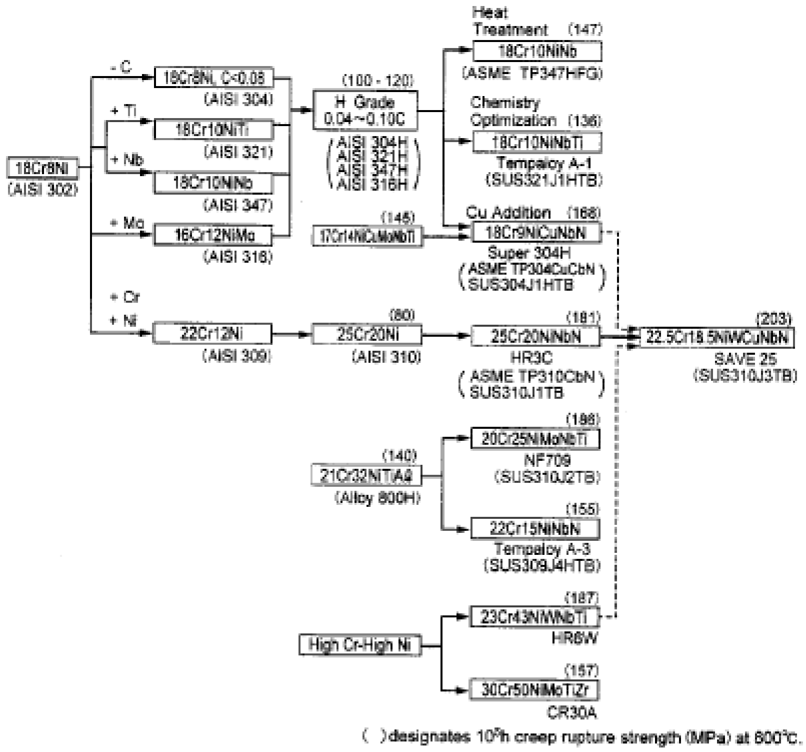

Fig. 2: Development Progress of Austenitic Steels for Boiler (8)

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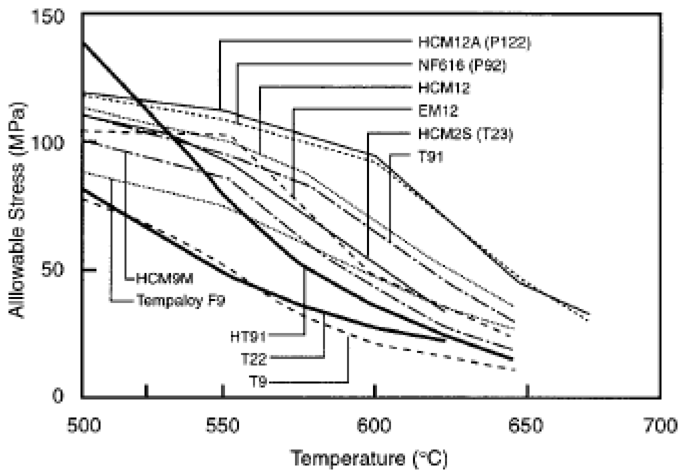

Fig. 3: Comparison of allowable stresses of ferritic steels for boiler (Based on Reference 8)

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

1. The high temperature strength of the advanced alloys, e.g. NF616, HCM12A and E911 (P-92, P-122, E911) is essentially the same as that of low-end 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.
2. Post weld heat treatment (PWHT) is always required for welded joints of advanced 9 to 12 Cr 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 PWHT costs minimal.
3. In the weldment of dissimilar alloys, material selection must be based on consideration of PWHT 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.
4. 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) 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.

