

# High temperature steels in pulverised coal technology

Kyle Nicol

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## **Preface**

This report has been produced by IEA Clean Coal Centre and is based on a survey and analysis of published literature, and on information gathered in discussions with interested organisations and individuals. Their assistance is gratefully acknowledged. It should be understood that the views expressed in this report are our own, and are not necessarily shared by those who supplied the information, nor by our member countries.

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### Abstract

Pulverised coal combustion (PCC) power plant with supercritical (SC) steam parameters have been operational for over forty years and ultra-supercritical (USC) PCC plant have been operational for just over twenty years. This significant amount of operating experience is valuable regarding the performance of high temperatures steels. For example 9–12% chromium martensitic steels have had problems with cracking and some have not been as strong as they were projected to be. Additionally, PCC power plant have been operated outside of design parameters, such as severe cyclic operation, which has resulted in unforeseen problems for high temperature steels. This report assesses the performance, problems, solutions and research efforts for high temperature steels used in SC and USC technology.

# Acronyms and abbreviations

ASME	American Society of Mechanical Engineers
AUSC	advanced ultra-supercritical
AVT[O]	all-volatile treatment oxygenating
AVT[R]	all-volatile treatment reducing
CMMS	computerised maintenance management system
COST	CO-operation in the field of Science and Technology
CTF	component test facility
DMW	dissimilar metal weld
FAC	flow accelerated corrosion
FSDP	full-scale demonstration plant
GMAW	gas shielded metal arc welding
GTAW	gas tungsten arc welding
HAZ	heat affected zone
НР	high pressure
HRSG	heat recovery steam generators
ICHAZ	inter-critical fine grain zone of the heat affected zone
IP	intermediate pressure
LHV	lower heating value
LP	low pressure
MARBN	MARtensite plus boron plus nitrogen
NIMS	National Institute for Materials Science
OFA	over-fire air
ОТ	oxygenated treatment
PCC	pulverised coal combustion
PBHT	post bend heat treatment
PWHT	post weld heat treatment
SAW	submerged arc welding
SC	supercritical
SCC	stress corrosion cracking
SEM	scanning electron microscope
SMAW	shielded metal arc welding
TEM	transmission electron microscopy
TIG	tungsten inert gas welding
USC	ultra-supercritical
WSF	weld strength factor

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Introduction

#### **1** Introduction

Increasing the net electrical efficiency of pulverised coal combustion (PCC) plant guarantees lower coal consumption, resulting in reduced fuel costs and emissions; and helps sustain valuable coal resources. Increasing the superheated steam temperature is the single most effective way to increase the efficiency of PCC plant. The maximum superheated steam temperature is limited by steels, used to make high temperature components in the steam circuit, able to operate at this temperature for a service lifetime of 20–40 years. Developing new high temperature steel components is complex, expensive, time consuming and risky. New steels need to be qualified for over a decade in numerous mechanical and chemical tests. However, the increase in efficiency justifies this effort.

This development in steels has increased the maximum steam temperature from subcritical steam temperatures, to supercritical (SC), to the present state-of-the-art ultra-supercritical (USC). Supercritical (SC) pulverised coal-fired (PCC) power plant operate with superheated steam at 540–580°C and 21–25 MPa using low alloy ferritic steels, 9–12% chromium martensitic steels and austenitic steels. The net electrical efficiency of SC PCC plant lies between 35–40% (LHV) with coal consumption at 320–380 g/kWh. Since 1959, hundreds of SC plant have been commissioned globally.

Ultra-supercritical (USC) PCC power plant operate with superheated steam at 580–605°C and 22–29 MPa using low alloy ferritic steels, improved 9–12% chromium martensitic steels and austenitic steels. The net electrical efficiency of USC PCC plant lies between 40–47% (LHV) with coal consumption at 340–320 g/kWh. The first USC unit, Tsuruga 2, was commissioned in 1992 in Japan. From 1992–2006, twelve USC units in Japan and two in Denmark were commissioned. From 2007, the US, Germany, Italy, Russia China, South Korea and now India have USC units. According to Platts, PCC plant operating in August 2013 include ~165 operational USC units, ~645 operational SC units and >7883 operational subcritical units (IEA, 2012; Breeze, 2012; Nalbandian, 2008; Platts, 2013).

Despite extensive testing, new high temperature steels in service for over a decade can encounter unforeseen problems. These problems often result in reduced availability and reliability, thus increasing maintenance costs and decreasing operational profit. SC and USC PCC power plant have now been operational for up to forty years and twenty years respectively. This substantial base of operating experience is valuable for qualifying the performance of high temperatures steels.

Problems have been encountered with new steels since their commercial use. These problems include stress corrosion cracking (SCC) of T24 ferritic steel, Type IV cracking and long-term creep degradation of 9–12% chromium martensitic steels. These problems are now understood and preventative measures to avoid failure have been developed. In some cases these problems have been used as the basis to develop stronger steels.

Since the 1990s in Europe, the energy industry has been deregulated and privatised and there has been a substantial increase in the capacity of intermittent renewable power (such as wind, and solar), which can fluctuate within minutes. In order to balance the load in a power gird with intermittent resources and

maximise profits, PCC power plant which have been designed to provide base-load power, have been forced into cyclic operation. This cyclic operation has resulted in more unforeseen creep-fatigue damage mechanism of high temperature steels (Shibli, 2012b).

Figure 1 shows the average component failures in steam boilers by Thielsch Engineering of the USA (Smoske and Barbaro, 2013).



#### Figure 1 – Average component failures in steam boilers (Smoske and Barbaro, 2013)

This report will assess the problems, solutions and research efforts for high temperature steels used in SC and USC technology.

#### 2 Steel selection

The following sections will review the following items regarding high temperature steels in pulverised coal combustion (PCC) power plant; the degradation mechanisms, developments, welding procedures, codes and standards, and provide detailed tables of commercial steels and the chemical composition for steels.

#### 2.1 Damage mechanisms

High temperature steels will last for a finite service lifetime in PCC plant. Ultimately, the combination of chemical attack, stresses and erosion on steels in service will result in material failure. For the purpose of this report, high temperature steels in service are gradually degraded by the following damage mechanisms; chemical attack, in the form of fireside corrosion and steamside oxidation, and stress, in the forms of constant and cyclic stresses.

#### 2.1.1 Steamside oxidation

Steamside oxidation is the oxidation of metal surfaces exposed to the steam in the steam loop; this will be most prevalent in higher temperature locations, such as pipes, tubes, valves and steam turbines. The rate of steamside oxidation is proportional to the metal temperature. Steamside oxidation consists of three stages. Firstly, oxide scale builds up causing materials to overheat, which decreases material strength. Secondly, the oxide scale eventually exfoliates, gradually reducing the cross-sectional area of steel, which again decreases material strength. Finally, the oxide scale fragments and erodes the entire steam loop, further decreasing strength. In short, steamside oxidation will lower steam turbine efficiency and the decrease in material strength may lead to pipe blockages, *see* far left picture and middle picture on Figure 22 (page 43). To avoid build-up of scale in the steam cycle, power plant operators have developed methods to periodically flush out scale into the condenser (Viswanathan, 2008a).

#### 2.1.2 Fireside corrosion

Fireside corrosion is a term used to describe the degradation of material surfaces in boilers by flue gases and molten coal ash containing elements such as sodium, sulphur and chlorine. The accumulation of corrosion by-products on metal surfaces, *see* far right picture on Figure 22, has two effects. Firstly, heat transfer rates are decreased resulting in reduced thermal efficiency. Secondly, material strength is reduced through overheating and the gradual reduction of cross-sectional area. Generally, the rate of fireside corrosion increases with flus gas temperature. For coal combustion, fireside corrosion occurs in the high temperature gas phase, high temperature gas and liquid phase and low temperature liquid phase as explained subsequently (Moreea-Taha, 2002):

 high temperature gas phase – at high temperature, sulphur (sulphur dioxide and hydrogen sulphide) and chlorine species (in the form hydrogen chloride and chlorine) can corrode steels by reduction or oxidation mechanisms – common products of corrosion are sulphates, sulphides and chlorides. High temperature gas phase corrosion involving chlorine is called chlorination and with sulphur it is sulphidation.

- high temperature gas and liquid phase various salts formed during combustion condense on steels as a liquid film. New salts are then formed from reaction with other salts and with various elements from metal surfaces. Some of these new salts can then evaporate, depleting steels of certain elements, which potentially leads to secondary corrosion mechanisms. The corrosion rate depends on the affinity of the alloying elements to salts.
- low temperature liquid phase low temperature corrosion may result from the condensation of sulphuric acid, sulphurous acid and hydrogen chloride in the colder areas of the boiler. The resulting corrosion is usually manifested as pitting.

Cofiring other fuels, such as biomass, are with coal alters the fireside corrosion chemistry. Such chemistry is complex and beyond the scope of this report, however Table 1 summarises fireside corrosion rates of different fuels on a scale of 1 to 10, which has been developed by Metso of Finland (Silvennoinen and others, 2013).

Table 1 – Fireside corrosion rate of different fuels (Silvennoinen and others, 2013)									
Fuel	Concern	Fireside corrosion rate							
Natural gas, heavy oil	-	1							
Bituminous coal	-	2							
Wood (Nordic softwood, forest residuals, spruce bark)	-	2							
Fossil+ (Coal washing reject, petcoke)	High ash content (<80% mass), high sulphur (8% mass)	3							
Wood+ (Willow, eucalyptus bark)	Chlorine, alkali, ash	4							
Agricultural biomass (straw, hull, kernels)	Chlorine, alkali, phosphorus, silicon, nitrogen	7							
Recycled wood	Chlorine, alkali, heavy metals	7							
Solid recoverable fuels	Chlorine, alkali, lead, zinc, ash	8							

#### 2.1.3 Constant and cyclic stress

Constant stress, induced by physical load and pressures, at high temperatures over long time periods results in creep damage. Creep damage is where the material microstructure transforms resulting in cracking. Catastrophic failure can occur if rapid crack propagation occurs. Two useful rules of thumb for creep damage are, a short time period at elevated temperature will result in similar creep damage to a long time period at lower temperature and the creep life for most steels will halve for a 10°C increase in temperature. Cyclic stresses, induced by high thermal gradients, seen as the difference in flame temperature to steam temperature, result in fatigue damage, seen as cracks on the material surface.

#### 2.2 Development of steels

Since the 1950s extensive high temperature steel research has developed four generations of steels with increased strength and resistance to chemical attack. Figure 2 shows the increase of creep resistance from 35 MPa to 130 MPa (over 100,000 hours at 600°C) for ferritic and martensitic boiler steels from the 1960s to 2013 (100,000 hours translates to 11.41 years).



#### Figure 2 – Development of boiler steels from the 1960s to 2013 (Subanovic and Schneider, 2012)

Figure 3 shows a Gantt chart of some significant high temperature steel research programmes from 1985 with projections to 2026. Some of these programmes will be expanded upon later in the report.



Figure 3 – Gantt chart of high temperature steel research programmes 1985-2026

Figure 4 shows a cross-section of a pipe fabricated from different steels. The figure compares the pipe thicknesses of different steels required to operate with steam at 593.3°C and 320 bar (USC steam parameters). Weaker steels, such as P22, X2012CrMoVNb and P91 require thicker walls to operate with USC steam. Thick walls are impractical as they are difficult to weld, have lower heat transfer rates which limit ability to operate in cyclic mode, and have a higher chance of failure due to a large thermal co-efficient of expansion (Shibli, 2012a).



Figure 4 – Comparison of nominal pipe thickness for different steels (Shibli, 2012a)

#### 2.3 Welding procedure

Welding steels is essential for manufacturing components – the other manufacturing route is casting which is more problematic. Welding can introduce undesirable changes to the microstructure in the heat affected zone (HAZ) of the parent material adjacent to the weld material. The material properties of the HAZ and filler material are different to those of the parent material and welds often contain residual internal stresses. For some steels post weld heat treatment (PWHT) may be necessary to prevent permanent changes in the steel microstructure and reduce internal stresses caused by welding. However, for many steels, welds remain the weakest link.

The following types of welding procedures are used for high temperature steels in PCC plant components. Depending on the material type, a different filler material may be required for each welding procedure (Stultz and Kitto 2005):

- submerged arc welding (SAW);
- shielded metal arc welding (SMAW);
- gas shielded metal arc welding (GMAW), also referred to by its subtypes, metal inert gas (MIG) welding or metal active gas (MAG);

• gas tungsten arc welding (GTAW), also referred to as tungsten inert gas welding (TIG).

The ratio of creep resistance of the welded joint to the creep resistance of the base metal is called the weld strength factor (WSF). WSF are the most important information for welds in the material design codes. In general, boilers require a WSF of 0.8–0.85 over 100,000 hours (11.41 years). Figure 5 shows WSF for steels from 100,000 hour cross-weld uniaxial creep tests. The hatched areas show results for 10,000–50,000 hour tests (1.14–5.7 years). Some design codes use other tests, such as cross weld multi-axial creep tests, to define weld properties. However, fatigue damage, and therefore creep-fatigue damage, has not been factored into the design codes for older coal-fired power plant (Hueggenberg and others, 2012). Hueggenberg and others (2012) have developed a geometrical weld model which determines local stress and strains, and thus selects appropriate steels.



Figure 5 - Weld strength reduction factors (Hueggenberg and others, 2012)

Steel selection

#### 2.4 Codes and standards

Steels used in power plant must pass certain material requirements set by material code administrative agencies. These requirements include conducting tests in order to project a safe material service life. Mechanical tests asses the following material properties: fatigue resistance, creep resistance, toughness, bending and welding ability. Chemical tests assess resistance to steamside oxidation and fireside corrosion.

