# Materials for Ultrasupercritical Coal Power Plants—Turbine Materials: Part II

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The efficiency of conventional boiler/steam turbine fossil power plants is a strong function of the steam temperature and pressure. Research to increase both has been pursued worldwide, since the energy crisis in the 1970s. The need to reduce  $CO_2$  emission has recently provided an additional incentive to increase efficiency. Thus, steam temperatures of the most efficient fossil power plants are now in the 600 °C (1112 °F) range, which represents an increase of about 60 °C (108 °F) in 30 years. It is expected that steam temperatures will rise another 50 to 100 °C (90 to 180 °F) in the next 30 years. The main enabling technology is the development of stronger high-temperature materials, capable of operating under high stresses at ever-increasing temperatures. Recently, the EPRI performed a state-of-the-art review of materials technology for advanced boiler/steam turbine power plants (ultrasupercritical power plants). Results of this review pertaining to boilers are reported in a companion paper in this volume. This paper describes the results relating to steam turbines.

Keywords creep, materials, power plants, supercritical, turbines

# 1. Introduction and Background

The goal of improving the efficiency of pulverized coal power plants has been pursued for many decades. While fuel conservation was the major driver in the past decades, concerns about reducing  $CO_2$  emissions have added further incentives in recent years. Worldwide developments with respect to plant construction have been reviewed in part I of this paper. Development of turbine materials has focused around 31 to 35 MPa (4500 to 5000 psi) and 565 °C (1050 °F), 593 °C (1100 °F), 620 °C (1150 °F), or 650 °C (1200 °F) inlet steam conditions. These developments are described in this paper.

# 2. Candidate Material Selection

The key components of steam turbines around which material development has centered include high pressure (HP)/intermediate pressure (IP) rotors, rotating buckets,<sup>1</sup> bolting, and inner cylinder. These components are exposed to the highest temperature in the turbine and therefore have to meet the most exacting requirements.

Candidate materials for use in steam turbines of advanced supercritical plants are listed in Table 1. The rationale behind these selections on a component-specific basis is described in the following sections.

<sup>1</sup>The terminology of buckets or blades is used by different manufacturers to denote the same components.

### 2.1 HP/IP Rotors

HP/IP rotors are large steel forgings carrying the buckets (blades) and are located in the high pressure or intermediate pressure reheat turbine. They are subject primarily to centrifugal loads during operation at high temperatures and overspeed testing at low temperatures and to thermal stresses during start/ stop transients. The most important material properties for this application are creep strength, low-cycle fatigue strength, and fracture toughness. High creep strength is required to resist deformation and crack initiation in the bore or in the blade attachment areas. The low-cycle fatigue strength is required to prevent cracking from thermal stresses due to cycling. The fracture toughness is needed to contain the possibility of brittle fracture during transient conditions, *i.e.*, startup/shutdown. Ferritic steels are invariably preferred to the austenitic steels to minimize risk of thermal fatigue.

The variety of compositions that have been explored to improve the creep strength are listed in Table 2. The workhorse steel of the industry for conventional power plants operating up to 545 °C  $(1012 \text{ °F})^2$  has been the 1%Cr1%Mo0.25%V steel. At higher temperatures, 12%Cr steels are needed for creep strength as well as for corrosion resistance. The evolution of rotor steels has followed a path very similar to that of the boiler steel, as shown in Fig. 1. The earliest 12%Cr steel was the 12CrMoV steel X21CrMoV 121, capable of operation up to about 560 °C (1040 °F).<sup>[1]</sup> The next stage of development consisted of adding Nb + N or Ta + N or W, resulting in three alternate versions of the 12Cr steel. The Ta + N version was used in Japan; the Nb + N version was used by the General Electric Company; and the W-added steels 12CrMoVW were used by the Westinghouse Electric Corporation in the United States.<sup>[2,3]</sup> This class of steels gave an advantage of another 15 °C (27 °F) over the conventional 12CrMoV steel, but were only successfully exploited up to 565 °C (1050 °F). The Nb and Ta

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<sup>&</sup>lt;sup>2</sup>All temperatures are metal temperatures.

Phase 0	31 MPa (4500 psi) 565/565/565 °C 1050/1050/1050 °F	31 MPa (4500 psi) 593/593/593 °C 1100/1100/1100 °F	31 MPa (4500 psi) 620/620/620 °C 1150/1150/1150 °F	34.5 MPa (5000 psi) 650/650/650 °C 1200/1200/1200 °F
HP/IP rotor	CrMoV AISI 422 SS TOS 101 11Cr1MoVNbN (GE original)	TR1100 X12CrMoVWNbN101-1 TOS107 GE-modified steel	X18CrMoVNbB91 TOS 110 EPDC alloy B TR1200 HB1200	HR1200
Blade	AISI 422 SS 12Cr1Mo1WV (Westinghouse) 11Cr1MoVNbN (GE original)	TOS 202 GE-modified steel	TOS 203 Candidate steel D (EPDC)	M252 Refractalloy 26 Nimonic 90 Juco 718
Bolting	CrMoV AISI 422 SS Refractalloy 26	M252 Refractalloy 26	Nimotic 80 Inco X 750 Refractalloy 26	Nimonic 80 Refractalloy 26
Inner cylinder	CrMo steel (cast)	9%Cr steel cast	Advanced 9–12%Cr steel (cast) Similar to P92, P122, E911 GX12CrMoWNiV NbN 10-1-1	316 austenitic stainless steel
Nozzle box	CrMo steel (cast)	9%Cr steel cast	Advanced 9–12%Cr steel cast Similar to P92, P122, E911 GX12CrMoWNiV NbN 10-1-1	316 austenitic stainless steel