Figure 4 is a plot of the allowable stresses vs temperatures for comparing the temperature capabilities of ferritic alloys with austenitic steels and Ni base alloys[11]. The Figure also shows the actual stresses at several steam pressures. The Ni base alloys are superior to the austenitic steels, which, in turn are better than ferritic steels. The nickel base alloys Inco740, Haynes 230, IN625, IN617, HR6W and HR120 have much higher temperature capability, in decreasing order as listed compared to austenitic steels, followed by the ferritic steels. Purely from the creep strength point of view, at a pressure of 5500 psi for a 2" x 0.5" tube (stress 8.6 ksi), ferritic steels are useful up to about 620°C (1150°F) (metal temperature), austenitic steels up to about 675°C (1250°F). At metal temperatures higher than about 675°C (1250°F), nickel base alloys (see Table 5) are needed. The alloy Inco740 appears capable of reaching 788°C (1450°F). Since the thick walled components are used over a range of conditions, all of the above categories of materials area likely to be used at different locations in an ultra supercritical plant.

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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 fire-side 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 6. The rationale for these selections is discussed in the following sections.

2.3.1 Creep Rupture Strength

In terms of creep rupture strength, application for tubes follow the same logic as for the headers/pipes discussed earlier. The principal difference is that in the tubes, the inside metal temperature can be higher than the steam temperature by as much as 25 to 39°C (50 to 70°F). Thus, tubes made of T22 should be limited to steam temperature of 538°C (1000°F); Alloys T91, HCM12, EM12, HCM9M and HT91 limited to steam temperature of 565°C (1050°F); Alloys T-92, P-122 and E911 limited to steam temperature of 593°C (1100°F) (or metal temperature of 620°C [1150°F]), while the developmental ferritic alloys NF12 and SAVE12 may permit steam temperatures up to 620°C (1150°F). Under corrosive conditions however, even the best ferritic steel may be limited to 565°C (1050°F) temperature and austenitic steels are needed in the metal temperature range 620-675°C (1150-1250°F). Above 675°C (1250°F) nickel base alloys are needed.

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 17-14 CuMo 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 intermediate between ferritic steels and high Cr austenitic stainless steels. Several high-creep-strength alloys containing more than 20% Cr, such as NF707, NF709, HR3C, and SAVE 25 have been developed, and offer low-cost alternatives to Incoloy 800 for use in the temperature range from 620 to 675°C (1150 to 1250°F). Clearly, SAVE 25, NF709, HR3C and Super304H are leading candidates for use in the highest-temperature applications. At temperatures exceeding 675°C (1250°F) nickel base alloys are candidates (see Table 7). The highest temperature capability at a given stress is exhibited by Inco740, Haynes 250, HR6W and Inco617 in decreasing order. A new alloy “Marco” is reported to have been developed in Germany as a modified version in IN617, possessing higher strength than IN617.

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Table 5: Nominal Chemical Composition of Ni Base Alloys for USC Boilers

Alloy	Fe	Ni	Cr	Co	Mo	W	Ta	Nb	Al	Ti	Mn	Si	C	B	Zr	Other
IN 617	–	54	22	12.5	9	–	–	–	1	–	–	–	0.07	–	–	–
IN 625	2.5	61	21.5	–	9	–	–	3.6	0.2	0.2	0.2	0.2	0.05	–	–	–
HR 230	3	Bal	22	5	2	14	–	–	0.3	–	–	0.4	0.1	–	–	0.2 La
HR 120	33	37	25	3	2.5	2.5	–	0.7	0.1	–	0.7	0.6	0.05	0.004	–	0.2 N
HR 160	4	Bal	28	27	–	–	–	–	–	–	–	2.75	0.05	–	–	–
800	40	30/35	19/23	–	–	–	–	–	0.15/0.6	0.15/0.6	1.5	1.0	0.1	–	–	0.75 Cu
800HT	40	30/35	19/23	–	–	–	–	–	0.5	0.5	1.5	1.0	0.08	–	–	(Al + Ti)0.85-1.2
INCO 740	0.7	48	25	20	0.5	–	–	2	0.9	2	0.3	0.5	0.06	–	–	–
45TM	23	45	27.5	–	–	–	–	–	–	–	1.0	3.0	0.08	-	-	0.3 Cw

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Table 6: Candidate Alloys for USC Plants

