

Recent Advances in Steels for Coal Fired Power Plant: A Review

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Received: 22 January 2013 / Accepted: 5 May 2013 / Published online: 3 July 2013
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Abstract The current status of the development of materials for advanced ultra supercritical power generation technology is considered in the light of changes in the priorities and opportunities worldwide for high efficiency power plant fired by coal. These include the slower economic growth, the emphasis on renewable sources, and technical setbacks with the new materials necessary for high temperature operation. Currently martensitic steels are restricted to about 620 °C and since Ni-base alloys cannot be used economically below about 700 °C, the utility industry has had to abandon the traditional incremental approach to the increasing of steam temperature. The major theme of the paper will be the potential of further materials research to identify steels with “Gap Closing” potential i.e. with sufficient strength to operate between the current limit for martensitic steels and the lowest temperature at which the Ni-base alloys become viable. Alloys with some potential in this regard are mentioned and representative properties described.

Keywords Boilers · Turbines · Ultra supercritical · Martensitic steels

1 Introduction

The worldwide effort to introduce higher steam temperatures in coal fired power plant began in the 1980's with the launch of the COST 501 Project in Europe to rival the EPRI programme in the USA and that of the EPDC in Japan. The work was driven originally by the need to use the finite and expensive (at least in Europe and Japan)

resources of fossil fuel more effectively. Subsequently the realisation that emissions of carbon dioxide from the combustion of fossil fuels and other sources had a potentially detrimental effect on climate change brought added emphasis. The key to higher operating temperatures as in all power plant technology lies in the availability of appropriate materials with good strength at high temperature and with costs of manufacture and fabrication that will yield a cost of electricity acceptable to the consumer.

More recently it was recognised that higher efficiencies of generation could compensate for energy losses associated with Capture of carbon dioxide and Sequestration (CCS) thus minimising the effect of the introduction of this technology on the overall cost of electricity. Clearly increased costs of electric power would have a potentially harmful effect on national economic performance.

Against this background extensive programmes of materials development were initiated focused on the further improvement of the high strength martensitic steels of which the well-known alloy P91 was the forerunner. This work resulted in the emergence of improved materials produced in the main by the European and Japanese steel companies with enhanced performance at the highest temperatures. These alloys are required for pipe and other thick section parts and also for steam turbine rotors and other components. Developments in austenitic steels for superheater and reheater applications yielded improved alloys with increased strength and good corrosion and oxidation resistance.

2 Current State-of-the-Art in USC (~600 °C Steam) Technology

The Eddystone plant which was built in the 1960's with main steam conditions of 36.5 MPa and 654 °C and double reheat

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Table 1 Characteristics of some USC plants operating worldwide

Plant	MW	Steam parameters	Fuel	Years	Efficiency (%)
Niederaussem	975	265 bar; 565 °C/600 °C	Lignite	2002	>43
Torrevaldaliga Nord	660	250 bar; 600 °C/610 °C	PC	2008	44.7
Isogo 2	600	280 bar; 600 °C/620 °C	PC	2009	>43
Haimen	2 × 1,036	250 bar; 600 °C/600 °C	PC	2009	~44
Ninghai	2 × 1,000	262 bar; 600 °C/600 °C	PC	2009	~45
Suizhong	2 × 1,000	250 bar; 600 °C/600 °C	PC	2010	
Leqing	660	250 bar; 600 °C/600 °C	PC	2010	
John W Turk	690	261 bar, 602 °C/608 °C	PC	2012	

at 565 °C represented a major advance in power plant technology. The unit which was designed and built by Combustion Engineering (a predecessor of Alstom Power) had a generating capacity of 325 MW and was thus the largest and most efficient plant in operation anywhere in the world at that time. However in order to improve availability the main steam conditions were subsequently reduced to 29.7 MPa and 608 °C and it is only relatively recently that these steam conditions have been matched in plants in Japan and Europe.

The more recent development towards higher steam temperatures was led by Japan with a USC coal fired plant commissioned in 1997 and was closely followed by the introduction of similar technology in Europe where the Danish company Elsam was prominent.

The current state-of-the-art in USC coal fired power plant is summarised in Table 1, where it can be seen that efficiencies of ~45 % can now be achieved with single reheat, optimised steam turbine blade designs, and seawater cooling. With double reheat and relatively minor changes in the design it is possible to raise the efficiency to about 49 % without the need for any more advanced technology.

Thus advanced ultra supercritical technology (A-USC) will be required to provide efficiencies, which are significantly greater than those currently achievable if economic operation is to be achieved, bearing in mind the costs associated with the advanced materials required to cope with the higher steam temperatures and pressures.

3 Limitations of Materials Performance

Traditionally advances in power engineering technology have been accomplished incrementally with changes in steam temperatures and pressures and the introduction of new materials occurring gradually over a period of years. This was true of the advance from steam temperatures of ~540 °C in the 70's to around 610 °C currently so that risk was minimised and new materials and operating conditions could be introduced gradually.

Initially it was anticipated that the advanced 9–12 % Cr martensitic steels, which were developed for service at the

higher steam temperatures, would have strength characteristics that would allow applications up to about 650 °C. This turned out to be somewhat optimistic so that a temperature of about 620 °C was the maximum that could be achieved with the steels that were developed and code approved in the late 1990's.

The limits achievable with the various classes of alloy are illustrated in Fig. 1 which defines the strength characteristics of the martensitic steels, the austenitic steels and also the Ni-base alloys that were considered for A-USC applications [1].