The creep rupture tests are the most time consuming. Short-term creep rupture tests take 10,000–30,000 hours (1.14–3.5 years) and long-term tests take 100,000 hours (11.41 year). Using results from creep rupture tests, computer models fit a variety of creep projection equations, such as the Manson-Heford and Larson-Miller, to determine which equation can be used to most accurately extrapolate creep resistance to a service life of up to 40 years. A safety factor is of course fitted to the lower bound data. The models, equations and safety factors used depend on the material standard. Based on operating experience in power plant, steels tend to have a much longer life than projected. However, failures from creep damage have been seen in power plant which have been operated outside of design conditions, resulting in hot spots within the boiler or excessive fireside corrosion (Fleming and Foster, 2001). It is important to remember that until a material has served a complete service lifetime, the material is considered new.

Globally, there are many material code administrative agencies, such as those set by the Japanese Industrial Standards and the British Standards. However, the Boiler & Pressure Vessel Code, set by the American Society of Mechanical Engineers (ASME), are used internationally. The ASME designation uses prefixes, such as T, P or F. T stands for tube or thin and accounts for thin-section components and P stands for pipe and accounts for thick-section components. P91 for example is grade 91 with a specific chemical composition for forged pipes, there is also T91 for seamless tubes, WP91 for pipe fittings, F91 for forgings, FP91 for forged and bored pipe and Gr 91 for alloy steel plates. Additionally, there are different filler materials for each type of grade 91. Austenitic steels are only applied to thin-section components for mechanical reasons so they do not currently use the pre-fix T or P.

In addition to material codes, there are country-specific design standards for components manufactured from the code approved steels. Design standards will dictate minimum requirements for components, examination methods and inspection routines. Two approaches are used to design components, the 'design by analysis' approach, used in Europe, and the 'design by rule', used in the US. The 'design by rule' approach usually results in heavier wall thicknesses and does not cover all design situations (Narula and others, 2013).

#### 2.5 Commercial steels

Tables 2 and 3 lists the steels used for high temperature boiler and steam turbine components, respectively, in commercially operating USC PCC power plant. Both tables list the relative resistance required to the four main forms of damage, fireside corrosion, steamside oxidation, creep and fatigue. Additionally, the comments on the far right hand column mention the problems associated with the components manufactured from the stated steels, all of which will be expanded on in this report. All

temperatures mentioned in this report are that of the steam, not of the metal or flame. Stronger steels are more expensive, martensitic steels are two to three times more expensive than ferritic steels and austenitic steel are three to ten times more expensive than ferritic steels. Thus lower strength steels are used where possible to keep costs down; this increases the number of steels used in steam circuits (Wheeldon and Shingledecker, 2013).

Boiler component and steam temperature	Steels	Fireside corrosion resistance	Steamside oxidation resistance	Creep resistance	Fatigue resistance	PWHT	Comments	
Tube: Waterwall <480°C	Ferritic: T11, T12	Low	Very Low	Very Low	Very Low	No	High fireside corrosion	
Tube: Waterwall <565°C	Ferritic: T22, T23, T24	Moderate	Low	Low	Low	No	with OFA SCC of T24	
Tube: Superheater and reheater 550–575°C	Ferritic: T22, T23, T24	Moderate	Moderate	Low - Moderate	Low - Moderate	No	SCC of T24	
	Martensitic: T91			moderate	Woderate	Yes	Type IV	
Tube: Superheater and reheater <600°C	Martensitic: T92, E911, T122, NF12, SAVE12	High	High	Very High (superheat)	Very High (superheat)	Yes	Type IV	
	Austenitic: 347HFG, 310			High (reheat)	High (reheat)	Yes	DMW	
Tube: Reheater <620°C	Austenitic: Super 304H, Esshete 1250, 17–14 CuMo, Sanicro 28, NF709, HR3C, SAVE 25	Very High	Very High	Moderate	Moderate	Yes	DMW	
Pipe: Headers <580°C and <22 MPa	Martensitic: P91	Moderate	Moderate	High	Moderate	Yes	Type IV	
Pipe: Header <600°C and 22-25 MPa	Martensitic: P92, E911, P122	High	High	Very High	High	Yes	Type IV	
Pipe: Headers <620°C and <10 MPa	Martensitic: NF12, SAVE12	Very High	Very High	High	Moderate	Yes	Type IV	
Pipe: Superheat <600°C and 22–25 MPa	Martensitic: P92, E911, P122	None	High	Very High	Very High	Yes	Type IV	
Pipe: Reheat <620°C and <10 MPa	Martensitic: NF12, SAVE12	None	Very High	Moderate	Moderate	Yes	Type IV	
Furnace floors, upper furnace walls, convection pass enclosures and economisers	Ferritic: High carbon grades, chromoly steels	Moderate	None	Low	Low	Yes	None	
Baffles, supports, hanger fittings, oil burner impellers, soot-blower clamps and hangers	Austenitic: 25Cr–20Ni, 25Cr–12Ni	High	None	Moderate	Moderate	Yes	None	

 Table 3 – Steels for valves and steam turbine components (Narula and others, 2013; Stultz and Kitto 2005; Viswanathan, 2008b; Blum, 2009; Modern Power Systems, 2009b)

Steam turbine component	Steels	Steamside oxidation resistance	Creep resistance	Fatigue resistance	Comments
HP/IP Rotor <620°C	Martensitic: 9-12CrMoVNbN, 9–12CrWCo, E, FB2, TR1150, TOS110	High	High	High	
HP/IP Rotor <593°C	Martensitic: TR1100, TOS107	Moderate	Moderate	Moderate	
HP/IP Rotor <566°C	Ferritic: 1CrMoV Martensitic:, 11CrMoVTaN (TOS101), 12CrMoVW, 12CrMoVNbN, 26NiCrMoV11.5	Low	Low	Low	Single material to avoid DMW.
LP Rotor <600°C	Martensitic: 3.5NiCrMoV	Moderate	Moderate	Moderate	
LP Rotor <566°C	Martensitic: NiCrMoV	Low	Low	Low	
Blades <620°C	Martensitic: 9-12CrWCo	High	High	High	Coatings may be applied
Blades <593°C	Martensitic: 9CrWCo, R26	Moderate	Moderate	Moderate	to protect against
Blades <566°C	Ferritic: 1.25CR–0.5Mo (cast) Martensitic: Alloy 422, 10CrMoVNb	Low	Low	Low	erosion, but not corrosion.
Inner casing and vale body <620°C	Martensitic: 9CrMo(W)VNbN, CB2, 12CrMoVCbN (cast or forged), 9–12CrW, 12CrWCo (cast) Austenitic: 19Cr12.5NiNbMoC (CF8C–Plus)	High	High	High	
Inner casing and vale body <593°C	Martensitic: 9Cr1MoVNb, 10CrMoVNb	Moderate	Moderate	Moderate	Thermal coefficient of
Inner casing and vale body <566°C	Ferritic: 2.25CR–1Mo (cast), 1.25CR–0.5MoV (cast), 1.25CR–0.5Mo (cast) Martensitic: 10CrMoVNb, 9CrMoVNb	Low	Low	Low	casings must be similar.
Outer casing <600°C	Ferritic: 2.25Cr–1Mo (cast)	Negligible	Moderate	Moderate	
Outer casing <566°C	Ferritic: 1.25Cr-0.5Mo (cast)	Negligible	Low	Low	
Valve internals and turbine nozzles <620°C	Martensitic: 9-10CrW, 12CrWCo	High	High	High	
Valve internals and turbine nozzles <593°C	Martensitic: 9Cr1MoVNb cast, 10CrMoVNb, 12Cr1MoVNbN	Moderate	Moderate	Moderate	
Valve internals and turbine nozzles <566°C	Ferritic: 2.25CR-1Mo (cast), CrMoV Martensitic: 10CrMoVNb (cast)	Low	Low	Low	
Bolts <620°C	Martensitic: 9-12CrMoV, Nickel alloy: IN718, A286	Negligible	High	High	Thermal coefficient must
Bolts <593°C	Martensitic: Refractory 26 Nickel alloy: Nimonic 85A	Negligible	Moderate	Moderate	be similar to that of casings.
Bolts <565°C	Martensitic: Alloy 422, 9-12CrMoV, Nickel alloy: Nimonic 80A, IN718	Negligible	Low	Low	resistance

Figure 6 shows a typical waterwall, in the process of having tubes welded, Figure 7 shows a typical header and Figure 8 shows a typical superheater.



Figure 6 – Typical waterwall (McCauley, 2012)



Figure 7 – Typical header (Viswanathan and other, 2008a)



Figure 8 – Typical superheater (Hernblom, 2012)

#### 2.6 Steel composition

Table 4 lists the designation and chemical composition of the ferritic, martensitic and austenitic steels used in pulverised coal-fired power plant.

Table 4 – Designation and chemical composition of steels										
Material type	Nominal composition	EN (Europe)	ASME (USA)	JIS (Japan)	References					
Ferritic	1.25Cr0.5Mo	10CrMo5-5	T11		Hikes and Gross, 2013					
Ferritic	1Cr0.5Mo	13CoMo4-5	T12		Hikes and Gross, 2013					
Ferritic	2.25CrMo	10CrMo9–10	T22		Hagen and Bendick, 2013					
Ferritic	2.25Cr1.6WVNb	7CrWVMoNb9–6	T23	HCM2S	Hagen and Bendick, 2013					
Ferritic	2.25Cr-1MoVTiB	7CrMoVTiB10–10	T24		Hagen and Bendick, 2013					
Ferritic				SAVE12	Holcomb, 2012					
Martensitic		X20CrMoNiV11-1		650HV10	Hagen and Bendick, 2013					
Martensitic	9CrMoWVNbN	X11CrMoWVNb9-1-1	E911	HCM12	Hagen and Bendick, 2013					
Martensitic		X11CrMo9–1	т/Р9		Hagen and Bendick, 2013					
Martensitic	11Cr2WMoVNbCu		T/P122	HCM12A	Hagen and Bendick, 2013					
Martensitic	9CrMoVNb	X10CrMoVNb9-1	т/Р91		Hagen and Bendick, 2013					
Martensitic	9Cr2WMoVNbN	X10CrWMoVNb9-2	т/Р92	NF616	Hagen and Bendick, 2013					
Martensitic		HR100			Gibbon, 2013					
Martensitic		HR1200			Gibbon, 2013					
Martensitic		COST B			Gibbon, 2013					
Martensitic	10CrMo(W)VNbN	COST E			Blum, 2009; Gibbon, 2013					
Martensitic		COST F			Gibbon, 2013					
Martensitic	9CrMoCoVNbNB	COST FB2			Blum, 2009; Gibbon, 2013					
Martensitic	9CrMoCoVNbNB	COST CB2			Gibbon, 2013					
Martensitic		MARBN			Gibbon, 2013					
Martensitic		MARN			Gibbon, 2013					
Martensitic		BH			Gibbon, 2013					
Austenitic	25Cr20NiNbN	X6CrNiNbN 25–20	TP310HCbN	HR3C	Nippon Steel and Sumitomo Metal, 2013					
Austenitic	18Cr9i3CuNbN	X10CrNiCuNb 18-9-3	2520	Super304H	Nippon Steel and Sumitomo Metal, 2013					
Austenitic	20Cr25Ni1.5MoNbN		A213 – TP31MoCbN	NF709	Nippon Steel and Sumitomo Metal, 2013					
Austenitic		X7NiCrWCuCoNbNB25– 23–3–3–2	A312	Sanicro 25	Sandvik, 2013					
Austenitic	18Cr12NiNb	X6CrNiNb 18–10	347H		Nippon Steel and Sumitomo Metal, 2013					
Austenitic	18Cr11Ni0.6Nb	X8CrNi19–11	347HFG		Nippon Steel and Sumitomo Metal, 2013					
Austenitic				Sanicro 28	Gibbon, 2013					
Austenitic				SAVE25	Gibbon, 2013					