TRADE DESIGNATION	NOMINAL COMPOSITION	ASME Code/ CodeCase	Preferred Application	Temp. of Application (metal)
Ferritic Steels				
HCM2S	2-1/4Cr-1.5W-V	2199	WW*	
Tempaloy F-2W	2Cr-1W-Mo-V-Nb		WW	
HCM12	12Cr-1Mo-1W-V-Nb		WW	
NF12	11Cr-2.6W-2.5Co-V-Nb-N		H	Up to 650°C (1200°F)
SAVE 12	12Cr-W-Co-V-Nb-N		H	
NF 616 (P-92)	9Cr-2W-Mo-V-Nb-N	2179	H	Up to 620°C (1150°F)
HCM12A (P-122)	12Cr-1.5W-Mo-V-Nb-N-Cu	2180	H	
E911	9Cr-1Mo-1W-V-Nb-N		H	
Austenitic Steels				620°C–675°C (1150°F–1250°F)
SAVE25	23Cr-18Ni-Nb-Cu-N		T	
NF709	20Cr-25Ni-NB-Ti-N		T	
HR3C	25Cr-20Ni-Nb-N	2113	T	
Super304A	18Cr-8Ni-W-Nb-N		T	
347HFG	18Cr-10Ni-Nb	2159	T	
800HT	21Cr-32Ni-Al-Ti	1987	T	
HR120	Ni-33Fe-25Cr-N	2315	T	
Ni Base Alloys				675°C–788°C (1250°F–1450°F)
INCO740	25Cr-20Co-2Ti-2Nb-V-Al		P,T	
230	22Cr-14W-2Mo-La	2063	P,T	
Marco Alloy				
625	21.5Cr-9Mo-5Fe-3.6Nb-Al-Ti	1409	P,T	
617	22Cr-12.5Co-9Mo-1.2Al	1956	P,T	
HR6W	23Cr-6W-Nb-Ti		P,T	
45TM	27Cr-23Fe-2.75Si	2188	P,T	

**WW - water wall; T - superheater/reheater tubes; P - pipes and headers

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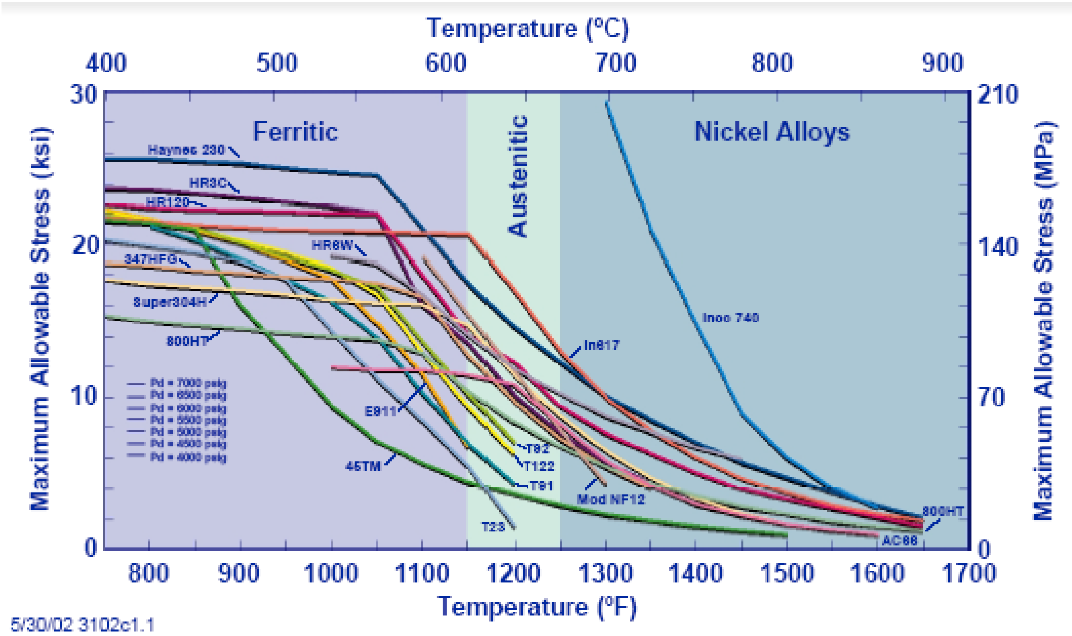

Fig. 4: Boiler Materials for USC Plant(11)

2.3.2 Fire-side Corrosion

Fireside corrosion results from the presence of molten sodium-potassium-iron trisulfates. Because resistance to fire-side 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. 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 Figure 5[12]. 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%.