For a 100,000 h creep rupture strength of 100 MPa the temperature limit for the martensitic steels is about 625 °C and the equivalent temperature for the weakest of the Ni-base alloys is about 700 °C and the austenitic steels fill the gap between these limits. However for a modern power plant cyclic operation is a major requirement and the poor thermal conductivity and the high coefficient of thermal expansion typical of austenitic alloys will result in high thermal stresses during cyclic operation and is a significant limitation in this regard. Thus the austenitic alloys have fallen out of favour for thick section boiler parts and for steam pipe. Consequently the designer of A-USC plant was faced with the need to resort to Ni-base alloys for these pressure parts. However in order to achieve efficiency gains sufficient to justify the high capital costs when these alloys were used it was necessary to operate with steam temperatures of at least 700 °C. Thus the initial plans for A-USC plant involved a significant step change in steam temperature to justify the Ni-base alloys, which was hardly an incremental approach as had been the case with developments in the past. Such an increase in steam conditions and the use of alloys not previously applied in steam power plant carried a significant additional element of risk for the OEM's and the utility customers.

4 Current Status of A-USC Developments

In Europe, which led the worldwide drive to develop advanced USC technology, much of the materials

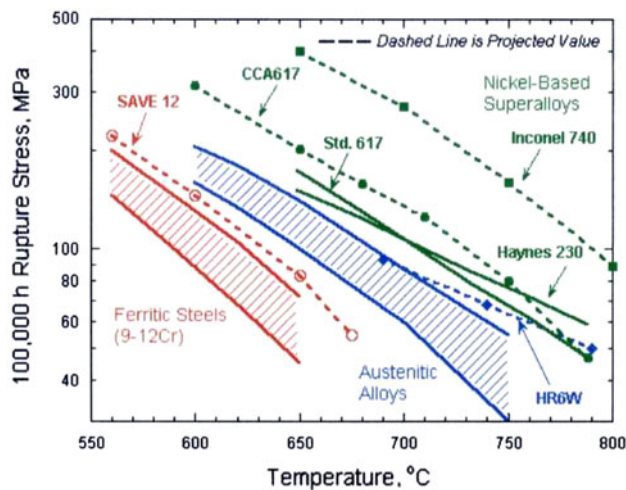


Fig. 1 Illustration of the strength characteristics of alloys for A-USC applications [1]

development and characterisation work was carried out in the various phases of the original COST Project. However the latest phase, COST 536, was not renewed at the end of 2011. Consequently formal collaborative work on materials development has effectively been abandoned in Europe.

In parallel with the materials development work a consortium of German utilities was established to support a component test facility, ComTes 700, to enable components manufactured from the new alloys to be tested for an extended period in realistic conditions. The test facility [2] was installed in a working boiler at the Scholven power plant of E.ON Kraftwerk GmbH and operated for about 20,000 h at the conditions of temperature and pressure consistent with the target parameters for a unit operating with a main steam temperature of ~ 700 °C.

However it turned out that the results were disappointing in that cracks developed in the thick section parts [3] manufactured from the Ni-base alloy IN617. The outcome was that E.ON shelved plans for a demonstrator unit and arrangements were made for a further programme to carry out long term testing of welds in thick section parts. This facility was to be installed in a working boiler in Italy and is currently in the planning stage.

In the USA the work of the Consortium of materials manufacturers, utilities and research organisations established to characterise materials performance and to develop fabrication techniques for boiler and turbine parts with financial support from the Department of Energy has now been largely completed. The next phase will involve establishment of a components test facility and this is in the planning stage.

In Japan the emphasis originally was in the refurbishment of existing elderly plant with poor operating efficiencies and replacement with units working at higher steam temperatures and pressures [4], with the aim of obtaining a relative

decrease in harmful emissions such as carbon dioxide. This appears to remain the overall strategy [5] and work on A-USC plants is now subsumed into the broadly based “Cool Earth Project” an innovative energy technology programme the aim of which is to improve the efficiency of energy usage in the major Japanese heavy industries. Retrofitting with A-USC plant is claimed to give a 15 % reduction in CO_2 .

In China [6] the National Innovation Alliance for Advanced Coal-Fired Power Plant, was organised by the National Energy Resource Bureau, in June 2011, with the head of the Chinese DoE as Chairman. The plan was for a 600 MW unit with target parameters for main steam of at least 35 MPa and 700 °C. A Council and a Technical Committee with three Technical Advisers has been established and the participants involve seventeen materials research institutes, power equipment manufacturers and power management and operation companies.

A materials evaluation programme in India is currently being planned.

5 State-of-the-Art in Steels for High Temperature Power Plant

5.1 Membrane Walls

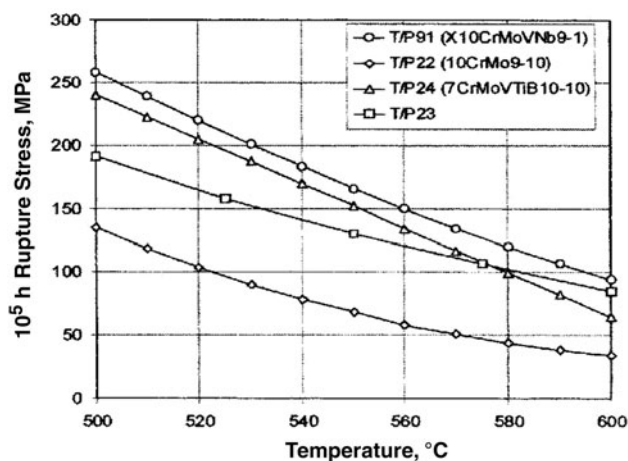
Similarly to waterwalls in a conventional unit the membrane walls in a supercritical boiler enclose the furnace and in the lower section where the heat flux is high the membrane is spiral wound and behaves as an evaporator. Higher up the furnace in the convective heating area a vertical tube design is usual and this section of the membrane behaves as a first stage superheater.