Table 4 con	tinued																			
Known by	Fe	С	Cr	Мо	Ni	Si	Mn	Al	W	Ti	V	Nb	В	N	Р	S	Та	Nd	Cu	Со
T11	Bal	0.10	1.25	0.50		0.32	0.68													
T12	Bal	0.13	1.00	0.50		0.70	0.60													
T22	Bal	0.08-0.15	2-2.5	0.9–1.2		0.15-0.4	0.3-0.7	<0.04												
T23	Bal	0.04–0.10	1.9–2.6	0.05–0.30		<0.5	0.10-0.60	<0.03	1.45-1.75		0.2-0.3	0.02-0.08	0.0005- 0.006	<0.03						
T24	Bal	0.05-0.10	2.2–2.6	0.9–1.1		0.15-0.45	0.3-0.7	<0.02		0.05-0.10	0.2-0.3		0.0015- 0.007	<0.01						
SAVE12	Bal	0.01	11.00			0.30	0.20		3.00		0.20	0.07		0.04			0.07	0.04		
650HV10	Bal	0.17-0.23	10-12.5	0.8-1.2	0.3–0.8	<0.5	<1				0.25-0.35				<0.025	<0.015				
E911	Bal	0.09-0.13	8.5–9.5	0.9–1.1	0.1-0.4	0.1-0.5	0.3–0.6	<0.04	0.9–1.1		0.18-0.25	0.06-0.10	0.0005– 0.0050	0.050– 0.090						
т/Р9	Bal	0.08-0.15	8.0–10	0.9–1.1		0.25-1	0.3-0.6	<0.04							<0.025	<0.02			<0.3	
T/P122	Bal	0.07-0.13	10-12.5	0.25-0.6	<0.5	<0.5	<0.7	<0.04	1.5-2.5		0.15-0.30	0.04-0.10	<0.005	0.04-0.1					0.3–1.7	
T/P91	Bal	0.08-0.12	8-9.5	0.85-1.05	<0.4	0.2-0.5	0.3-0.6	<0.04			0.18-0.25	0.06-0.1		0.03-0.07						
Т/Р92	Bal	0.070.13	8.5–9.5	0.3-0.6	<0.4	<0.5	0.3–0.6	<0.04	1.5-2.0		0.15-0.25	0.04-0.09	0.001- 0.006	0.030–- 0.070						
HR100	Bal	0.12	120	1.20	0.60				0.38		0.17	0.05		0.05						
HR1200	Bal	0.09	11.00	0.23	0.51				2.70		0.22	0.07	180ppm	0.02						
COST B	Bal	0.18	9.00	1.50							0.25	0.05	100ppm	0.02						
COST E	Bal	0.12	10.00	1.00					1.00		0.20	0.05		0.05						
COST F	Bal	0.12	10.00	1.50							0.20	0.05		0.05						
COST FB2	Bal	0.13	9.00	1.50								0.07	100ppm	0.02						
COST CB2	Bal																			
MARBN	Bal	0.08	8.90						2.85		0.20	0.05	135ppm	80ppm						
MARN	Bal	0.00	9.20						2.96		0.20	0.06	70ppm	490ppm						
BH	Bal	0.03	9.12	0.15					2.40		0.20	0.05	60ppm	500ppm						
HR3C	Bal	0.04-0.10	24–26		19-22	1-1.5	<2					0.2–0.6		0.15	<0.045	<0.03				
Super304H	Bal	0.07-0.13	19.00		10.50	0.30	1.00	0.03				0.60	0.01	0.12	0.04	0.01			3.50	
NF709	Bal	0.05	20.00		11.00	1.00	2.00		2.60		0.50	0.50		0.25	0.04	0.03				
Sanicro 25	Bal	0.10	22.50		25.00	0.20	0.50		3.60			0.50		0.23	0.03	0.02			3.0	1.50
347H	Bal	0.06-0.01	17–20			0.75–1	2.00					some			0.04– 0.045	0.03	some			
347HFG	Bal	0.06-0.01	17–20		9 to 13	0.75–1	2.00					some			0.04 <del>-</del> 0.045	0.03	some			
Sanicro 28	Bal	0.02	27.00	3.50	31.00									some					1.00	
SAVE25	Bal	0.08	27.00	3.50	31.00				1.50					some					3.00	

#### 3 Mechanical behaviour of steels

This Chapter assesses the performance, problems and solutions regarding mechanical behaviour for high temperature ferritic, martensitic and austenitic steels.

#### **3.1 Ferritic steels**

Ferritic steels have a ferrite microstructure (iron arranged in body centred cubic) due to a low proportion of alloying (<0.025% carbon). Ferritic steels have been strengthened with the following strengthening mechanisms, solid solution and dislocation strengthening, which are explained in the following subsections. Generally, ferritic steels have good weldability and do not require post weld heat treatment (PWHT) and thus offer considerable financial savings (Stultz and Kitto 2005).

Ferritic steels, called the CMn and Mo steels, were used in PCC plant reaching superheated steam temperatures of 500°C until the 1960s. Improvements in ferritic steels were then achieved with increased alloying of chromium and molybdenum in the CrMo steels, or chromoly steels, which include T/P11 (1.25Cr–0.5Mo) and T/P22. In the 1960s, 570°C superheat temperatures were attainable in supercritical plant largely using chromoly steels and some of the first martensitic steels (Hagen and Bendick, 2013; Subanovic and Schneider, 2012). Since the 1980s, ferritic steels, such as the new T/P23 and T/P24, have been further developed for lower temperature application, such as waterwalls and other low temperature applications in SC and USC plant, due to their ease of fabrication and welding. Modern ferritic steels are capable of dealing with steam at 565°C (Narula and others, 2013). At higher temperatures the low chromium content of chromoly steels results in excessive steam side oxidation (Gibbons, 2013).

#### **3.1.1** Solid solution strengthening

Solid solution strengthening is where small amounts of more than two other alloying elements are diffused into the microstructure of a parent metal in order to increase strength of the material (whilst keeping a single phase). The alloying element is smaller or larger than the surrounding parent atoms, creating distortions which disrupt the microstructure, making it more difficult for layers of the microstructure to slide over each other. This makes the alloy less ductile and therefore stronger than the pure metal (NDT Resource Center, 2013). In steels, tungsten, molybdenum and cobalt cause solid solution strengthening (Narula and others, 2013).

#### **3.1.2** Dislocation strengthening

Dislocation strengthening, or cold working, is a method of strengthening a metal by plastic deformation at low temperature. The strain deforms the grains in the microstructure, creating more dislocations and tangling the dislocations, which prevents movement of microstructure during constant stress, and thus strengthens the material. However, this process has limited strengthening ability, as exposure to high temperatures restores the microstructure. This restoration can be divided into three stages, recovery, re-crystallisation and grain growth. The recovery phase is where atoms diffuse from high strain areas to low strain areas within the deformed grains, or sub-grains, which removes any defects in the microstructure. Creep resistance eventually lowers through the reduction in the dislocation density and the movement of dislocations to lower strained areas. Re-crystallisation follows recovery, where new strain free grains form throughout the material. These new grains then grow. Figure 9 shows these three stages. Shot-peening is a process that uses cold work to increase resistance to chemical attack. The process shoots round metal/glass/ceramic particles onto the material surface to induce cold work (Subanovic and Schneider, 2012; NDT Resource Center, 2013).



Figure 9 – Recovery, re-crystallisation and grain growth after dislocation hardening (NDT Resource Center, 2013)

#### 3.1.3 Ferritic steels T23 and T24

T23 and T24 were specifically designed and qualified in Europe, partly under the material research programme 'applications of advanced low alloy steels for new high temperature components' (ALOAS), for use in waterwalls, supporting tubes and superheater tubes (<550°C) of thermal power plant, particularly ultra-supercritical coal-fired power plant. T23 and T24 evolved from T12 with the addition of elements such as vanadium, niobium and titanium. T23 is strengthened by the dispersion of fine M<sub>6</sub>C and MC carbides and T24 is strengthened by vanadium carbides. The main advantage of T23 and T24 over martensitic alloys is that they do not require PWHT. To do this, T23 and T24 have a wall thickness lower than 10mm and lower carbon content than T12 and T22, which reduces the martensitic content. T23 and T24 have creep resistance approaching that of the 9% chromium martensitic steels, however the limited chromium content will limit their maximum temperature application (Fleming and Foster, 2001; Ullrich and others, 2012).

#### 3.1.4 Stress Corrosion Cracking of T24

T24 first began operation in ultra-supercritical coal-fired power plant in 2010. Shortly after commissioning in two boilers in Europe, multiple cracks developed in T24. Subsequent evaluation showed the cracking mechanism to be stress corrosion cracking (SCC). Uniquely, cracks caused by SCC

show little or no deformation. For SCC to occur the material must have certain properties, it must reach critical tensile stresses and be exposed to a certain fluid composition. There are three main types of SCC, anodic SCC, hydrogen-induced SCC and Anodic Hydrogen Embrittlement, all of which interact in complex mechanisms and are explained in detail by Ullrich and others (2012).

In a laboratory, slow tensile tests in controlled high temperature water at different strain rates were used to test the SCC sensitivity of T24 to tensile varying fluid compositions and stresses. The following conclusions were made and later confirmed with a test waterwall operating at E.ON's Staudinger coal-fired power plant over 1336 hours and 21 start-ups (Ullrich and others, 2012):

- T24 welds are susceptible to SCC in high temperature water with an increased oxygen concentration in the steam cycle. For oxygen concentrations up to 450 ppb, it was found that SCC susceptibility occurred independently of the applied strain rate;
- Anodic SCC was found to be the mechanism for SCC initiation, with hydrogen playing a role in later crack propagation;
- heat treatment (>600°C for 2 hours with high oxygen concentration) can suppress SCC.

The following measures can be taken in order to minimise the risk of future SCC of T24 (Ullrich and others, 2012):

- 1. Adapt the chemical cleaning process:
  - optimisation of the process of chemical cleaning and the mixing with de-ionised water;
  - omitting chemical cleaning for the waterwalls and the supporting tubes;
  - intensive cleaning of the waterwalls and heating surfaces by flushing.
- **2.** Reduce the critical tensile stress of T24 with heat treatment (which relaxes the external and residual stresses):
  - externals heaters are used to heat treat the entire boiler at 450–500°C;
  - warm air is passed through all external pipework and internal tubes (waterwalls, superheaters, reheaters) and headers;
  - additionally, residual weld stresses are reduced by 20% from improvements in the welding procedure.
- 3. Adjust the water chemistry and the start-up procedure:
  - start-up with increased temperature gradient to minimise time in critical temperature range;
  - adapting the commissioning to ensure the target temperature of > 300°C for a longer period;
  - conditioning the pH-value and the oxygen content in the feed water according to VGB guide line 450 L for AVT-conditions. The target is to keep the dissolved oxygen in the water below 10 ppb.

**4.** to reliably achieve the above modifications, an external auxiliary steam generator and mobile water treatment with chemical binding of oxygen must be installed.

Ultra-supercritical coal-fired power plant commissioned since 2011, such as Neurath BoA unit's 2 and 3 (Germany), have implemented these measures and, to date, no SCC of T24 has been detected.

#### 3.1.5 Welding procedure of T24

T24 is amongst the highest strength commercial steel that do not need PWHT, provided strict observation of correct welding parameters is practised. In general PWHT is not required for T24 if the hardness values of T24 are below 350 HV10. V&M (Germany) have shown that T24 parent material lies between 310–360 HV10 after fabrication and the filler material lies between 340–360 HV10 with no PWHT. Parent material pre-heating and inter-pass temperatures must be undertaken properly for a weld that does not require PWHT. The following three paragraphs explain how gas tungsten arc welding (GTAW), shielded metal arc welding (SMAW) and submerged arc welding (SAW) should be carried out (Heuserand and Tak, 2013).

With GTAW, to ensure that PWHT is not required, the parent material has to be pre-heated to 100–150°C, the inter pass temperature must be 200–250°C and the welding must involve thin beads and a narrow scatter band of current at welding speed. If this welding process is not followed then PWHT is required to prevent the risk of failure – 740°C for 2 hours reduces the hardness of the filler material to <250 HV10. GTAW must be performed properly otherwise the material can be too brittle. GTAW requires a multiple-layer technique for all tube thicknesses so that the layer beneath experiences an annealing effect. End crater cracking in the root of GTAW can be avoided by not reducing the amperages of the electrodes by >50% to prevent the critical area of the root cooling too quickly. Purging gas is highly recommended when welding the root and during the hot pass.

SMAW of T24 requires PWHT if the stick electrode has a carbon content of  $\geq 0.08\%$ , which lowers toughness. A carbon-reduced (0.06 %) stick electrode has been developed for use without PWHT. In both cases, the parent material should be preheated to 100°C and the inter-pass temperature should be 200–250°C.

For SAW of T24 waterwalls (tube to fin), parent and filler materials must have a carbon content of 0.07–0.09%. Flux (BB 305/UV 305) must be used and rebaked before use. Sources of hydrogen must be eliminated during SAW of the waterwall to minimise risk of hydrogen induced SCC. Again, preheating the parent material between 80–100°C and re-heating via a soaking treatment directly behind the welding station, to reduce the cooling rate, are required to avoid PWHT.

#### **3.2** Martensitic steels

Increasing the chromium content of low alloy ferritic steels above 7% chromium combined with rapid quench and tempering from the austenitic condition during fabrication, results in a hard martensitic microstructure (iron arranged in body centred tetragonal) which is shown in Figure 10. The martensitic

microstructure has a high dislocation density and finely dispersed carbide and nitride precipitates, also known as carbonitride precipitates. Martensitic steels are strengthened with precipitation strengthening as well as solid solution and dislocation strengthening.

Generally, 9–12% chromium martensitic steels have high creep and fatigue resistance, low coefficient of thermal expansion, high thermal conductivity and good fabricability. Modern martensitic steels are capable of dealing with steam at 620°C (Narula and others, 2013). However, they require post weld heat treatment (PWHT), they are susceptible to cracking (Type IV) and are ultimately limited by their steamside oxidation resistance, due to the maximum allowable chromium content.



Figure 10 - Microstructure of martensitic steels (Maile, 2012)

#### 3.2.1 Precipitation strengthening

Precipitation strengthening is where the amount of alloying, with at least two other elements, is increased so that they can no longer diffuse into the microstructure and create a second phase, or precipitates. Finely and homogeneously distributed precipitates throughout the material microstructure impede movement at dislocations, which prevents growth of sub-grains, and thus strengthens the material. A material with more than two phases is known to have poly-phase. Greek letters are commonly used to distinguish the different solid phases in a given alloy (NDT Resource Center, 2013). Precipitation strengthening is the dominant form of strengthening.

The chemical compositions of the precipitates depend on the alloying elements. Each type of precipitate has certain properties. Heat treatment will determine the shape, size and distribution of precipitates. Precipitates found in 9–12% chromium steels include chromium carbides and vanadium and niobium carbon-nitrides, such as M<sub>23</sub>C<sub>6</sub> (Cr<sub>23</sub>C<sub>6</sub>, Fe<sub>21</sub>Mo<sub>2</sub>C<sub>6</sub> or [Cr, Fe]<sub>23</sub>C<sub>6</sub>), MX (V[C,N] and Nb [C,N]), Laves phase, or M<sub>2</sub>X nitrides.

MX and M<sub>23</sub>C<sub>6</sub> precipitates are the most favoured for increasing long-term creep resistance as their coarsening rates are low; Laves phase and M<sub>2</sub>X nitrides are undesirable (Subanovic and Schneider, 2012). The amount of carbon has to be optimised for the most precipitation strengthening and good weldability characteristics (Narula and others, 2013). Figure 11 shows transmission electron microscopy (TEM)

images of heat treated VM12-SHC. The image on the right is a zero peak loss image of the microstructure and the image on the left shows a red, green and blue (RGB) image.