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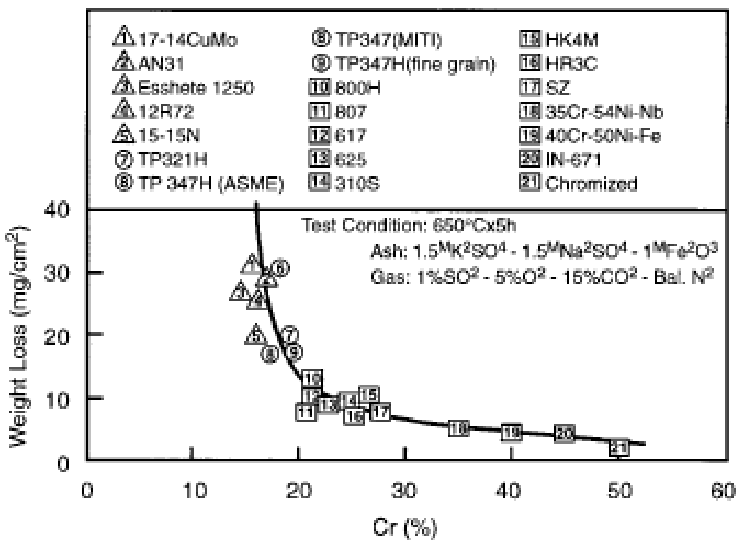

Fig. 5: Relationship between Hot-Corrosion Weight Loss and Chromium Content for Various Alloys [(12)]

A ranking of the performance of various austenitic alloys in the presence of trisulfates has been provided by Ohtomo et al[13] on the basis of short-term laboratory tests (see Figure 6). The plots of weight loss versus temperature exhibit a bell-shape curve. At temperatures below 600°C (1110°F), corrosion is 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 are 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 17-14 CuMo 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[14]. In addition to alloy selection, other "fixes' to minimize fire-side corrosion, such as shielding of the tubes coatings and claddings may also be applied, if economical[15].

Results of extensive field tests have also been reported by Blough[16]. This was based on a collaborative study by EPRI, IHI and F-W who carried out extensive laboratory and field tests in 3 boilers, two of them fueled with somewhat corrosive Eastern bituminous US coal, one fueled with a supposedly non-corrosive Western low sulfur sub-bituminous coal. The experiments were carried out using air cooled, retractable probes, inserted in finishing superheater or reheater areas. Metal temperatures were maintained in the 600-690°C range (1250-1300°F). Exposure time was 16,000 hrs with samples removed after 4000, 12,000 and 16,000 hrs. Figure 7 shows metal losses observed in one of the boilers, using an Eastern bituminous coal, Figure 8 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

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became more protective, but in all alloys internal oxidation and sulfidation occurred in Cr depleted zones below the scale.