In conventional units low alloy steels are typically used in this application and these are characterised by good fabricability including no requirement for post-weld heat treatment, which is an important attribute particularly when field assembly is required. Advanced variants of the low alloy steels viz T23 and T24, as shown in Table 2, have greatly increased strength at high temperature [7] and are similar to T91 in creep rupture strength, Fig. 2. However at the higher temperatures the low content of Cr in these steels results in excessive oxidation in steam and ultimately limits the maximum temperature capability of the alloys. Internal coating could improve the oxidation resistance. It should be noted that for steam temperatures of 700 °C, metal temperatures in the membrane wall would be in the range 500–600 °C. For these conditions it is claimed [8] that T91 and T92 can be used for membrane wall applications and fabrication techniques have been successfully developed.

Clearly operation with a lower steam temperature e.g. around 650 °C would reduce the demands on the membrane

Table 2 Nominal compositions of steels T23 and T24

Alloy	Composition in mass%, bal. Fe								
	C	Cr	Mo	V	Ti	W	Nb	B ^a	N ^a
T23	0.07	2.5	0.3	0.25	–	1.6	0.05	60 ^b	300 ^b
T24	0.07	2.5	1.0	0.25	0.07	–	–	70 ^b	100 ^b

^a ppm^b max**Fig. 2** 10^5 h stress rupture properties for low alloy steels with data for T/P91 for comparison [7]

wall materials and would enable the use of low alloy steels such as T23 and T24.

A critical factor in the choice of materials for membrane walls is the ability to carry out welding in the field i.e. without post weld heat treatment, and this requirement effectively sets a limit on the maximum temperature capability of the waterwall since the stronger alloys usually require heat treatment after welding. Also, as already mentioned, with the ferritic materials the oxidation limit frequently sets the maximum temperature of operation.

5.2 Superheater and Reheater Tubing

For the higher temperatures in these applications austenitic steels are necessary to provide the required creep strength but also to cope with the corrosive conditions of the flue gases on the fireside and to resist steam oxidation on the internal tube surfaces. These degradation mechanisms can lead to loss of wall thickness on the outside of the tube and to a build up of oxide leading to higher metal temperatures on the steam side. Clearly higher contents of Cr will contribute to increased resistance to degradation but will also result in increased cost.

Typically the austenitic steels used for steam temperatures up to about 600 °C are variants of the familiar Type

304 and 347 steels used widely in the power generation industry. A more recent development in this category is the alloy Super 304H and in this case a small addition of Cu gives enhanced creep performance as a result of the precipitation of fine particles of a Cu-rich phase. This phase is precipitated during ageing at 650 °C and because the lattice parameter misfit with the Fe–Cr–Ni matrix is small the particles are coherent and highly stable and show relatively slow rates of growth. Thus it is claimed [9] that even after ageing for 50,000 h at 650 °C the particle size is ~35 nm. As a result the creep rupture strength of the alloy is superior to other alloys in this class, Table 3, while any impact on material cost will be small. Super304H is used in many of the coal-fired USC plants built recently in Japan [10] and with steam temperatures of up to 613 °C.

The relatively poor oxidation and corrosion resistance associated with Cr contents in the range 17–20 % can limit the performance of these alloys. In this context a modified version on Type 347 viz 347 HFG has a fine grain size and it is claimed that the fine grains increase diffusion rates of Cr and enhance corrosion resistance. During cyclic operation oxides formed on the steam side tend to spall and in extreme cases the spalled material can accumulate and tube blockages may occur. Furthermore when spalling occurs the underlying substrate tends to be depleted in Cr so that rapid attack may occur until a new oxide layer can be established. Recent work [11] to model the failure mechanisms in oxides in both ferritic and austenitic materials has provided a basis for estimating times to onset of oxide spallation.

In conditions where degradation due to fireside corrosion or to oxidation in steam is expected to be severe advanced austenitic steels such as HR3C, Sanicro 28, NF 709 and SAVE 25 may be used. The compositions of these alloys are given in Table 4.

5.3 Pipe and Thick Wall Components

For the current generation of USC plants with steam temperatures up to a maximum of ~610 °C the high strength martensitic steels P91, E911 and P92 have been used extensively with some usage of P122 in Japan. The nominal compositions are given in Table 5.

The temperature capability of these alloys has been less than anticipated when the development work began and currently P92 is the strongest alloy in this class of material, which has been approved in the ASME Code. It should be explained that originally each of the new steels in Table 5 met the target creep strength criterion, at least on the basis of data extrapolated from 10,000 h in the case of the ASME approval process; however when longer-term data became available subsequently, the strength level of P92

Table 3 Comparison of the creep rupture strength of some austenitic steels

Parameter	Steel		
	Tp347H	Super 304H	HR3C
10 ⁵ h Rupture strength (MPa)	86.9	104	98.1

Table 4 Nominal compositions of austenitic steels with good corrosion resistance

Steel	Composition in mass%, bal. Fe								
	C	Cr	Ni	Mo	W	Ti	Nb	Cu	Others
NF709	0.15	20	25	1.5	–	0.2	0.25	–	N, B
HR3C	0.07	25	20	–	–	–	0.4	–	N
SAVE25	0.08	27	31	3.5	1.5	–	–	3.0	N
Sanicro28	0.02	27	31	3.5	–	–	–	1.0	N

was significantly reduced. Thus the 100,000 h rupture stress at 600 °C was reduced by the ECCC (European Creep Collaborative Committee) from 123 MPa in 1999 to 113 MPa in 2005 and consequently the margin of advantage over P91 has been eroded somewhat as longer term creep data have become available.