Figure 11 – TEM images of heat treated VM12-SHC showing precipitates (Subanovic and Schneider, 2012)

In steels, vanadium and niobium cause precipitation strengthening. Vanadium precipitates as VN during tempering or under constant stress, boron promoted nucleation of VN. Vanadium and niobium are effective when combined in the ratio 0.25% vanadium and 0.05% niobium. Boron reduces the coarsening rates of MX precipitates. Chromium is a solid solution strengthener and increases resistance to chemical attack (Narula and others, 2013).

#### 3.2.2 Martensitic steel P91

The first martensitic 9–12% chromium steel, X20CrMoNiV11.1, was developed in Germany and became commercial in the 1960s. X20CrMoNiV11.1 achieved its strength and high oxidation resistance through molybdenum, vanadium and 11% chromium alloying (Hagen and Bendick, 2013).

The iconic P91 was developed by Oak Ridge National Laboratory (USA) from 1970-90s for fast breeder nuclear power plant. From 1992, P91 was used commercially in thin and thick section components to achieve superheated steam at 580°C, starting a new generation of higher steam temperatures known as ultra-supercritical (USC). With regard to current design rules, the WSF of P91 drops below 0.8 at temperatures above 580°C. Compared to X20CrMoV11.1, P91 has high creep resistance and better weldability due to niobium alloying, optimised vanadium and reduced carbon (Subanovic and Schneider, 2012; Gibbons 2013; Bader and others, 2013).

#### Schkopau and Weisweiler PCC plant

Units A and B of Schkopau PCC plant were commissioned in 1995–96. The superheater tubes, headers and pipes (550°C/285 bar) and reheater tubes, headers and pipes (565°C, 70 bar) are entirely constructed

from T/P91 and are designed for 200,000 hour (22.82 years), service lifetimes. In 2013, the high temperature steels had been operating for 100,000 hours (11.41 years) without any noticeable problems. The 18 year old Mannesmann (now V&M) lifetime monitoring system predicts that the lifetime consumption as 26%.

In 2010 a material evaluation programme was undertaken. The evaluation consisted of non-destructive testing (NDE) with ultrasonic testing (UT) and magnetic-particle testing (MT). Additionally, a steels testing programme, with sampling for impact tests, tensile tests, weld bending tests, hardness tests, and metallographic investigations for parent and filler material, was undertaken. The programme classified the T/P91 components as 2a according to the VGB–TW 507. The VGB–TW 507 evaluated creep damage with the following rankings; 0 is a new material, 1 has been exposed to creep damage but has no cavities, 2a has isolated cavities, 2b has numerous cavities without preferred orientation, 3a has numerous cavities with directional orientation, 3b has chains of cavities or grain boundary separations, 4 has microscopic cracks and 5 has visible cracks. Both damage evaluation methods show that the T/P91 components have roughly 100,000 hours left, which is in accordance with its designed 200,000 hour lifetime (22.82 years).

In 2006 after 250,000 hours (28.5 years) of service, the reheat pipework of units G and H of Weisweiler PCC plant (Germany) was replaced with longitudinally welded and then heat-treated P91 (535°C and 45.2 bar). No problems had been found up to mid-2013, such as significant reduction in creep resistance (Bader and others, 2013).

#### 3.2.3 Martensitic steels P92 and P122

In the 1980s, the Japanese modified T/P91 by reducing molybdenum (0.5%), adding boron and increasing tungsten (1–2%) to create the stronger NF616, or T/P92 under ASME. To increase steamside oxidation resistance of NF616, the chromium level was increased to 12% to create HCM12, or T/P122 under ASME. HCM12 has two phases, mostly martensitic with up to 30% sigma ferrite. HCM12A is HCM12 with the addition of 0.9% copper for a fully martensitic microstructure (Subanovic and Schneider, 2012; Kuhn and others, 2012). Presently, P92 has the highest creep resistance of the martensitic steels for the temperature range of 580–620°C. However, P92 cannot be used in components above 620°C due to limited steamside oxidation resistance (Bader and others, 2013).

#### 3.2.4 COST 501

The CO-operation in the field of Science and Technology (COST) collaborative material research programme in Europe started in 1986 and ended in 2008. COST aimed to develop new steels for high temperature applications.

COST 501 (1986–2001), titled 'Advanced materials for power engineering components – high efficiency, low emission systems', aimed to develop advanced steels for use at 625°C. Test loops were installed in unit G at the Weisweiler PCC plant (Germany) - the loop produced steam at 650–720°C and 160–180 bar. COST 501 took 15 years and went through the following stages (Osgerby, 2007):

- stage 1 (1986–1989, 3 years): investigation of trial materials;
- stage 2 (1989–1990, 1 year): two prototype rotors were manufactured;
- stage 3 (1990–1993, 3 years): characterisation of these materials led to their selection for the Skaerbaek and Nordjylland PCC plants (Denmark);
- stage 4 (1993–1997, 3 years): machines were manufactured and commissioned;
- stage 5 (1998–2001, 3 years): test pieces from the rotor forgings used for these turbines were included in a long-term testing programme funded by VGB (Germany).

COST 501 achieved the following (Subanovic and Schneider, 2012; Jiang, 2012; Hagen and Bendick, 2013; Gibbons, 2013; Maile, 2012):

- modified T/P91 with 1% more tungsten and some boron to create E911 which has creep resistance similar to that of T/P92 and is limited to 620°C by steamside oxidation resistance;
- VM12-SHC was developed by V&M Tubes (France), it has 11% chromium for high steamside oxidation resistance and MX precipitation for high creep resistance. Additional strengthening was achieved through optimised additions of tungsten, cobalt and boron;
- developed alloys B, E (contains tungsten), and F for large turbine components. Alloys E and F have been up used to forge steam turbine rotors with steam temperatures up to 610°C in Europe and Japan;
- qualified the steels T91, T92 and VM12 for use in waterwalls.

#### 3.2.5 COST 522

Titled 'Power generation in 21st century, ultra efficient, low emission plant', COST 522 started in 1998 and finished in 2003. The research project developed a new 12% chromium martensitic steel called 12CrCoMo for use at 620–650°C and up to 30MPa (VGB, 2013b: Moreea-Taha, 2002).

#### 3.2.6 Laves phase weakening

9–12% chromium martensitic steels suffer from a long-term weakening mechanism, known as Laves phase. In service, tungsten and molybdenum will precipitate out as large and coarse intermetallic Laves phase [(Fe, Cr)<sub>2</sub> (W, Mo)], which reduces the effects of solid solution strengthening and precipitations strengthening (Subanovic and Schneider, 2012).

In 1999, P92 was code approved with creep resistance of 123 MPa at 600°C, which was extrapolated from a 10,000 hour creep test (1.14 years). However, when the 100,000 hour creep test (11.41 years) finished in 2005, the creep resistance reduced to 113 MPa at 600°C. This accelerated drop in creep resistance makes P92 not that much stronger than P91 (Gibbons, 2013).

#### 3.2.7 COST 536

Titled 'Alloy development for critical components of environmental friendly power plant (ACCEPT)', COST 536 started in 2004 and ended in 2009. The project encompassed all stages in the development and validation of advanced steels, and coating concepts, for large components capable of operation at up to

650°C. The total cost was £2 million, including £0.8 million provided from former Department of Trade and Industry in the UK. The lead contractor was Mitsui Babcock (now Doosan and Babcock) and collaborators included ALSTOM Power Limited, Corus UK Limited Cranfield University, E.ON UK, Loughborough University, Metrode Products Limited, National Physical Laboratory and TWI Limited (Nalbandian, 2008).

COST 536 developed Alloy FB2 and Alloy FB3 for large turbine forgings, and Alloy CB2 for large turbine castings, which are slightly stronger than P92 (Allen and others, 2013). Alloy FB2 has achieved significantly higher creep resistance than Alloy E or F through the addition of Boron. Alloy FB4 was also developed in COST536 and can now be used commercially in thick-section components up to 620°C. Alloy FB4 has no cobalt alloying, compared to Allot FB2, which has 1.2% cobalt, and therefore has a lower capital cost (Blaes and others, 2010). These new steels are shown in Figure 12 (Blum, 2009).



#### Figure 12 – Large turbine forging and casting (Blum, 2009)

COST 536 also optimised 12% chromium steel VM12-SHC for applications up to 625°C. Böhler Schweisstechnik developed filler materials matching VM12-SHC for the GTAW and SMAW processes (Heuserand and Tak, 2013).

#### 3.2.8 Z-phase weakening

Steels with chromium levels of 11–12%, such as VM12, VM12–SHC, NF12 and P122 have steamside oxidation resistance to 650°C. However, COST 536 found that 11–12% chromium martensitic steels have an accelerated drop in long-term creep resistance to below that of P92 or P91. This accelerated drop in strength is more than can be explained by the precipitation of Laves phase alone. This accelerated drop in strength is due to the precipitation of Z–phase, as well as Laves phase.

The higher chromium content causes increased precipitation of the coarse nitrides [Cr (V, Nb) N], known as Z-phase, which consumes the small strengthening precipitates, such as vanadium nitride and niobium nitride. Studies show that higher the levels of chromium result in higher levels of Z-phase formation

(Kuhn and others, 2012; Gibbons, 2013). Z-phase weakening usually occurs after 10,000 hours (1.14 y) in high chromium martensitic steels (Blum, 2009). Figure 13 shows the microstructure martensitic steels before and after creep damage showing Z-phase formation (Maile, 2012).



initial state

after creep



TEM bright field image and elemental distribution map after creep

Figure 13 – Microstructure of martensitic steels before and after creep damage showing Z-phase formation (Maile, 2012)

#### 3.2.9 Martensitic steel NF12 and SAVE12

NF12 and SAVE12 are 12% chromium martensitic steels with the highest creep resistance amongst the 9–12% chromium martensitic steels. NF12 contains 2.5% cobalt and 2.6% tungsten. SAVE12 contains 3% cobalt and 3% tungsten and minor amounts of tantalum and niobium. High strength is gained from finely precipitated and stable nitrides (Narula and others, 2013).

#### 3.3 Type IV cracking of martensitic steels

Creep damage is often detected as cracks adjacent to welds. The cracks have been characterised into four types by their position in the weld as shown in Figure 14 (Fleming and Foster, 2001):

- Type I cracks are wholly within the weld metal and run both transverse and parallel to the weld;
- Type II cracks both transverse and parallel to the weld but propagate into the HAZ and beyond into parent metal;
- Type III cracks initiate in the coarse grained HAZ close to and parallel to the fusion boundary and lie both in this region and also extend into the parent metal;
- Type IV cracks located in the HAZ adjacent to the parent metal running parallel but offset from the fusion line.



#### Figure 14 – Classification system for weld cracking mechanisms (Fleming and Foster, 2001)

Figure 15 shows a scanning electron microscope (SEM) of a type IV crack in P91.



Figure 15 – SEM of Type IV crack in P91 (Shibli, 2012a)

#### 3.3.1 Case studies of type IV cracking

Type IV cracking of P91 has been significant in the UK and Germany, with failures occurring within 20,000 hours of service (Bader and others, 2013; Chalk and others, 2012). The following two paragraphs give examples of Type IV cracking. Brett and others (2010) present a pragmatic guide to estimate the earliest appearance of Type IV cracking of P91 in power plant.

After 35,520 hours of operation, T91 tube to P91 header welds have failed at the West Burton PCC power plant (UK). Non-destructive examination (NDE) of other P91 tube-header welds has shown extensive creep damage. Type IV cracking was attributed to incorrect PWHT. Additionally, four T91 superheater

transition bottle welds failed at the same plant, the earliest at 20,000 hours. However, in this case, the failure was due to incorrect heat treatment of the parent material during fabrication (Chalk and others, 2012).

Another example in a PCC plant (UK) is a P91 header installed in 1992, designed to operate at 580°C and 17.5 MPa for a service life of 150,000 hours. In 2004, small cracks were found after only 58,000 hours of service. Despite repair welding the cracks reappeared in 2006 and the header was replaced in 2008. Inspection of the removed header identified Type IV cracking in areas of the parent material with insufficient alloying – the nitrogen to aluminium ratio was too low. This led to a better understanding of the microstructural evolution of P91 and improved measuring, modelling and simulation of steels (Thomson, 2009).

#### 3.3.2 Cause of type IV cracking

Type IV cracking of martensitic steels can be caused by the following errors in the fabrication, welding procedure, PWHT or post bend heat treatment (PBHT).

#### Fabrication:

- material is insufficiently austenitised in the heat treatment during fabrication. The martensite that forms has low carbon content and does not have the required creep resistance (Bader and others, 2013);
- insufficient alloying, for example the nitrogen to aluminium ratio is too low (Thomson, 2009);
- solid forging is cooled too slowly in air or furnace following normalising (Bader and others, 2013).

#### Welding:

during the welding procedure the inter-critical fine grain zone of the HAZ (ICHAZ), or adjacent parent material, reaches a sufficiently high temperature (>830°C) for the martensite to transform to austenite. On cooling, there may be insufficient time for the carbides to dissolve into the martensite that forms, the amount of dissolved carbon is low (under-alloyed) and strength is reduced. Correctly applied PWHT restores strength (Gibbons, 2013). The temperature profiles of the welding procedures for P91, P92 and VM12-SHC are explained in the next section.

#### **PWHT and PBHT:**

- heat treatment of the material, through tempering and normalising, results in fully tempered martensite with the correct amount of dissolved carbon. However, incorrect PWHT/PBHT leads to phase transformation, grain size alteration and change of precipitation characteristics of the parent and weld material. The temperature profiles of PWHT/PBHT for P91, P92 and VM12-SHC are explained in the next section. The following list explains the consequences of incorrect PWHT/PBHT (Chalk and others, 2012):
  - over-tempering: too high a temperature coarsens precipitates leaving a part martensite, part austenite, microstructure, which is weak and known and the 'soft zone';

- under-tempering: too low a temperature limits precipitation, rendering the material susceptible to brittle fracture and SCC, as well as Type IV cracking;
- heating in the inter-critical region during hot or cold work (Chalk and others, 2012):
- inductively bent pipes are not fully tempered, but only stress relieved (Bader and others, 2013).