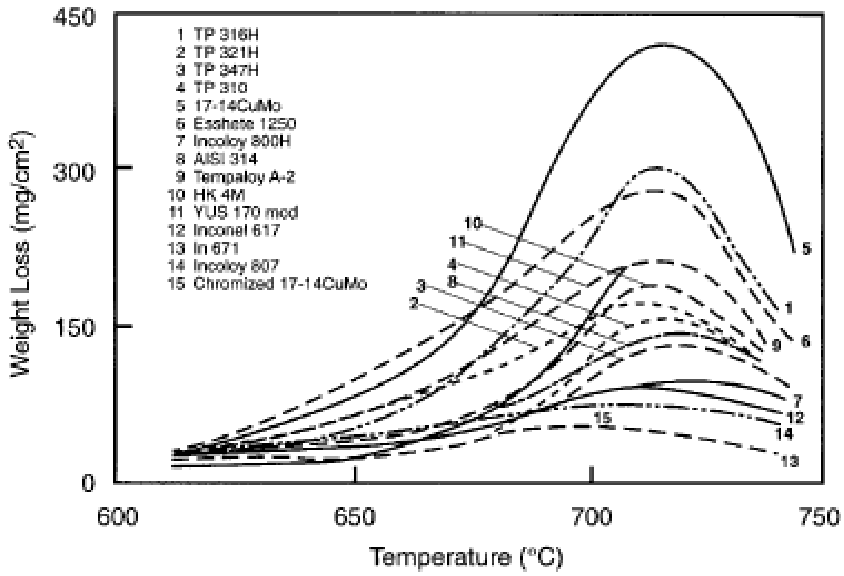

Fig. 6: Comparison of Fire-side Corrosion Resistance of Various Alloys[13]

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, while 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 tight to ferritic/martensitic steels, but spall readily from all austenitic steels.

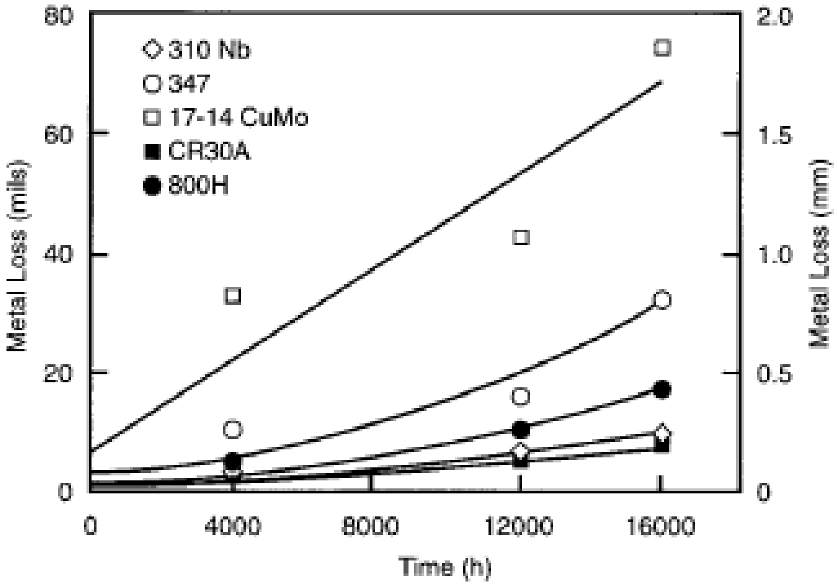

Fig. 7: Metal Losses of Various Superheater Steels in a Boiler using Bituminous Eastern US Coals[16]