With P122 however the strength dropped off more rapidly and consequently this steel has been less widely used although the higher Cr content in this case gives improved resistance to oxidation in steam and this is a useful attribute for the tubular version of the steel.

Welded martensitic steel structures are susceptible to a type of failure known as Type IV cracking which is a consequence of the phase transformation. During welding there will be a zone in the parent metal, which reaches a sufficiently high temperature, i.e. above 830–850 °C, for the transformation to austenite to occur. However since the time at temperature will be too short for all the carbides to dissolve the martensite that forms on subsequent cooling will be low in carbon and therefore the hardness and creep

strength will be reduced. The formation of this zone of weakness can be avoided by carrying out a full normalise and temper heat treatment following the welding. If a full heat treatment is impractical it will be important to design the weld such that stresses are reduced relative to the parent metal to avoid premature failure.

A well-known problem with the 9–12 % Cr steels is that after long times (~60,000 h) at high temperatures serious deterioration in creep performance can occur due to microstructural instability so that long term stress rupture data are necessary in order to validate the high temperature performance of these alloys. Recently it has been shown, following the work of Strang and co-workers [12], that the drop off in stress rupture performance experienced with some of these steels is due to the formation of a Cr (V, Nb)N intermetallic known as modified “Z” phase. The formation of coarse particles of “Z” phase is accompanied by dissolution of the MX particles, which contribute much of the creep resistance of these steels. This process occurs after long exposure at high temperature and since the coarse “Z” phase particles make no contribution to creep strength, weakening of the alloy results. It appears that steels with higher levels of Cr levels such as P122 are more susceptible to “Z” phase formation whereas in 9Cr steels such as P92 the rate of precipitation is relatively slow.

A material, which should at least be mentioned even although it may not be generally categorised as a steel, is the Fe–Ni–W alloy HR6W, Table 5. This was originally developed [13] for superheater tubing for service at 650 °C and is strengthened by Fe₂W (Laves phase) and by M₂₃C₆ particles. The alloy has good strength (Table 6) with microstructural stability at 650 °C in contrast to the martensitic steels and is considered suitable for thick section boiler parts including high-energy piping, Fig. 3.

Critical factors in determining the potential for widespread application of this material will include cost and the coefficient of thermal expansion which is claimed to be about 15 % lower than that of the austenitic steels.

Table 5 Nominal compositions of martensitic steels and of HR6W

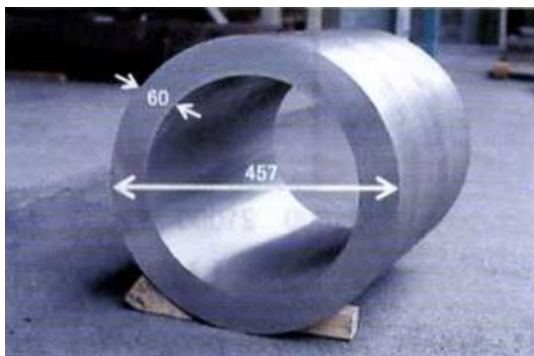
Alloy	Composition in mass%, bal. Fe, except for HR6W												
	C	Si	Mn	Cr	Mo	W	Ni	V	Nb	Ti	N	B ^a	Cu
P91	0.1	0.4	0.4	9.0	1.0			0.2	0.08		0.05		
P92	0.07	0.06	0.45	9.0	0.5	1.8		0.2	0.05		0.06	40	
E911	0.11	0.4	0.4	9.0	1.0	1.0		0.2	0.08		0.07		
P122	0.11	0.1	0.6	12.0	0.4	2.0	0.3	0.25	0.05		0.06	30	1.0
HR6W	0.08			23		7.0	45		0.02	0.1		50 ^b	

^a ppm

^b est

Table 6 Rupture strength of alloy HR6W

Temp (°C)	10 ⁵ h Rupture strength (MPa)
650	120
700	88
750	65

**Fig. 3** Section of extruded pipe in HR6W (dimensions in mm) [13]

5.4 HP/IP Steam Turbine Rotors

The developments in Europe and in Japan that led to the emergence of new high strength martensitic steels for steam turbine rotors owed much to the pioneering work in this area by Professor T Fujita. The compositions of some of the alloys are shown in Table 7. The alloys HR 1100 and HR 1200 were the original alloys proposed by Professor Fujita and alloys B, E, and F were developed in the initial phase of the COST programme. Steel FB2 was a later development.

The similarities are evident and it turned out that of the original European alloys only E and F became commercial steels even although alloy B was superior in terms of strength at high temperature. A modified version of HR 1200 was developed in Japan [14] with lower content of Ni and Co intended for service to 650 °C.

The heat treatment applied to steel E was 1,050 °C, oil quench (OQ); 570 °C, air cool (AC); 700 °C AC, although later work suggested that higher austenitizing temperatures were desirable to fully solution the boron nitride particles. This steel was used by Toshiba in collaboration with GE for the HP rotor in the Tachibana Bay power plant which is a 1,050 MW unit operating with steam conditions of 600 °C/610 °C, 25 MPa commissioned in 2000 and also in Isogo New 1 a 600 MW plant where the steam conditions were 605 °C/613 °C, 28 MPa. In each case the reported [15] efficiency was 42 %.