Newer components have reduced risk of Type IV cracking through designing the weld such that the stresses are reduced relative to the parent metal and so that the welding procedure and PWHT are easy to undertake.

#### 3.3.3 Temperature profiles during fabrication and welding

Figure 16 shows the correct temperatures for preheating, welding and PWHT with time of P92 and VM12–SHC. The following two paragraphs explain in detail the welding procedures for P92 and VM12–SHC, respectively (Heuserand and Tak, 2013).



# Figure 16 – Temperature profile of welding procedure and PWHT for P92 and VM12-SHC (Heuserand and Tak, 2013)

Welding procedures for P92 include GTAW, SMAW, SAW and flux cored arc welding. Matching filler materials for P92 are not yet standardised. For filler materials with a similar composition to P92, the weld should be left to cool to 20–100°C to allow a fully tempered martensite microstructure before welding. Welded components can be left to cool to room temperature. Provided they are stored dry and stress free, PWHT can be performed at a later stage. However, to prevent hydrogen induced cold cracking, soaking at 250–300°C for 2–3 hours immediately after welding allows the hydrogen to diffuse – this is not necessary for thin-section welds with GTAW or GMAW procedures (Heuserand and Tak, 2013). PWHT at 760°C, the holding time determined by the wall thickness and welding process (4 hours for SAW in all cases),

reduces the hardness from roughly 400 HV10 to 250 HV10. The two important processes that happen here are stress relief annealing and tempering of the martensite. Exceeding 775°C for a significant time period can transform the tempered martensite to austenite, which then cools to un-tempered martensite. Therefore, accurate temperature measurement of the parent material is essential. The temperature must be measured at the pipe and the scatter band of measurements must be small. Thin welding passes improve toughness through improved tempering, especially in SAW (Heuserand and Tak, 2013). Bader and others (2013) have shown that P92 retains a strong tempered martensite microstructure with hardness values 190 HV for PWHT at 780°C and 8 hours.

VM12-SHC, qualified by Germany's VdTÜV for wall sizes up to 10 mm, requires PWHT at 770°C for at least 30 minutes with GTAW and at least 2 hours with SMAW and GMAW (Heuserand and Tak, 2013).

The welding procedure temperature profile of P91 is exactly the same as P92. For P91, hardness values between 170-185 HV have an extremely over tempered microstructure, resulting in a soft ferrite matrix with globular carbides (Bader and others, 2013). Goswami (2012) goes into detail on the required PWHT for P91, as well as other design, fabrication and operational issues. The author concludes with the remark 'when utilised properly, P91 is an exceptional high temperature material.

The PWHT temperature for P92 is typically 780°C. This is just below the temperature at which the microstructure changes from martensitic to austenitic (austenitisation). However, the tolerances in the chemical composition of the weld material can result in a certain composition that will undergo austenitisation during PWHT at 780°C. Additionally, too long PWHT will also soften a material. Using a combination of modelling and experimental observations, the ETD (UK) has derived an equation to predict the austenitisation temperature of P92 material as a function of chemical composition. This information allows correct PWHT temperatures and thus prevents austenitisation. The equation used can also be applied to other steels to improve heat treatment such as tempering and normalising (Chalk and others, 2012).

#### 3.4 Austenitic steels

When over 8% nickel is added to stainless steel the microstructure transforms to austenite (iron arranged of face centre cubic). Austenitic steels also have high chromium levels, often above 18%, which classifies them as stainless steels. Austenitic steel have high fireside corrosion and steam oxidation resistance and high creep resistance but have a high coefficient of thermal expansion and low thermal conductivity. The high coefficient of thermal expansion limits application to thin-section superheaters and reheaters, due to excessive fatigue damage in thick-section components (Wheeldon and Shingledecker, 2013). It is important to note that a header is 25 m long and weighs 18 t. Modern austenitic steels are capable of dealing with steam at 665°C and 310 MPa may be suitable up to 750°C depending on resistance to chemical attack – NF709 may be suitable up to 770°C (Narula and others, 2013).

#### 3.5 Creep-fatigue damage of steels

Creep damage and fatigue damage can interact synergistically to create creep-fatigue damage, which can result in failure faster than with either creep or fatigue damage alone. Cyclic operation causes higher fatigue damage, and therefore increases creep-fatigue damage as well. Figure 17 shows how creep, fatigue and creep-fatigue damage occur, situations a) to f) are explained below. The honeycomb structure represents the crystalline structure of a material (Holdsworth, 2012):

- a) fatigue damage;
- b) inter-granular creep damage with some fatigue damage, which occurs within steels with low creep-ductility;
- c) trans-granular creep damage with some fatigue damage, which occurs within steels with high creep-ductility;
- d) creep-fatigue damage with consequential creep damage;
- e) creep-fatigue damage with simultaneous creep damage, which occurs within steels with low creep- ductility;
- f) creep damage and fatigue damage but no creep-fatigue damage, which occurs within steels with high creep-ductility.



#### Figure 17 – Creep-fatigue damage mechanisms (Holdsworth, 2012)

Some material codes assess the effect of fatigue damage separately to creep damage, however separate creep and fatigue tests will not account for the more destructive creep-fatigue damage. In the European standard EN12952–3, 'Water tube boilers and auxiliary installations – Part 3: Design and calculation for pressure parts'; fatigue analysis is to be carried out when a boiler will be subject to cyclic operation (Robertson, 2012). ASME Boiler and Pressure Vessel Code (Case N–47) recognises the significance of creep-fatigue damage and provides guidance on creep-fatigue damage of steels and its related life

expectancy, however this is not mandatory (Shibli, 2012b). Figure 18 shows an example of how the ASME quantifies creep-fatigue strength with bi-linear damage summation loci – a straighter line indicates better resistance to creep-fatigue damage (Shibli, 2012a).



#### Figure 18 – Martensitic steel T91

In combined cycle gas turbines, waste heat from the gas turbine is passed to a heat recovery steam generator (HRSG). The HRSG is exposed to relatively clean flue gas from the gas turbine, comprised of nitrogen, carbon dioxide and water vapour, to generate steam for a steam turbine. Fireside corrosion is negligible, however oxidation is probable. Steels used in a HRSG have been derived from PCC plant boilers.

There have been reports of cracking at the toe on the tube side of the tube-to header welds in T91 superheater and reheaters in HRSG. An example is shown in Figure 19. The failure mechanism has been identified as fatigue or creep-fatigue damage, caused by differential thermal expansion of neighbouring tubes and/or thermal quenching caused by un-drained condensate in old horizontal gas-path HRSG and some vertical gas-path HRSG with inadequate drainage. This problem can be solved by improving drainage and effectively managing condensate removal (Shibli, 2012b). Figure 19 also shows bulging of the tube in what is known as the soft zone, due to over-tempering during PWHT (Shibli, 2012a).



Figure 19 – Creep-fatigue cracking of P91 tube-to header weld (Shibli, 2012b)

#### 3.6 Cracking of dissimilar metal welds

Dissimilar metal welds (DMW) are welds between different types of materials, such as low alloy ferritic steel and austenitic steel. There is a high risk of cracking at DMW as explained by the following three reasons (Stultz and Kitto 2005; Shibli, 2012a, b):

• thermal co-efficient of expansion: different steels can have a different thermal co-efficient of expansion. When steels are exposed to high thermal gradients, the forces generated by the difference in thermal co-efficient of expansion can physically break the welds. Cyclic operation places high thermal gradients on steels. Figure 20 shows the difference in the thermal co-efficient of expansion between ferritic, martensitic and austenitic steels as a function of chromium alloying. The risk of cracking is higher for thicker-section components, as there will be a higher difference in expansion or contraction. This is the reason why austenitic steel is limited to superheater and reheater applications, as it has a high thermal coefficient of expansion;

- **carbon diffusion:** carbon will diffuse across DMW from areas of high carbon concentration to areas of low carbon concentration. This is likely as different steels have different carbon concentrations. The change in carbon levels can lower the strength of both steels;
- **steamside oxidation resistance:** differences in resistance to steamside oxidation between two steels can create localised oxidation. An oxide wedge will form on the inside and outside of the material at the DMW, creating a notch, which is an ideal place for crack initiation.

Severe cyclic operation of older PCC plant has placed high thermal gradients on DMW and has resulted in failures. An almost complete circumferential crack was found in a DMW in a HRSG (USA) between the P91 main steam pipe and a 1<sup>1</sup>/<sub>4</sub>Cr1Mo<sup>1</sup>/<sub>4</sub>V control valve casting, welded using 2<sup>1</sup>/<sub>4</sub>Cr1Mo filler material, after less than 5000 hours of operation. The crack was found in a carbon depleted zone in the HAZ of P91, as shown in Figure 21 (Shibli, 2012b).



Figure 20 - Thermal co-efficient of linear expansion of steels (Shibli, 2012a)



10 1.11

Figure 21 – Cracking in HAZ of P91 (Shibli, 2012b)

### 4 Chemical attack of steels

This Chapter assesses the performance, problems and solutions for high temperature ferritic, martensitic and austenitic steels when exposed when chemically degraded. Figure 22 shows severe examples of steamside oxidation and fireside corrosion.



**Figure 22 – Steamside oxidation (left and middle) and fireside corrosion (on right)** (Mao, 2012; Stein-Brzozowska, 2012)

#### 4.1 Over-fire air

Recent studies in the USA have shown that retrofitting boiler with over-fire air (OFA), to reduce emissions of nitrogen oxides, can result in excessive corrosion, up to 2 mm/y, of ferritic steels near the burner (Zhang, 2013).

#### 4.2 Fireside corrosion of T92, HR3C and 347HFG

Laboratory testing at Cranfield University measured the fireside resistance of T92, 347HFG, HR3C and 625 in simulated air-fired and oxy-fired boiler environments at 600–750°C. All steels showed a bell-shaped curve of fireside corrosion damage with increasing temperature, with peak damage occurring at 650°C in air-fired conditions, but 700°C in oxy-fired conditions due to higher levels of sulphur oxides. The steels tested can be ranked as follows, from the most fireside corrosion resistant steels to the least, 625> HR3C>347HFG> T92 (Hussain and others, 2013).

#### 4.3 Cleaning boiler deposits

Excessive slagging and fouling will reduce boiler efficiency and lengthen boiler start up times, through reduced heat transfer. It will also cause material over-heating and place increased loads on tubes, which both increase creep damage. Figure 23 shows an example of severe slagging inside a boiler – deposits can reach 21 metres long. Fortunately, boilers can be kept clean online, with soot blowers, and can be cleaned offline. SC and USC boilers usually have soot blowers, but may still require some offline cleaning.



#### Figure 23 – Severe slagging inside boiler (Martino, 2013)

Soot blowers use compressed air, steam or water to knock off deposits. New intelligent soot blowers are retractable, can vary the steam/water/air pressure and use heat transfer sensors to determine when cleaning is required. This combination allows for maximum cleaning, minimum water usage and tube damage. As with installing most new technology, it is important that the intelligent soot blowers are set-up according to their manufacturer and this will differ from boiler to boiler. Intelligent soot blowers include Diamond Power's 'HydroJet' and 'SMART Clean' systems. Typical payback periods for Diamond Power's intelligent soot blowers are around 6–12 months, and can eliminate the need for offline boiler cleaning for up to 20 years.

Offline cleaning methods include the use of high pressure water and dynamite. Any large deposits fall into the hopper, flow into the grinder and out of the sluice area. Modern cleaning with dynamite can be done in 36 hours, much quicker and less water intensive than high pressure water cleaning.

Cold starts can expand boiler tubes up to 46 cm, which effectively dislodge deposits. Therefore, an unforeseen consequence of cyclic operation is reduced need to clean the boiler (Martino, 2013).

#### 4.4 Flow accelerated corrosion

Despite numerous failures, and fatalities, flow accelerated corrosion (FAC) still occurs in >70% of fossil-fuelled power plant and represents >40% of all tube failure in HRSG. Feedwater conditioning with oxygen scavengers and an alkaline additive is known as all-volatile treatment reducing (AVT[R]). Oxygen scavengers, predominantly hydrazine, carbohydrazide and methyl ethyl ketoxime, de-aerate water to <7 ppb and passivates oxidised areas of material, forming more protective magnetite (Fe<sub>3</sub>O<sub>4</sub>). Ammonia or amine is added to keep the feedwater mildly alkaline, pH 9.1–9.3 for mixed alloy steam circuits, and more for all-ferrous systems.

However, it was found that oxygen scavengers cause single-phase Flow Accelerated Corrosion (FAC). The combination of a reducing environment coupled with high turbulence and optimum conditions, low pH at  $\sim$ 8.75 and low temperature at 149°C, cause dissolution of ferrous ions

(Fe+2) from the metal, eventually resulting in catastrophic failure. Areas susceptible to singlephase FAC include elbows in feedwater and economisers, valve perturbations and feedwater heater drains. Figure 24 shows wall thinning by single-phase FAC. Catastrophic failure of an elbow in the condensate system at Slurry nuclear power plant (VA, USA), due to this failure mechanism, resulted in four deaths and significant financial losses in repair cost and lost revenue in 1986. Many operators of PCC power plant use AVT(R) and in 2007, an FAC induced failure at an attemperator line in a PCC plant resulted in two deaths and a seriously injury.