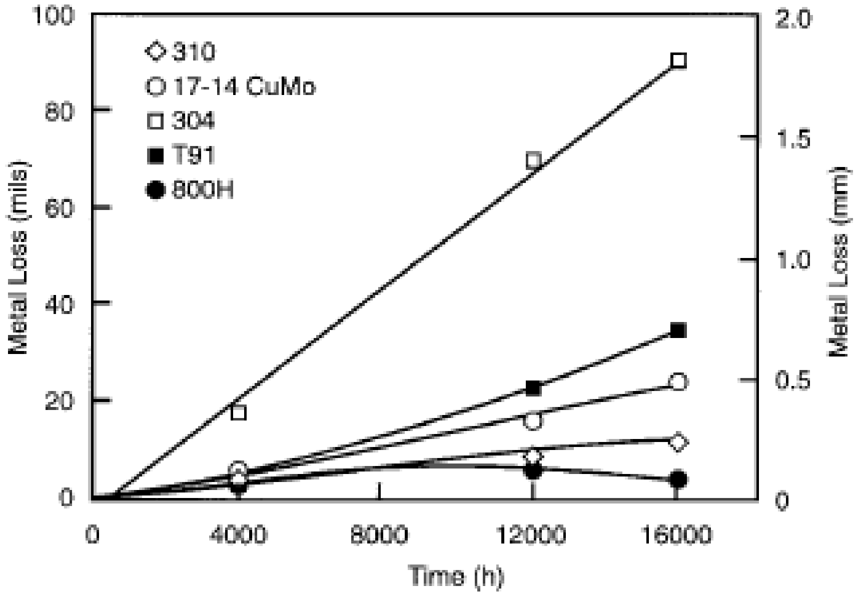

Fig. 8: Metal Losses of Various Superheater Steels in a Boiler Subbituminous Western US Coals[16]

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)[17]. 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/yr (10 mils/yr) corrosion. However in one area, about 10 tubes wide and 10 ft (3m) high, corrosion rates ranged from 0.5 – 1.25 mm/yr (20-50 mils/yr). 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 – 0.5 mm/yr (5 – 20 mils/yr). It is concluded that increasing the Cr content of the alloy from 18-20% to 23-25% will only significantly increase corrosion resistance, when the corrosivity of the deposits is moderate, i.e. ≤ 0.5 mm/yr (20 mils/yr for 18-8 stainless steels). For more corrosive conditions, co-extruded tubes or weld overlay claddings containing at least 40% Cr are strongly recommended. For metal temperatures exceeding 675°C (1250°F), nickel base alloys such s INCO740, Haynes 230, INCO 617 and HR6W need to be considered.

Extensive field experience at EPRI and TVA has shown 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, balNi) and In671 (48Cr, balNi), are commercially available, although improved application methods and reduced costs are desirable. Candidate alloys for tubing after transitions from Ni alloys are the austenitic steels followed by the ferritic.

2.3.3 Steam-side Oxidation

Steam-side 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 steam-side scale-growth characteristics of the ferritic tubing alloys. In a study by Sumitomo Metal Industries[18], 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 hr 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[19]. 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[20]. In addition to the inherent resistance of HCM12M steel to steam-side oxidation, Masuyama et al suggest that the tendency toward exfoliation of oxide scale would also be less for this alloy than for austenitic steels[19, 20]. Additional improvements in 9 to 12% Cr steels may be possible by extending the chromizing[21, 22] and chromate conversion treatments[23] 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[24]. Steamside oxidation results on Ni base alloys are not available and the upper temperature limits have not been defined.

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2.4 Choice of Materials for Waterwalls

2.4.1 Metal Temperature Concerns

This issue has been discussed originally by Blum[25]. In boilers operating at 625°C/32 MPa, maximum midwall temperatures can be as high as 500-525°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[26], 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 12Cr% respectively developed by Sumitomo and MHI are more promising in that they do not require preheat or postweld heat treatment[25-27]. 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. It 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 US 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 US retrofitted with such systems have reported severe corrosion of low alloy steel waterwalls, with metal losses in the 1-3 mm/yr (40-120 mil/yr) 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[28] has shown that corrosion rates in gas mixtures, actually found in boilers, containing 500-1500 pm H_2S and 5-10% CO, are generally less than 0.5 mm/yr (20 mils/yr) 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. When corrosion is a problem there is no alternative to overlay coatings or cladding with high Cr alloys such as IN671 or IN72.

The temperature of waterwalls is driven by the steam pressure. Present maximum waterwall temperatures are in the 470°C range for steam pressures of 24.5 MPa (3500 psi). If this is increased to 35 MPa (5000 psi), the expected maximum waterwall temperature will increase by 50 to 75°C (to 500–525°C [932–977°F]). 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.

3.0 US Project on Boiler Materials for USC Plants

Table 1 illustrates the efficiency advantages to be gained by going to higher steam conditions. Compared to the efficiency of subcritical steam plants of 37% and that by conventional supercritical plants of 40.9%, the steam conditions of 5500 psi/1400°F/1400°F envisaged in the DOE/OCDO project offers an efficiency of 46.5% (HHV); For a double reheat cycle it is

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increased to 47.5 (HHV). It is to be noted however that efficiency is a function of numerous variables and the values reported in Europe are generally higher compared to the US by 3 to 4 points. An attempt has been made to achieve an apples-to-apples comparison as described in the table.