Steels E and F were widely used for HP turbine applications for the USC plants built in Europe with steam

temperatures up to 610 °C and have been in operation successfully for several years.

6 Steels with 650 °C Capability

6.1 Introduction

The limitation in the temperature performance of the advanced martensitic steels focused attention on the Ni–Cr alloys for the A-USC applications even although it was recognised that the use of these alloys for thick section parts would greatly increase the cost of a plant to operate with 700 °C steam. However development work on the martensitic steels continued in both Japan and Europe with different approaches being used in each case. In Japan the emphasis was on introducing small amounts of boron, which had earlier been shown, to be advantageous in the rotor steels developed in the COST Project and in Europe a novel approach involved an effort to use the precipitation of “Z phase” as a strengthening mechanism in 12 % Cr steels which would have superior oxidation resistance compared to the 9 % Cr alloys. There was also further effort to improve the 9 % Cr steels by modification to the heat treatment and optimisation of minor element composition.

6.2 Thick Section Parts for Boiler Applications

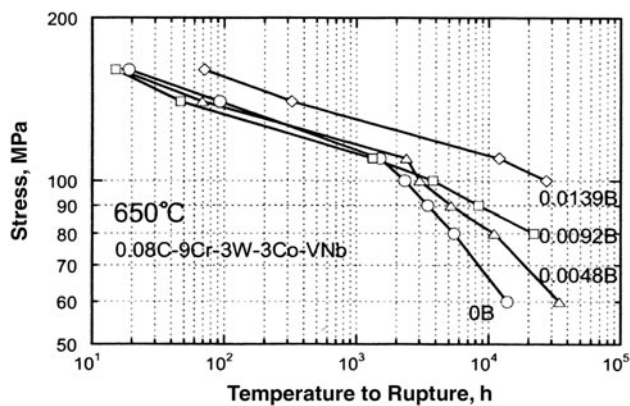
The most comprehensive work on the effect of boron additions to 9 % Cr steels has been carried out in NIMS by Abe [16]. Specifically they showed that improved performance could be achieved by optimising the boron and nitrogen additions in a 9Cr–3W–3Co–0.2V–0.05Nb–0.08C steel. It was claimed that the boron improved the long-term creep rupture strength by reducing the coarsening rate of the $M_{23}C_6$ during creep while the addition of up to about 80 ppm of nitrogen further enhanced creep strength through the formation of fine particles of MX nitrides. At high levels of nitrogen boron nitrides form and this has a deleterious effect on properties by reducing “effective” boron. Creep rupture data at 650 °C for steels containing additions of boron and nitrogen are shown in Fig. 4.

Commercial variants of steels of this type have been produced, viz, MARN, MARBN, and BH and the compositions are shown in Table 8 and stress rupture properties at 650 °C are given in Fig. 5 with data for P92 for comparison [17]. Heat treatment involved normalising in the range 1,050–1,150 °C and tempering between 770 and 800 °C. The steels are currently on trial in Japan prior to Code submission.

While the MARN and MARBN appear promising the available data are fairly short term and early trials have revealed some difficulties in welding with MARBN so that

Table 7 Nominal compositions of martensitic steels for rotor applications

Alloy	Composition in mass%, bal. Fe									
	C	Cr	Mo	W	Co	Ni	V	Nb	N	B ^a
HR1100	0.12	10.2	1.2	0.38	–	0.6	0.17	0.05	0.05	–
HR1200	0.09	11	0.23	2.7	2.5	0.51	0.22	0.07	0.02	180
B	0.18	9	1.5				0.25	0.05	0.02	100
E	0.12	10	1.0	1.0			0.2	0.05	0.05	
F	0.12	10	1.5				0.2	0.05	0.05	
FB2	0.13	9.0	1.5		1.0			0.07	0.02	100

^a ppm**Fig. 4** Effect of boron on the stress rupture performance of a martensitic steel [16]

further development may be necessary. However it is likely that an attempt will be made to commercialise a martensitic steel containing boron. Data for durations up to 70,000 h have been obtained for steel BH developed by Babcock Hitachi in collaboration with Professor Fujita so that this alloy is perhaps the most promising [18].

The other promising development in this area is the 12 % Cr martensitic steel, which turns the presence of “Z” phase to some advantage by forming a fine distribution of particles, which serves as a strengthening addition [19]. The work is at an early stage but laboratory experiments have shown that a fine distribution of Z-phase can be achieved in steels containing 12 % Cr and with additions of either Nb or Ta to produce NbN or TaN, which can be transformed to fine particles of Z-phase. It is important to avoid vanadium additions. Both the steel containing Ta and that containing Nb form fine distributions of Z-phase which persist for thousands of hours of annealing. The distribution is somewhat finer in the alloy with Ta, which also seems to be stronger in preliminary evaluations. An important point here is that the higher Cr content in this alloy will provide greater resistance to steam oxidation than that of the 9 % Cr steels and this would be a major advantage. The work, which has the support of VGB,

represents a novel approach in terms of the strengthening mechanism in 12 % Cr steels.

Other work [20] has focused on the potential to improve the performance of P92 by modifications to heat treatment and by fine tuning the composition with the C:N ratio a critical parameter. This work has shown some promise at least on the basis of relatively short-term stress rupture data.