#### Figure 24 – Wall thinning caused by single-phase FAC (Buecker, 2013)

Alternative feedwater treatments for all-ferrous once-through PCC plant include oxygenated treatment (OT) and all-volatile treatment oxygenating (AVT[O]). OT involves the deliberate injection of oxygen into the condensate or feedwater network to establish oxygen concentrations <300 ppb. The high oxygen content in pure water (cation conductivity  $\leq 0.15 \ \mu$ S/cm) creates a protective ferric oxide hydrate (FeOOH) over the magnetite, lowering feedwater iron concentration to <1 ppb and minimising single-phase FAC. AVT[O] does not inject oxygen but allows air in-leakage, usually found in steam circuits, to achieve the following feedwater characteristics, pH range 9.2–9.6 to minimise FAC, dissolved oxygen at 1–10 ppb to form a ferric oxide hydrate layer on the magnetite, and cation conductivity  $\leq 0.2 \ \mu$ S/cm which occurs with the in-leakage of carbon dioxide. An old rule of thumb for air in-leakage is 1 standard cubic feet (0.0283 m<sup>3</sup>) of air per minute of operation per 100 MW.

Two-phase FAC occurs where water and steam exist simultaneously, such as in feedwater heat exchangers, heater drains and de-aerators. When water flashes to steam, oxygen departs with the steam, thus water in contact with metal does not maintain an oxidising environment. Additionally, the pH of entrained water droplets in steam usually have a lower pH than bulk water. The low oxygen and pH caused in two-phase flow favour FAC. Prevention is difficult and therefore regular inspection is important.

Water quality and quantity is maintained by an ion-exchange, full-stream, condensate polishing unit, with make-up water addition, located downstream of the condenser. The feedwater purity must meet required cation conductivity otherwise contaminants from air in-leaks, condenser leaks or improper water treatment chemicals for example, can cause excessive steamside oxidation and corrosion, such as hydrogen damage (the chemistry behind this is complex and beyond the scope of this report). Typical feedwater quality must meet the following parameters, total organic content <100 ppb, silica <10ppb, chloride, iron, sodium and sulphate all <2 ppb.

With all feedwater treatment strategies, continuous online water quality monitoring is vital to detect problems and quickly correct them. Important monitoring parameters include sodium concentration, cation conductivity, dissolved oxygen and acidity/alkalinity measurement. Monitoring at the condensate pump discharge, condensate polisher effluent and evaporator water is essential. Isokinetic sample nozzles and proper plumbing of sample lines is required for accurate analysis.

For more information on feedwater treatment, please see the website for the 'The International Association for the Properties of Water and Steam' at <u>http://iapws.org/</u>. Another way to prevent single-phase and two-phase FAC is with the use of higher chromium ferritic steels, up to 2.5% chromium, in low temperature sections, as opposed to straight mild steel (Buecker, 2012, 2013; Wheeldon and Shingledecker, 2013).

#### 4.5 Cleaning oxide scales

Scales from steamside oxidation can cause hot spots, increasing stress damage, and lower heat transfer rates, lowering efficiency. These scales can be removed with hydrochloric acid, ethalene diamene tetracedic acid (EDTA), hydroxyacetic formic acid or citric acid. To remove 0.45 kg of iron, 6.17 kg of ETDA, 1.13 kg of citric acid or 0.72 kg of hydrochloric acid is required. ETDA is environmentally friendly, but at twice the cost of other acids. The cleaning process takes 2–3.5 working days and may need doing every two years (Martino, 2013).

#### 4.6 Steamside oxidation at Waigaoqiao PCC plant

Exfoliation of steamside scales is high with cyclic operation. In China, damage from steamside oxidation has been seen to decrease net electrical efficiency by 4% points after two years of operation. Waigaoqiao Number 3 PCC plant (China) has implemented a series of sophisticated measures to keep the oxide scales in flow to a minimum. These measures include a steam cycle cleaning system, shortened start-up times and minimal thermal shock during start-up. After 30 months of operation, the tubes in the third superheater, the second reheater and the turbine IP blades show no sign of steamside oxidation damage, shown in Figure 25, or reduction in electrical efficiency (Feng and Yu, 2012).



Figure 25 – Tubes and blades at Waigaoqiao Number 3 PCC plant (Feng and Yu, 2012)

#### 5 Steel lifetime assessment

Steels only last for a specific amount of time in service. The older the steel the better the projected lifetime is. As explained in the previous Chapters, cyclic operation causes more fatigue damage and creep-fatigue damage, and increases the risk of DMW cracking, especially for PCC plant that have been operated in a more sever cyclic mode than designed for. Cyclic operation can significantly reduce the projected lifetime of high temperature components. Figure 26 shows the relative lifetime decrease for high temperature components in the global average fleet of PCC plant with the introduction of cyclic operation. This curve is known in the industry as the 'bathtub failure curve'. Looking at the x-axis, the first stage is the break in stage for newly commissioning errors coupled with shortcomings in quality control. The second stage is the most predictable and accounts for the majority of component life. The third stage is where the component will eventually fail due to time dependent damage mechanisms. Due to cyclic operation stage two has been shortened significantly.



#### Figure 26 – Bathtub failure curve (Klenk and Maile, 2012)

If PCC plant are operated in cyclic operation beyond their design specification and kept online according to the original lifetime, then there is a high chance of catastrophic failure in the steam circuit. It can be economically favourable to repair or replace components before failure. To do this the corrected lifetime is needed.

Old software packages and material examination tools for steel lifetime assessment are difficult to implement and are unreliable, as they fail to include all of the factors involved in PCC power plant.

The onset of cyclic operation has placed a high demand for accurate steel lifetime assessment methodologies. Extensive operational experience has improved the understanding of microstructural degradation and at the same time material examination tools and computer modelling have developed significantly. Therefore, modern software packages and material examination tools can be used to accurately measure steel lifetime accounting for other operational changes, such severe cyclic operation or fuel change.

Corrected steel lifetimes are part of preventative maintenance strategies for the entire plant. This is explained in more detail in Section 5.8 later in this Chapter.

#### 5.1 Wilshire equations

The Materials Research Centre at Swansea University has developed the Wilshire equations for predicting the lifetime of a range of materials (Whittaker and others, 2012).

#### 5.2 RemLife

The Australian Nuclear Science and Technology Organisation (ANTSO) have developed the RemLife Software, which can be used to assess component damage, due to cyclic operation, and then predict component lifetime and assess the costs of the chosen cycling regime. The use of RemLife software at Loy Yang PCC plant (Australia) has lowered running costs through optimised operation and maintenance (Payten 2012).

#### 5.3 ETD

The ETD specialise in life assessment of high temperature steels in base load and cycling plant. Material properties can be evaluated and determined through advanced techniques, such as small punch creep testing, monitoring components during service and accurately measuring damage development. Proper life assessment ensures optimal plant performance, by minimising the chance of forced outages, and minimises running costs through an effective operation and maintenance programme and design modifications.

A number of non-destructive examination (NDE) techniques have been developed for martensitic steels and used successfully to determine the integrity and lifetime of martensitic steels. NDE techniques include a model relating hardness drop to consumed life fraction and high resolution on-site microscopes to examine the fine microstructure of martensitic steels. The ETD lead a project called 'P91 Integrity'. This project deals with NDE of P91 and aims to develop on-site tools. The ETD also has an international P91 users group (Chalk, 2012).

#### 5.4 COST 558

COST 558 developed an 'integrated toolbox' to accurately and reliably assess the remaining life of critical components in European thermal power plant before repair or replacement. The 'integrated toolbox' is comprised of:

- advanced measuring techniques (intermittent/continuous, invasive/non-invasive) to assess degradation of steels;
- improved material lifetime modelling tools (microstructure modelling);
- extensive steels and components database.

Fifty one projects in industry and academia across Europe made up COST 558. Progress was made in most areas, although there is still work to be done. By 2008, the 'integrated toolbox' was implemented nine times. The projects included 'modelling crack development', 'life assessments of parent materials' and 'prediction of deposits'. Additionally, the 'integrated toolbox' will correct the material remnant life with on-going monitoring and thus quantify the change in component remnant life with operational changes. This information will improve future plant (COST 538, 2013).

#### 5.5 Dong Energy

Dong Energy (Denmark) has extensive and successful experience with 9% chromium martensitic steels in ultra-supercritical coal-fired power plant. Dong Energy has developed their own material quality check and control parameters for 9% chromium martensitic steels, which are listed below (Chalk, 2012):

- always check thermocouple records of heat treatment, both austenitising and tempering;
- often check thermocouples used by the supplier of the material;
- check hardness and do random dimension checks;
- buy extra material (0.5 to 1 t for each unit) for future tests;
- austenitising and tempering temperatures: 1070°C and 750+-10°C respectively;
- prefer lower Al/ N ratio;
- Si and Cr should never be too high as they affect strength;
- plant containing P91 cycle on average one cycle a week;
- for pipe bends check full records of heat treatment and always get replicas;
- checked for microstructure;
- all bends fully austenitised and tempered after bending;
- PWHT = 750 +0/-10°C (1382°F);
- full ultrasonic and X-ray checks on all welds;
- carefully check and re-check thermocouples.

#### 5.6 Schaeffler

The Corus steelmaking site in Scunthorpe (UK) generates 53 MW of power by burning waste gases. During routine maintenance of turbine number 5, a blade was missing and there were cracks and a fracture in the retaining ring. This discovery raised concerns regarding the sister turbine, number 4, at the plant. A hazard and operability analysis (HAZOP) of steam turbine number 4 identified the need for a protective cover to ensure personnel safety and a failure protection system, which detects onset of blade failure and thus prevents catastrophic failure of the steam turbine.

The FAG DTECT X1 online vibration monitoring system, made by Schaeffler, was installed on the exciter and turbine end bearings of turbine number 4. Failures are detected when the vibration of the component goes out of the specific frequency band. The FAG DTECT X1 can be used on a variety of components and conventional sensors and probes can be attached to record process values such as acceleration, speed, temperature, pressure and proximity

Shortly after installation the FAG DTECT X1 detected a rotor blade failure. The broken rotor blade was replaced quickly and at low cost, as opposed to lengthy down-time and high repair costs. The saving in lost generation was £35,000 per day. As energy prices remain high, the Corus steelmaking plant is progressing towards a comprehensive failure protection system (Modern Power Systems, 2009a).

#### 5.7 Metso

With increased coal blending and cofiring of non-fossil fuels in boilers designed to burn coal, superheaters and reheater failures due to higher fireside corrosion are becoming significant. Metso of Finland has developed a commercially proven control package that monitors fireside corrosion rates on superheater and reheaters, and can lower these rates to an acceptable level, through plant optimisation and boiler additives. Metso's fireside corrosion control package focuses on reducing fireside corrosion rates by managing alkali-chlorides and consists of three items, an analyser, process control and a combustion additive system.

Direct analysis of fireside corrosion rates is not practical. However, fireside corrosion rates on boiler steels can be determined with knowledge of the fuel flow rate and composition, measurements of the flue gas composition and an extensive database of material properties and fireside corrosion rates of flue gas elements. Metso use their Corrored analyser to measure the sulphur and chlorine content of flue gases in 10–15 minute intervals. The Corrored analyser comprises the SDG-100 sampler unit and an analyser unit. The sampler unit is located in the superheater area in the boiler, typically at temperatures between 550–950°C. The analyser unit is located outside the boiler. The molar ratio of sulphur to chlorine is used to quantify material wastage and predict the remaining lifetime of superheaters/reheaters. This information helps avoid unforeseen shutdowns and allows effective maintenance of superheaters/reheaters.

Process control aims to optimise the combustion atmosphere for minimal fireside corrosion through fuel blend, fuel flow rate, use of additives, and controlling steel temperatures through steam temperature. However, process alteration has to be done without compromising stack emissions, fuel flexibility, plant availability, electrical efficiency or ash quality. The Metso DNA system covers all process control of multifuel boilers with plant performance analysis and optimisation.

The additives include CorroStop and CorroStop+. CorroStop additives are ferric and aluminium sulphate (Fe<sub>2</sub>[SO<sub>4</sub>]<sub>3</sub> and Al<sub>2</sub>[SO<sub>4</sub>]<sub>3</sub>), they reduce the corrosion rate of alkali-chlorides and are either mixed with fuel before injection into the furnace or directly injected into the upper part of the furnace. CorroStop+ additives are sulphur granulates which are dosed into the fuel flow. Both additives have an optimal

temperature window and require sufficient residence time and an excess of oxygen. The amount of additive used will be decided by the process conditions and fuel flow rate. Process optimisation may increase operating costs slightly but reduce maintenance costs significantly.

Metso's fireside corrosion control package was added to a small-scale, circulating fluidised bed boiler which burns highly corrosive fuels. With addition of CorroStop+, the fireside corrosion rate dropped 80%, from 0.5 mm/y to 0.1 mm/y (Silvennoinen and others, 2013).

#### 5.8 Computerised maintenance management system

Plant maintenance strategies have moved away from simply responding to component failure, towards preventative maintenance strategies which minimise down-time and maintenance expenditure. Preventative maintenance strategies rely on process measurements, to assess performance, and modern condition monitoring techniques, which provide adequate knowledge on component condition through vibration measurement, oil analysis, thermal imaging and other techniques. Process measurements and condition monitoring techniques can be offline or online. Sufficient knowledge of failure risk, including catastrophic failure risk and risk of adverse effects on personnel safety, pollution and performance, and the cost associated with maintenance options are used to make a decision on the most cost-effective maintenance route; this information can be put into a model for stream-lined operation. All risks are based on the plant operators' own engineering experience and historical data, although knowledge can be gained from other plant operators and even equipment or component suppliers. Preventative maintenance strategies have worked successfully for single components.

State-of-the-art preventative maintenance strategies integrate online and offline information from process measurement and condition monitoring, with models of risk and cost, for multiple components into a single computerised maintenance management system (CMMS). CMMS can give a quick overview of the entire plant condition, providing risk and cost information in order to make a pro-active decision. Additionally, CMMS will highlight unnecessary inspections or maintenance, saving resources, and can integrate the risks and costs of components that may affect each other, thus creating a holistic preventative maintenance strategy. If the CMMS detects a change in measurement that does not require immediate action, the programme can alter the inspection and maintenance routines accordingly.