This project was initiated about 6 months ago around October 2002 and is of 5 years' duration. It is funded by the USDOE/National Energy Technology Labs (15.2 Million US$), and the Ohio Coal Development Office of the Ohio Department of Development (2.0 Million US$). The participants also provide cost sharing to the tune of 2.7 Million US$.

The goals of the project include: identification of advanced materials that achieve cost competitive, environmentally acceptable coal based electric power generation that includes the use of high sulfur coals; and to enable domestic boiler manufacturers to globally compete for the construction and installation of high efficiency coal fired power plants.

The specific objectives of the Ultra Supercritical Materials Project are to:

- Identify materials performance issues that limit operating temperatures and thermal efficiency of coal-fired electricity generating plants;
- Identify improved alloys, fabrication processes and coating methods that will permit boiler operation of steam temperatures up to 760°C or 1400°F and steam pressures up to 5500 psi;
- Work with alloy developers, fabricators, equipment vendors and power generation plants to develop cost targets for the commercial deployment of alloys and processes developed;
- Define issues impacting designs that can permit power generation at temperatures greater than or equal to 870°C or 1600°F;
- Lay the groundwork for ASME Code approval.

The alloys that will be evaluated under the Ultrasupercritical Materials Program will have direct application in all advanced fossil-based power generation technologies that incorporate the Rankine steam cycle. This program will have an impact on ultrasupercritical coal combustion systems, integrated gasification combined cycle plants, hybrid cycles incorporating partial gasification and fluid bed combustion, and gasification fuel-cell/turbine systems. The near term benefits this research program could solve high-temperature materials problems in present power generation systems. The long term benefit would be the development of new high temperature materials capable of providing for higher efficiency cycles critical to the success of the Vision 21 concept pioneered by the US DOE.

The scope of work involves conceptual design, economic studies, and evaluation of candidate alloys' mechanical properties, steamside oxidation resistance, fireside corrosion resistance, weldability and fabricability. Coating and cladding technologies will also be evaluated. Detailed reviews of the State-of-the-Art with respect to alloy selection, mechanical properties, oxidation and coatings will be conducted right at the start. The impact of these technologies on code development will also be explored.

The consortium of members performing the various tasks include Alstom Power, Babcock Borsig Power, Babcock & Wilcox Co./McDermott Technologies, Foster Wheeler Development Corp. and the Electric Power Research Institute (EPRI). EPRI also oversees and manages the technical direction, while the Energy Industries of Ohio (EIO) is the prime contractor that has the overall management responsibilities. The Oak Ridge National Labs

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(ORNL) is informally part of the consortium structure as they provide complementary input to this project through a parallel contract.

4.0 Summary and Conclusions

Literature pertaining to materials technology for boilers in ultra supercritical pulverized coal power plants has been reviewed. Extensive development in strengthening of 9 to 12% ferritic steels have 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 (1080-1112°F) and pressures of 24 to 30 MPa (3400-4200 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 Mo 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) (metal temperature) 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 Cr 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 metal temperatures exceeding 675°C (1250°F). Candidate alloys for heavy section applications and the applicable limiting temperatures are shown in Table 7.

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 28-39°C (50-70°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 (1150°F) application, Super 304H, Tempalloy Al, Eshete 1250 and 17 Cu-MO are acceptable under non corrosive conditions while 20-25% Cr alloys such as HR3C, NF709, 347HCG, SAVE 23 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 both header and SH/RH applications close to 760°C Ni base alloys Inco740, Nimonic 230 and modified Alloy 617 are being evaluated. Additional cladding with high Cr alloys may be needed for tubing.

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 595-650°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 18-20% Cr.

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A new consortium project sponsored by USDOE and OCDO aims to evaluate materials for a USC boiler operating at 30.9 MPa (5500 psi)/760°C (1400°F)/760°C (1400°F). Details of the project are described.

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