Although austenitic steels are not popular with designers other than in superheater or reheater pendants for reasons that have been discussed earlier a recent development in this area may prove more attractive. Conventional austenitics tend to be chromia (Cr_2O_3) formers and consequently have limited resistance to oxidation in steam at high temperatures where the chromia can volatilise. By contrast alumina (Al_2O_3) performs well in this type of environment but design of suitable alloys is complicated by the need to balance additions that contribute to creep strength and those that protect against oxidation.

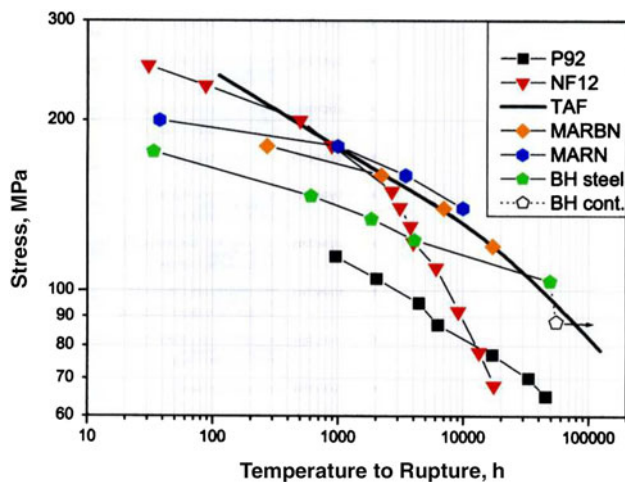
The AFA family of steels has been developed [21] using a combination of thermochemical modeling to establish phase equilibria and microstructural engineering to optimise overall materials performance. The result is a series of alloys with superior oxidation resistance to conventional austenitics in the temperature range 650–900 °C. The compositions of two alloys optimised for oxidation resistance and for high creep strength are given in Table 9.

The results of creep testing are shown in Fig. 6 and it can be seen that both alloys show good creep properties although as anticipated OC5 is somewhat superior at least as far as can be judged from the limited testing carried out so far. Data for alloy 617 and for NF 709 and Tp347 are also shown and it is evident that the AFA alloys are comparable in strength to the conventional austenitics while somewhat weaker than IN617. Clearly these are encouraging results and a preliminary estimate of the likely temperature for a 10^5 h rupture life at 100 MPa is about 660 °C.

An interesting feature is that unpublished measurements indicate that the thermal expansion coefficient for these

Table 8 Nominal compositions of some advanced martensitic steels

Steel	Composition in mass%, bal. Fe								
	C	Cr	Mo	W	Co	V	Nb	N ^a	B ^a
MARBN	0.08	8.9	–	2.85	3	0.2	0.05	80	135
MARN	0.002	9.2	–	2.96	3.09	0.2	0.06	490	70
BH	0.03	9.12	0.15	2.4	1.8	0.2	0.05	500	60

^a ppm**Fig. 5** Stress rupture properties at 650 °C for steels under development [17]

alloys tends to be somewhat lower than for conventional austenitics. However it remains to be seen whether this will be sufficient for alloy steels of this type to be used in the demanding conditions, including cyclic loading and rapid start-up, demanded of modern power plant.

6.3 Steam Turbine Rotors

In this case the effort in Europe has been concentrated on the effects of boron additions to improve the strength of the martensitic steels used for this application [22]. In the production of large forgings the risk of segregation of the boron addition is a concern but steelmaking techniques have been modified to minimise this risk. In the most recent phase of the COST programme the aim was to try to improve on the performance of the alloy FB 2, which had

demonstrated a clear advantage, compared with the earlier steels E and F which were used in applications up to 600 °C. As a first step full-scale rotor forgings were manufactured in the FB2 composition (see Table 7) by the three major forging manufacturers in Europe each of which used a slightly different manufacturing process. The forgings were then evaluated and the results compared with the earlier data obtained from 500 kg experimental heats. It was shown that the results from all three forgings were in close agreement with the data from the experimental heats. In Fig. 7 stress rupture results for the three rotor forgings are shown along with data for the steels E and F and B2 and it is clear that the performance of the three FB2 forgings was similar despite the different processing routes and superior to that of the earlier steels.

Efforts continue to improve the properties further to provide a 650 °C capability and have involved substituting Ta for Nb and altering the boron: nitrogen ratio. Stress rupture data are only available so far to 10,000 h and further evaluation will be necessary. However it is clear that the 10⁵ h stress rupture criterion of 100 MPa at 650 °C will not be readily achieved.

More recently work in Germany [23] has been focused on developing increased strength in 11 % CrWCoMoVB rotor steels by optimising the compositions to give enhanced stress rupture performance. The steels with the highest creep rupture strength had relatively high contents of boron (200 ppm) and carbon (0.2 %) and reduced levels of W and Co and were characterised by fine, slow growing M₂₃C₆ particles. Testing has been carried out to over 40,000 h on experimental heats and the results are encouraging particularly for a relatively high Cr content.