One utility established CMMS across its twenty seven oil and gas fired units. The result was fewer forced outages, measured as a 30% reduction in equivalent forced outage rate, increased peak reliability by 7% and, after a few months, maintenance costs reduced. A utility in North America introduced a SKF @aptitude Decision Support System across nine coal-fired units – the system has identified unknown faults and has resulted in improved maintenance routines (Burge, 2010).

#### 6 Raising the steel barrier to 650°C

Here is a list of the highest temperature components in the steam circuit and the maximum steam temperatures commercial steels can withstand.

- **thin-section superheater and reheater (all pressures):** the temperature of the fireside superheater and reheater steels will exceed that of the steam by up to 55°C, although this figure is difficult to measure accurately (Wheeldon and Shingledecker, 2013). Narula and others (2013) say that state-of-the-art austenitic steels are capable of dealing with steam at 665°C;
- **thick-section**, **superheater header**, **pipe and valve (high pressure)**: 9% chromium martensitic steels are limited mostly by steamside oxidation resistance, but also by insufficient HAZ strength and fireside corrosion resistance, to 600°C;
- thick-section, reheater header, pipe and valves (low pressure): Reheat temperatures are generally higher than superheater temperatures at 620°C, but the steam pressure is at least 20 MPa lower, resulting in much lower stresses but higher steamside oxidation. 10–12% chromium martensitic steels, which have higher steamside oxidation, but lower creep resistance than 9–10% chromium martensitic, are therefore suitable (Heuserand and Tak, 2013);
- **steam turbine**: Many components make up the steam turbine in general they can operate with steam up to 650°C (Narula and others, 2013).

Therefore, the limiting factor to increasing superheated and reheated steam to 650°C is the unsuitability of steels for thick-section components - this concept is illustrated in Figure 27. Providing thick-section steels can be improved for 650°C superheat and reheat applications, this would increase net electrical efficiency by 1% to 3.5% points (LHV) for USC plant operating at 600°C superheat and 620°C reheat (Nicol, 2013).



#### Figure 27 – Highest steam temperatures, with state-of-the-art materials and 650°C steels

Martensitic steels with 11–12% chromium seem to be the most suitable candidate for 650°C, as they have inherently higher resistance to steamside oxidation. All attempts to create 11–12% chromium martensitic steels with long-term creep resistance similar to that of P92/FB2/CB2 have been unsuccessful. However, there are some new interesting concepts aiming to increase long-term creep resistance, which are explained in the following sections (Blum, 2009).

#### 6.1 KOMET 650

KOMET 650, also known as 'Power station options: developments in materials and measurement techniques and tests under operating parameters at 650°C', was a German joint research programme to research the use of steels up to 650°C. Using components at the time KOMET650 estimated that operating at 650°C would give a net electrical efficiency of >47% (LHV).

KOMET650 ran from 1999 to 2008. There were fifteen individual projects in the areas of materials, measurement techniques and modelling. Small-scale tests were conducted in the laboratory. Large-scale test were conducted at four steam loops placed in Westfalen PCC plant (Germany). Each steam loop tested ten different materials at temperatures up to 650°C and pressures up to 19 MPa. The total cost of the project was €10 million, which was funded through the COORETEC funding framework. KOMET650 was made up of twelve companies and published four reports, the findings of which are summarised in the following sections.

To summarise, KOMET650 concluded that of the materials tested, commercially available steels at the time could achieve maximum steam temperatures of 630°C and nickel alloys are required for steam temperatures higher than 630°C (VGBa, 2013).

# 6.1.1 Investigations of the operational behaviour of boiler materials and their welded joints at temperatures up to 650°C

This report details the findings from the four steam loops that were placed in Westfalen PCC plant. The steam loops trialled numerous materials for use in superheaters. The investigations found the following practical material limits with respect to steam temperature: <550°C for martensitic grades E911 and NF 616, <570°C for austenitic grades 1.4910, 1.4941, Esshête 1250 and Super 304 H, <600°C for austenitic grade 347HFG, <620°C for austenitic grade NF709, <630°C for austenitic grade AC66 and >630°C for nickel alloy Inconel 617.

# 6.1.2 Findings on the operational behaviour of the pipe materials used, and assessment of the overall design in the light of the current regulations

The objective was to determine material and component behaviour at elbows in various heat-resistant materials and their welded joints, and then to examine the design and measurement principles under realistic operating conditions for steam pipes in the temperature range to 650°C. A steam pipe was fabricated from a selection of martensitic and nickel alloys, with elbow, DMW and similar welds. The pipe was installed in the Westfalen PCC plant and tested for eight years (22,170 hours). This study concluded that it is still relevant to test the creep deformation for the 9% chromium steels using the 'replication method' surface microstructure testing. Realistic estimates of pipeline life can be obtained only on the basis of pipeline monitoring. A pipeline monitoring process should at least ensure that the average relaxation level can be estimated and that the mounting components, such as hangers and springs, can be checked.

#### 6.1.3 Investigation of materials for use in steam turbines at temperatures up to 650°C

A bypass of steam taken from the test pipe section installed in Westfalen PCC plant was directed onto test pieces installed in two modules, one at 620°C and the other at 650°C. After a year of operation the test pieces were removed and examined using metallographic and scanning electron microscope. The study concluded that steels, especially ferritic and martensitic steels, have a linear growth rate of oxidation and subsequent spallation. As the temperature rises, the oxide layer becomes too thick for operation; this is known as the practical limit. The practical limit for 9–12% chromium martensitic steels is <600°C and for austenitic steels is <620°C. However, initial results have shown that surface treatments, such as coatings, could possibly increase the practical limit of steels.

#### 6.1.4 Operational experience with control valves in the high temperature range

This project investigated whether the tried and tested materials and fabrication methods for valves operating at 610°C could be used at 650°C. Thermal shock is a problem for valves as they are made up of components that vary in design, fabrication method and material – the valve body is a large thick-section component. Two valves were installed in parallel on a bypass of the test loop of Westfalen PCC plant. Numerous experimental and mathematical investigations into the long-term resilience and operating

safety of control valves showed that reliable and safe valves can be produced for steam parameters of 650°C and 18 MPa using material 1.4905 for the valve spindle, material 2.8877 for the piston rings, control and throttle elements.

#### 6.2 COST 556 and KMM-VIN WG2

COST 556 'Engineered Microstructures and nanostructures for Enhanced long-term high temperature materials Performance (EMEP)' was planned to start in 2009 and end in 2013. COST 556 was cancelled in 2011 and all funding was cut (Gibbons, 2013; KMM-VIN, 2013).

COST 556 continued forward with no guaranteed government funding under the name of KMM-VIN WG2. The European Virtual Institute on Knowledge-based Multifunctional Materials (KMM-VIN) was established in 2007 and aims to foster the creation of a powerful platform for research and development and industrial application of advanced materials. In 2012, KMM-VIN integrated the members and plans from the cancelled COST 556 EMEP project along with old KMM-VIN members interested in different materials for energy applications into its agenda to form Working Group 2: Materials for Energy (WG2). KMM-VIN WG2 is an unfunded collaboration seeking to promote and co-ordinate research into advanced steels. Individuals project are funded by private sources, national governments or the EC.

KMM-VIN WG2 is made up of 72 research establishments and 25 companies across Europe. The high temperature material projects facilitated by KMM-VIN WG2 co-ordination effort are detailed subsequently (KMM-VIN, 2013).

#### 6.3 Sub-grain strengthening

Long-term creep damage causes the sub-grains to migrate, reducing their size and dislocation density, thus lowering creep resistance. Sub-grains can be stabilised by micro-alloying or precipitation strengthening. The proportion of boron in steels has been altered previously with inconsistent results. Fujio Abe of National Institute for Materials Science (NIMS) of Japan found that alloying boron (>0.01%/100 ppm) with nitrogen in certain ratios achieves high creep resistance. This is because boron incorporates into M<sub>23</sub>C<sub>6</sub> precipitates, suppresses its coarsening rates and thus delays the recovery period of the sub-grain structure. This is known as sub-grain strengthening. The ratio of boron to nitrogen has to be correct otherwise large coarse boron-nitrogen precipitates form, which reduces creep resistance. P92, TAF steels and FB3 are commercial steels which utilise this strengthening mechanism (Subanovic and Schneider, 2012).

#### 6.3.1 V&M Tubes

V&M Tubes of France have developed martensitic steel with 12% chromium and optimised concentrations of boron, nitrogen and other alloying elements, along with optimised heat treatment. Initial test results show creep resistance considerably higher than P92 (Subanovic and Schneider, 2012).

#### 6.3.2 IMPACT

The new MARBN (MARtensite plus boron plus nitrogen) steels aim to exploit boron strengthening further. MARBN steel is being assessed in the IMACT project. Based in the UK, the 'Innovative Materials

Design and Monitoring of Power Plant to Accommodate Carbon Capture' (IMPACT) project is a joint venture between E.ON New Build & Technology (plant user), Doosan Power Systems (boiler and welding), Alstom (turbine and components), Goodwin Steel Castings (cast component supplier), National Physical Laboratory (monitoring technology) and Loughborough University (microstructural characterisation and modelling). The total budget is £1.8 million, partly government funded through the Technology Strategy Board, and the project ran from 2010 to 2013. There were three objectives within the project:

- develop of advanced welded MARBN steels for power plant;
- improve the design for welded components to reduce premature cracking;
- improve the strain and materials monitoring to allow high temperature operation.

The IMPACT project has optimised the composition of MARBN steel and short-term tests has shown that MARBN has 20–40% higher creep rupture resistance than P92 at temperatures up to 675°C. Heat treatment at 1200°C further increases the creep rupture resistance by 10–15%. Potentially, MARBN has 55% higher creep rupture resistance than P92. However, MARBN steel shows a substantial weld strength reduction and is susceptible to cracking in the HAZ. The proportions of the alloying elements in MARBN need not be exact – a wide range is acceptable for similar properties. In May 2012, Goodwin Steel Castings (UK) produced an eight tonne melt of MARBN, from which ingots and castings were fabricated and welded. These components are now in long-term tests (Allen and others, 2013).

#### 6.3.3 Technical University of Graz

Working with the IMPACT project and within the KMM-VIN WG2 initiative, the Technical University of Graz and Technical University of Chemnitz are characterising MARBN steel and the corresponding welding process (KMM-VIN, 2013).

Additionally, the Technical University of Graz have developed a 9% chromium steel alloyed with 120 ppm of boron. To date, 25,000 hour creep tests have shown strength 20% higher than that of P92 (Kuhn and others, 2012).

#### 6.3.4 STX-21

The Electrical Power Development Centre (EPDC), now JPower, in Japan led and funded a material research programme called STX-21. This programme contains a sub project called 'Advanced ferritic heat resistant steels for 650°C USC steam boilers' that focuses on the continued development of 9–12% chromium martensitic steels for 650°C steam parameters. This project is scheduled for a period of 15 years. The first 5-year phase (1997–2002), which involved a total of 35 researchers at the National Institute for Materials Science (Tsukuba, Japan), made significant progress with modifying martensitic steels with boron additions (Osgerby, 2007; Mayer, 2001; Gibbons, 2013).

#### 6.4 Z-phase strengthening

Chapter 3, Section 2.8, explains how higher chromium martensitic steels suffer from Z–phase weakening. The higher chromium content causes increased precipitation of the coarse nitrides, known as Z–phase, which consumes the small strengthening nitrides precipitates. However, Z–phase precipitation can be used as a strengthening mechanism. By promoting its formation during fabrication, small Z–phase precipitates, as opposed to coarse Z–phase precipitates, strengthens steel.

Promoting Z-phase can be achieved through optimised alloying, more specifically an increase in chromium and cobalt concentrations, a decrease of carbon content and the addition of niobium and tantalum. Test results from microstructural investigations have been successful, showing that nitride and carbide precipitates are instantly converted to Z-phase (Subanovic and Schneider, 2012; Kuhn and others, 2012).

Figure 28 shows how the Z–phase weakening and Z–phase strengthening mechanisms develop, with SEM of standard 12% chromium steel and new 12% chromium steel designed to favour finely dispersed Z-phase precipitates. Medium-term and long-term creep rupture testing started in 2009 (Blum, 2009).

![](_page_57_Figure_4.jpeg)

Figure 28 – Z-phase weakening and Z-phase strengthening (Blum, 2009)

#### 6.4.1 Z–Ultra

Z–Ultra is short for 'Z–phase strengthened steels for ultra-supercritical power plants'. Z–Ultra started in February 2013 and will finish in January 2016; it is partially funded by the European Commission under Framework Programme 7. Z Ultra was developed independently and is now part of the KMM-VIN WG2 initiative.

Z–Ultra aims to improve the creep resistance of 12% chromium martensitic steels, by increasing the amount of smaller Z–phase precipitates, allowing operation with 650°C superheat steam. Numerous 12% chromium martensitic steels, associated filler materials and welding procedures are being assessed. Microstructure modelling will be used extensively to hasten research, improve understanding, and

provide design tools and lifetime estimation methods for the operation of future PCC plant. The project co-ordinator is Fraunhofer IWM (Germany) and involves ten partners, some of which are non-EU (KMM-VIN, 2013).

#### 6.5 Laves phase strengthening

Ferritic steels with chromium contents higher than 15% resist steamside oxidation up to 650°C. However, the higher chromium content can promote the formation of the iron-chromium Sigma phase which makes steels brittle, and the creep resistance cannot be obtained through precipitation of carbides or nitrides, as carbon and nitrogen have low solubility in the ferritic matrix. Strengthening ferritic steels through oxides precipitates is ruled out as it requires expensive powder metallurgical manufacturing processes.