Another approach to bridging the gap between the between the maximum capability of the martensitic steels

Table 9 Nominal compositions of AFA alloys optimised for oxidation resistance (OC4) and for creep strength (OC5)

Alloy	Composition in mass%, bal. Fe												
	C	Mn	Si	Cr	Ni	Mo	Cu	W	V	Ti	Al	Nb	B ^a
OC4	0.1	2	0.14	14	25	2	0.5	1.0	0.04	0.05	3.6	2.5	8
OC5	0.1	2	0.13	14	25	2	0.5	1.0	0.05	0.05	3.0	1.0	78

^a ppm

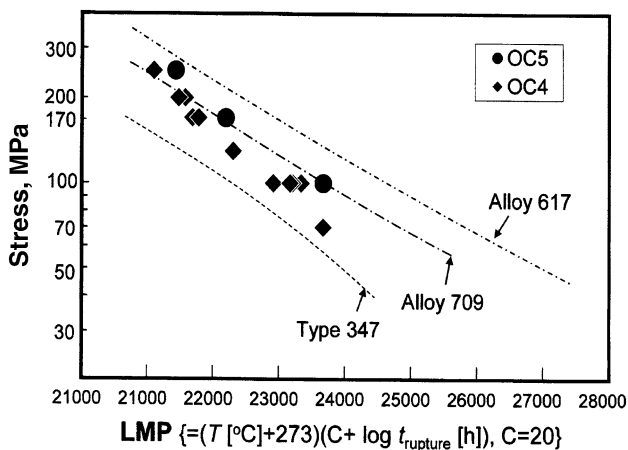


Fig. 6 Stress rupture properties of two AFA alloys with data for conventional austenitics and Alloy 617 for comparison [21]

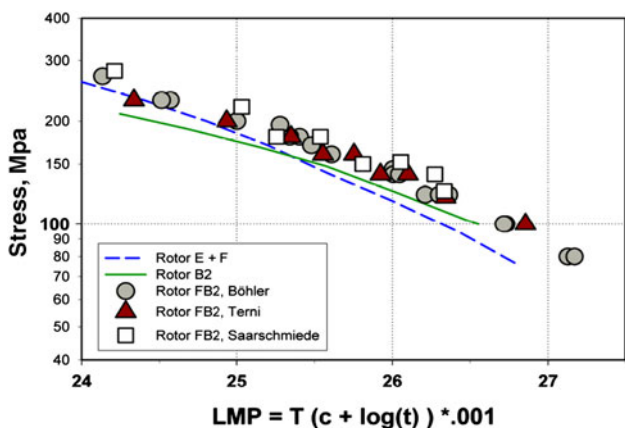


Fig. 7 Creep rupture data for three rotor forgings in alloy FB2 with data for earlier alloys for comparison [22]

and the superalloys for rotor materials has been to develop Fe–Ni–Cr alloys which may be less costly than the Ni–Cr alloys and therefore economically viable at temperatures below 700 °C and some work in this direction has been carried out both in Japan and in China.

Two alloys (neither of which is a steel) with interesting properties will be briefly discussed viz FENIX 700 developed in Japan [24] and GH 2984 developed in China [25] and the compositions are shown in Table 10 along with estimated values of the 10⁵ h stress rupture strength at 700 °C. Both of these steels are currently in the early stages

of development but it is clear that either one would easily meet the strength criterion of 100 MPa at 10⁵ h at 650 °C. The composition of FENIX 700 has been adjusted to give a strong stable alloy with a reduced tendency to segregation, which is an important attribute in the production of large forgings.

A significant point is that these alloys with reduced Ni and no additions of elements such as Co may be less expensive than some alternative alloys and may be viable at lower temperatures. In this context there could be some merit in designing a programme to investigate the potential for the development of a low cost Fe–Ni–Cr alloy, which could be applied in heavy forgings for service at 650 °C. A further point to note is that the availability of welded rotor technology in some of the turbine companies eases somewhat the task of providing an economically attractive solution to high temperature operation.

7 Conclusions

1. There is a significant effort worldwide aimed at the deployment of high efficiency power plant burning pulverised coal to produce electricity at a reasonable cost to the consumer.
2. Despite the investment of significant financial resources in the development and characterisation of advanced materials it is unlikely that an Advanced Ultrasupercritical (A-USC) power plant burning pulverised coal with a main steam temperature of ~700 °C, will be built in Europe or the USA in the near future.
3. The cracking of thick wall components manufactured in a superalloy material during exposure to 700 °C steam in a component test facility represented a serious technical setback and highlighted the risks involved in deploying the first A-USC plant.
4. In order to mitigate some of the risk, financial support from national governments is probably a necessary requirement in order for a demonstrator plant operating with high steam temperatures to be built and this seems unlikely in the current economic climate.
5. The power generation industry has hitherto introduced higher steam temperatures and new materials

Table 10 Nominal compositions and rupture strength of two Ni–Cr–Fe alloys

Alloy	Composition in mass% (bal. Ni)									10 ⁵ h Rupture stress, MPa at 700 °C
	C	Cr	Nb	Fe	Co	W	Mo	Al	Ti	
GH 2984	0.06	19	1.0	33	–	–	2.0	0.4	1.0	125
FENIX700	0.02	16	2.0	38	–	–	–	1.3	–	130

in an incremental fashion to reduce the risks involved and there may be some merit in returning to this approach.

6. Despite the limitations in the performance of the martensitic steels recent developments appear to offer options for modest increases in steam temperature thereby contributing to increased efficiency of power generation and a proportionate reduction in emissions such as CO₂.
7. Specific improvements in the performance of steels for critical components in boilers and turbines may offer a route to an incremental improvement in efficiency with reduced technical risk.
8. Innovative work involving a new approach to the strengthening of martensitic steels is at an early stage but may yield a high strength alloy with good oxidation resistance.
9. Novel austenitic alloys that form alumina as a protective oxide may provide a more attractive alternative to the more traditional chromia forming steels.
10. Current work has provided a useful basis of information from which further developments may be initiated and in particular some effort should be devoted to the development of a low cost Fe–Ni–Cr alloy for service at 650 °C.