Chapter 3, Section 2.6, explains how 9–12% chromium martensitic steels suffer from Laves phase weakening. Tungsten and molybdenum will precipitate out as large and coarse Laves phase, which reduces the strengthening effects of solid solution strengthening and precipitations strengthening. However, Laves phase precipitation can be used as a strengthening mechanism. By promoting its formation during fabrication, small Laves phase precipitates, as opposed to coarse Laves phase precipitates, strengthens steel.

ThyssenKrupp VDM and Forschungszentrum Jülich of Germany have developed a high chromium ferritic steel for high temperature fuel cells. This material has high creep resistance through Laves phase strengthening, can be produced in conventional electric arc furnaces and has good steamside oxidation resistance to 600°C (Kuhn and others, 2012).

#### 6.6 Super ferritic heat-resistant materials

The German project 'Super Ferritic Heat-resistant materials' tested 80 materials. The materials contained 8.4% to 14.4% chromium and 1% to 6% tungsten, micro-alloyed with various other alloying elements such as cobalt, copper and tantalum. The project identified one 12% chromium ferritic steel with creep resistance comparable to P92 – further details are yet to be published (Kuhn and others, 2012).

#### 6.7 CRESTA

The project called 'New Creep REsistant STAble steel for USC Power Plant' or CRESTA aimed to develop a steel and filler material that combines the benefits of between high creep resistance (between T91 and T92), high steamside oxidation and fireside corrosion resistance and good weldability (preferably no PWHT for waterwalls), using thermodynamic and kinetic modelling. Based in Europe, the participants include Centro Sviluppo Materiali, DONG energy, Technical University of Graz, Air Liquide Welding, Dalmine (of the Tenaris group) and CRMC (research arm of Industeel). The project started in 2008 and finished in 2012 and is split into the following stages. Results are yet to be published (CRESTA, 2013):

- WP1: alloy design;
- WP2: material production;
- WP3: industrial production of selected composition;

- WP4: prototype production;
- WP5: results analysis and guideline definition.

#### 6.8 Ferritic-martensitic steel

In 2000, research at NIMS found that some steels with two phases, comprised of a ferrite matrix with intermetallic martensite phase with carbide and nitride precipitates, perform better than the best commercial steels, such as T/P92. A two-phase material, with 6% tungsten and 3% cobalt, is estimated to have long-term creep resistance (100 MPa for  $1 \times 10^5$  h) up to 650°C. However, high amounts of tungsten may present difficulties in manufacture and data on steamside oxidation resistance is yet to be published (Kuhn and others, 2012).

#### 6.9 AFA steels

New austenitic steels, such as OC4 and OC5 (part of the AFA steels), are being developed that use aluminium to achieve steamside oxidation resistance in the temperature range 650–900°C and long-term creep resistance (100 MPa for 1 x 10<sup>5</sup> h) up to 660°C. Additionally, the thermal coefficient of expansion for AFA steels is lower than conventional austenitic steels (Gibbons, 2013).

#### 6.10 Coatings

High resistance to fireside corrosion and steamside oxidation can be achieved with the use of coatings. This reduces the need for such inherent material properties, which allows the use of lower cost steels. For steamside coatings however, a radical change in component design and manufacturing process could be required, depending on the method of coating application (Osgerby, 2007). Coating steels require strict process control otherwise the coating may not adhere. Boiler manufactures have avoided coatings as they have failed to work in practice (Holmström, 2012).

#### 6.10.1 Weld-overlays

As waterwall steels can be exposed to severe fireside corrosion, particularly near the burners, weldoverlays or cladding can be applied to protect the welds. Alloy 622 weld-overlay (containing >20% chromium) and SUS309 cladding have been used successfully at lower temperatures. Weld-overlays with higher chromium contents, such as Alloy 52, Alloy 33 and Alloy 72 (N72), can be used at higher temperatures. Weld-overlays are applied via pulsed-gas metal arc welding or by laser cladding. Weldoverlays cannot be applied to martensitic steels - thermal spray coatings or shielding would have to be used instead.

#### 6.10.2 Thermal spray coatings

Thermal (or plasma) spray coatings, using oxides, cemented carbides and metallic alloys, are currently in development. High chromium and nickel based thermal spray coatings have been successful, however the cost remains high (Narula and others, 2013; Wheeldon and Shingledecker, 2013).

#### 6.10.3 Aluminising

The ETD co-ordinate a sponsored group project titled 'T91 tube aluminising to extend the life of new or replacement tubes'. Aluminising is a type of thermal spray coating. The group includes V&M Tubes (France/Germany), Electricity Supply Board (Ireland) and Diffusion Alloys (UK). Existing tubes are cleaned of oxidation scales by sand blasting and acid pickling, after which they can be aluminised. Pilot-scale testing has been successful. The next step is commercial-scale application.

#### 6.11 Advanced ultra-supercritical (700°C)

The steel barrier presently lies at 620°C. However, further development of steels is thought possible to reach 650°C. Current research aims to use nickel alloys to reach 700°C superheated steam, known as advanced ultra-supercritical (AUSC) or 700°C technology, with a corresponding net electrical efficiency higher than 50% (LHV). However, nickel alloys are up to five to fifty times more expensive steels than used in USC technology (Wheeldon and Shingledecker, 2013).

The EU, USA, Japan, India and China all have material research programmes for 700°C technology. Nicol (2013) reviews the developments and status of these major material research programmes. The material research programmes consist of the following three main stages, which can overlap each other by a few years depending on technical readiness and funding availability:

- **Stage 1**: small-scale laboratory tests (8–13 y);
- **Stage 2**: large-scale components test facility (CTF).
  - Part A: design and build (4–5 y).
  - Part B: operate and evaluate (3–5 y);
- **Stage 3**: full-scale demonstration plant (FSDP) (500–1000 MWe).
  - Part A: design and build (4–6 y).
  - Part B: operate and evaluate (6 y).

Figure 29 shows a Gantt chart of the material research programmes. Assuming successful operation of a full-scale demonstration plant, a commercial 700°C PCC power plant could be operation in 2031, given favourable economics. This progress has been slower than expected, which has led to increased demand for 650°C steels.

![](_page_61_Figure_1.jpeg)

![](_page_61_Figure_2.jpeg)

### 7 Final remarks

#### 7.1 Mechanical behaviour of steels

Ferritic steels have a low amount of alloying and are strengthened with solid solution and dislocation strengthening. Ferritic steels are easy to fabricate and they have good performance all round up to 565°C, after which they are limited by their resistance to steamside oxidation. Ferritic steels are the only steel that does not require expensive and time consuming post weld heat treatment. Chromoly ferritic steels, such as T22, are well proven are used in waterwall and other low temperature applications. The installation of low NOx burners in the boiler can cause excessive corrosion of ferritic steels nearer the burners has been solved with protective high chromium weld-overlays.

T23 and T24 are new low-alloy ferritic steels for waterwalls and low temperature superheater applications. T24 was used to construct the waterwalls in a few new build pulverised coal combustion (PCC) plant in Europe. Shortly after commissioning in 2010, multiple cracks developed in T24. Subsequent evaluation showed that the cracking mechanism is stress corrosion cracking (SCC). After investigation and research, the following measures were introduced in 2011 to prevent SCC cracking of T24. During the commissioning stage, the critical tensile stress of T24 should be reduced with correct welding temperature profiles and additional heat treatment at 450–500°C after welding. Additionally, the chemical cleaning process was adapted and finally the water chemistry and the start-up procedure were adjusted to minimise risk of SCC. Ultra-supercritical coal-fired power plant commissioned since 2011 have implemented these measures and, to date, have not detected SCC of T24.

9–12% chromium martensitic steels have been widely used in PCC plant for just over two decades. High alloying of chromium molybdenum, nitrogen, niobium and vanadium achieve a significant amount precipitation strengthening. Generally, the 9–12% chromium martensitic steels have high creep and fatigue resistance, low coefficient of thermal expansion, high thermal conductivity and good fabricability. 9–10% chromium martensitic steels can operate up to 600°C and high pressures of up to 25 MPa, but are limited by their resistant to steamside oxidation. 11–12% chromium martensitic steels can operate up to 620°C and low pressures of less than 10 MPa, but are limited by their strength. However, martensitic steels require post weld heat treatment (PWHT); they are susceptible to cracking (type IV and creep-fatigue) and long-term weakening mechanisms (Z–phase and Laves phase transformation).

Type IV cracking of 9% chromium martensitic steels have been significant, with failures occurring within two years of operation. Type IV cracking can be avoided by sufficient alloying and correct temperature profiles during the fabrication, welding and PWHT procedures. Newer components have reduced the risk of Type IV cracking through improved design, to minimise

stresses on the weld, and so that the welding procedure and post weld heat treatment procedures are easier to carry out correctly.

Within a few years of service life, 9–12% chromium martensitic steels suffer from a long-term weakening mechanism, known as Laves phase. This is where the small strengthening precipitates transform to large weakening precipitates. P92 suffers from Laves phase, ultimately making it not that much stronger than P91. Higher chromium, 11–12% chromium martensitic steels suffer from Laves phase, but also suffer from Z-phase transformation, which is caused by the higher chromium level. The combined weakening mechanisms generally make higher 11–12% chromium martensitic steels weaker than lower 9–10% chromium martensitic steels.

Cyclic operation of older PCC plant has resulted in higher fatigue damage and creep-fatigue damage of high temperature components. Creep-fatigue damage is where creep damage and fatigue damage interact synergistically. Creep-fatigue damage can result in failure sooner than with either creep or fatigue damage alone, as has been the case for of 9% chromium martensitic steels. It is important to note that some material codes do not assess creep-fatigue damage.

Austenitic steels are used in the superheater and reheaters of ultra-supercritical power plant. Very high alloying with elements, such as chromium and nickel, achieve high solid solution and precipitation strengthening. They have excellent performance all around up to 665°C, but they have a high co-efficient of thermal expansion, which results in cracking when used in thick-section component, this austenitic steel are limited to thin-section components. Cyclic operation of older PCC plant has also resulted in failures of dissimilar metal welds (DMW), especially between austenitic and martensitic steels.

#### 7.2 Chemical attack of steels

Excessive slagging and fouling has increased creep damage on all high temperature steels. However, boilers can be kept clean with intelligent soot blowers whilst online. Intelligent soot blowers are retractable, can vary the steam/water/air pressure and use heat transfer sensors to determine when cleaning is required. This combination allows for maximum cleaning, minimum water usage and tube damage. Typical payback periods for intelligent soot blowers are around 6–12 months, and they can eliminate the need for offline boiler cleaning for up to 20 years. An unforeseen consequence of cyclic operation is reduced need to clean the boiler, as the increased expansion and contraction of steels effectively dislodges the deposits.

The feedwater treatment that uses oxygen scavengers to minimise steamside oxidation causes Flow Accelerated Corrosion (FAC). FAC has caused numerous failures and fatalities and still occurs in >70% of fossil-fuelled power plant. Feedwater treatment that involves the deliberate injection of oxygen or air into the feedwater, in order to create protective oxide layers on the steels, minimise the risk of FAC. In all cases, high water purity and continuous online water quality monitoring is essential to avoid corrosion. FAC can also be prevented with the use of higher chromium ferritic steels, up to 2.5% chromium, in low temperature sections, as opposed to straight mild steel.

#### 7.3 Steel lifetime assessment

If PCC plant are operated in cyclic operation beyond their design specification and kept online according to the original lifetime, then there is a high chance of catastrophic failure in the steam circuit. It can be economically favourable to repair or replace components before failure. To do this the corrected lifetime is needed. Modern software packages and material examination tools can be used to accurately measure steel lifetime accounting for other operational changes, such severe cyclic operation or fuel change. The corrected steel lifetimes are accurate, which allows components to be replaced just before failure, which minimises maintenance costs. This technique is known as condition monitoring.

Preventative maintenance strategies integrate information, from process measurements and condition monitoring, online and offline, for multiple components into a single computer programme, known as a computerised maintenance management system (CMMS). CMMS can give a quick overview of the entire plant condition, providing risk and cost information in order to make a pro-active decision. One utility in the USA established CMMS across its twenty seven oil and gas fired units. The result was 30% fewer forced outages, a 7% increase in peak reliability and after a few months maintenance costs reduced.

#### 7.4 Raising the steel barrier to 650°C

Commercially available steels for operating with superheat temperatures up to 600°C and reheat temperature up to 620°C. The limiting factor to increasing superheat and reheat steam temperature to 650°C is the unsuitability of steels for thick-section components.

Martensitic steels with 11–12% chromium seem to be the most suitable candidate for 650°C, as they have inherently higher resistance to steamside oxidation. Promoting fine and homogenous Z-phase and Laves phase precipitation during the fabrication steels can be used as a strengthening mechanism. A European project has estimated that Z-phase strengthened 12% chromium martensitic steel can operated with superheat steam at 650°C. Another European project has developed a Laves phase strengthened high chromium ferritic steel with good steamside oxidation resistance to 600°C. Sub-grain strengthening, by alloying boron with nitrogen in certain ratios, has been proven to increase creep resistance. Projects in Japan and Europe are assessing sub-grain strengthening. Short-term results show that sub-grain strengthened 12% chromium martensitic steels are stronger than P92 by up to 55%. New AFA austenitic steels, which have a low thermal co-efficient of expansion, are being developed for thick-section application up to 660°C. Coatings for martensitic steels are in the early stages of development.

Assuming thick-section steels can be improved; the increase of maximum steam temperatures from 600°C to 650°C will correspond with rise in net electrical efficiency of 1–3% points (LHV). 650°C could allow some pulverised coalfired power plant to reach close to 50% net electrical efficiency (LHV). Steam temperatures higher than 650°C can be achieved using exotic nickel alloys.

# 8 References

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