References

1. Shingledecker J P, Swindeman R W, Wu Q, Vasudevan V K, in Fourth International Conference on Materials Technology for Fossil Power Plants, Hilton Head Island, South Carolina, (2004). p 1198.
2. Tschaffon H, in 9th Liege Conference: Materials for Advanced Power Engineering, (eds) Lecomte-Beckers J, Centrepois Q, and Kuhn B, (2010) p 20.
3. Bader M, Energy Day 2010, Rome.
4. Fukuda M, Sone H, Saito E, Tanaka Y, Takahashi T, Shibashi A, Iwasaki J, Takano S, Izumi S, Advances in Materials Technology for Fossil Power Plants, in Proceedings of Fifth International Conference, (eds) Viswanathan R, Gandy D, Coleman K, Marco Island Florida (2007).
5. Fukuda M, in 9th Liege Conference: Materials for Advanced Power Engineering, (eds) Lecomte-Beckers J, Centrepois Q, and Kuhn B, (2010) p 5.
6. <http://www.cpecc.net/cpeccinternet/pages/CorrectWeb/cxlm/cxlm.aspx>.
7. Bendick W, Hahn B, Heuser H, Fuchs R, Advances in Materials Technology for Fossil Power Plants, in Proceedings of Fifth International Conference, (eds) Viswanathan R, Gandy D, Coleman K, Marco Island Florida, p 830.
8. Chen Q, Stamatelopolous G-N, Helmrich A, Heinemann J, Maile K, Klenk A, Advances in Materials Technology for Fossil Power Plants, in Proceedings of Fifth International Conference, (eds) Viswanathan R, Gandy D, Coleman K, Marco Island Florida, p 231.
9. Xie X, Chi C, Yu H, Yu Q, Dong J, Zhao S, Advances in Materials Technology for Fossil Power Plants, in Proceedings of Sixth International Conference, (eds) Gandy D, Shingledecker J, Viswanathan R, Santa Fe, New Mexico, (2010), p 30.
10. Masuyama F, in Materials for Advanced Power Engineering, (eds) Lecomte-Beckers J, Carton M, Schubert F, and Ennis P J, Liege (2006), p 175.
11. Sabau A S, Shingledecker J P, Wright I G, Advances in Materials Technology for Fossil Power Plants, in Proceedings of Sixth International Conference, (eds) Gandy D, Shingledecker J, and Viswanathan R, Santa Fe, New Mexico (2010), p 213.
12. Vodarek V and Strang A, in Proceedings of Materials for Advanced Power Engineering 2002, (eds) Lecomte-Beckers J, Carton M, Schubert M, and Ennis P J, Forschungszentrum Julich GmbH, pubs., Liege (2002), p 1223.
13. Semba H, Okada H, Igareashi M, Advances in Materials Technology for Fossil Power Plants, in Proceedings of Fifth International Conference, (eds) Viswanathan R, Gandy D, Coleman K, Marco Island Florida, p 168.
14. Arai M, Doi H, Fukui Y, Azuma T, Fujita T, in Proceedings of Materials for Advanced Power Engineering 2002, (eds) Lecomte-Beckers J, Carton M, Schubert F, and Ennis P J, Forschungszentrum Julich GmbH, pubs., Liege (2002), p 1269.
15. Masuyama F, in Fourth International Conference on Materials Technology for Fossil Power Plants, Hilton Head Island, South Carolina, (2004), p 35.
16. Abe F, Materials for Advanced Power Engineering, (eds) Lecomte-Beckers J, Carton M, Schubert F, and Ennis P J, Liege (2006), p 965.
17. Hald J, in 9th Liege Conference: Materials for Advanced Power Engineering, (eds) Lecomte-Beckers J, Centrepois Q, and Kuhn B, (2010), p 55.
18. Asakura K, Koseki T, Sato T, Arai M, Horiuchi T, Tamura K, Fujita T, *ISIJ Int* **52** (2012) 902.
19. Danielsen H K, and Hald J, in 9th Liege Conference: Materials for Advanced Power Engineering, (eds) Lecomte-Beckers J, Centrepois Q, and Kuhn B, (2010), p 310.
20. Morris P F, Sachadel U A, Clarke P D, in 9th Liege Conference: Materials for Advanced Power Engineering, (eds) Lecomte-Beckers J, Centrepois Q, and Kuhn B, (2010), p 554.
21. Yamamoto Y, Brady M P, Santella M L, Bei H, Maziasz P J, and Pint P J, *Metall Mat Trans A* **42A** (2011) 922931.
22. Kern T-U, Mayer K-H, Donth B, Zeiler G, DiGianfrancesco A, in 9th Liege Conference: Materials for Advanced Power Engineering, (eds) Lecomte-Beckers J, Centrepois Q, and Kuhn B, (2010), p 29.
23. Wang W, Kauffman F, Mayer K-H, Scholz A, Berger C, Maile K, in 9th Liege Conference: Materials for Advanced Power Engineering, (eds) Lecomte-Beckers J, Centrepois Q, and Kuhn B, (2010), p 86.
24. Fukuda M, in 9th Liege Conference: Materials for Advanced Power Engineering, (eds) Lecomte-Beckers J, Centrepois Q, and Kuhn B, (2010), p 5.
25. Jianting G and Xiukui D, *Acta Metall Sinica* **41** (2005) 1221.