## Table 1 Candidate materials for advanced steam turbines

#### Table 2 Nominal chemical compositions of candidate alloys for high-temperature rotors

Alloy designation	С	Mn	Si	Ni	Cr	Мо	v	Nb	Та	N	w	В	Со	Change	Limiting steam T °C(°F)
$X21CrMoV 121^{[5]}$ (same as alloy $13^{[1]}$ )	0.23	0.55		0.55	11.7	1.0	0.30								560 (1040)
11CrMoV TaN <sup>[1]</sup> (same as alloy 17, <sup>[1]</sup> TOS101)	0.17	0.60		0.35	10.6	1.0	0.22		0.07	0.05					575 (1070)
$GE - Original^{[2,3]}$ (same as alloy 16) <sup>[1]</sup>	0.19	0.50	0.30	0.50	10.5	1.0	0.20	0.08 5		0.06					
11CrMoV NbN (same as alloy 15) <sup>[1]</sup>	0.16	0.62		0.38	11.1	1.0	0.22	0.57		0.05					
Westinghouse <sup>[3]</sup> (same as AISI 422)	0.23	0.80	0.40	0.75	13.0	1.0	0.25				1.0				
10CrMoV NbN (same as TMKI <sup>[6,7,8]</sup> and TR(1100) <sup>[8]</sup>	0.14	0.50	0.05	0.60	10.2	1.5	0.17	0.06		0.04					593 (1100)
TOS 107	0.14			0.7	10.0	1.0	0.2	0.05		0.05	1.0				
X12CrMoWVNbN10-10-1 (COST steel E <sup>[5]</sup> )	0.12	0.4	0.01	0.75	10.5	1.0	0.19	0.05		0.06	1.0				
TMK2 (TR115 0) <sup>[6,7]</sup>	0.13	0.50	0.05	0.70	10.2	0.40	0.17	0.06		0.05	1.8				
X18CrMoVNb B91 <sup>[5,11]</sup> (COST type B) <sup>[5]</sup>	0.18	0.07	0.06	0.12	9.0	1.5	0.25	0.05		0.02		0.10			620 (1150)
TR1200 <sup>[6]</sup>	0.12	0.50	0.05	0.8	11.2	0.3	0.20	0.08		0.06	1.8				
TOS 110 <sup>[4]</sup> (EPDC alloy B) <sup>[14]</sup>	0.11	0.08	0.1	0.20	10.0	0.7	0.20	0.05		0.02	1.8	0.01	3.0		630 (1166)
HR1200 <sup>[9]</sup> (same as FN5) <sup>[5]</sup>	0.10	0.55	0.06	0.50	11.0	0.23	0.22	0.07		0.02	2.7	0.02	2.7		650 (1200)
The designations alloy 13, 15, 16, 17, etc	c. perta	ain to	develo	omenta	l allov	s desc	ribed i	n Ref	1.						

contribute to precipitation strengthening by formation of carbonitrides.

The next major development in the 1980s consisted of adding W to the Nb-N or Ta-N steel to improve the solid solution strength. This resulted in the development of TOS 107 in Japan<sup>[4]</sup> (also referred to as General Electric modified in Ref 3) and X12CrMoVWNbN 101-1 steel (E-type) in Europe under the COST 501 project.<sup>[5]</sup> These alloys increased the permissible operating temperatures to 593 °C (1100 °F). An alternate route of increasing the Mo content to 1.5% from 1% and reducing the carbon content was claimed to have resulted in equivalent

properties at 593 °C (1100 °F), due to solid solution strengthening of Mo and its ability to stabilize  $M_6C$  and  $M_{23}C_6$  carbides.<sup>[6,7,8]</sup> This higher Mo alloy, TMK1 or TR1100, entirely resembles the previous class of steels and the alleged superior properties are inadequately documented.

Further improvements to the X12CrMoVWNbN alloys were made by two routes. In the European COST 501 research, B additions, even in the absence of W, were found to lead to superior creep properties with required creep strength up to 620 °C (1150 °F).<sup>[5]</sup> This alloy was named X18CrMoVNbB91. The Japanese researchers, on the other hand, achieved higher



Fig. 1 Evolution of HP/IP steam turbine rotor alloy showing compositional changes and increasing temperature capability



Fig. 2 Larson-Miller rupture curves for commercial and developmental 12%Cr rotor steels

creep strength by further increasing the W content to 1.8% from 1%, resulting in alloy TMK2 (TR 1150).<sup>[7]</sup>

The next stage of alloy modification involved further increasing the W content from 1.8 to 2.7% and adding 3%Co and 0.01B. This resulted in alloys HR 1200<sup>[9]</sup> and FN5,<sup>[5]</sup> which are potentially capable of operation up to 650 °C. Trial rotors have been made and properties evaluated for all the alloys described above including HR 1200. At the time of this writing, no trial rotor data have been reported for the composition FN5. The limiting temperature for the alloy is generally based on a design criterion of 10<sup>5</sup> h rupture life at 125 MPa. More recently, Fujita has reported on a modified version of HR 1200 with Al content below 20 pm and Ni below 0.1%, which exhibits substantial improvement over the conventional HR 1200.

Stress rupture data representative of each class of steels is presented using the Larson-Miller parametric approach in Fig. 2. CrMoV and X21CrMoV 121 rotors have been in service and considerable long-time data are available. The CrMoV(Ta)NbN type rotors have also been in service since 1973. Toshiba reports introduction of TOS 101 in the year 1973 and nearly 20 rotors are currently in service.<sup>[4]</sup>

With respect to the tungsten-containing CrMoVWNbN steels, TOS 107 was first introduced in service in 1991.<sup>[40]</sup>



Fig. 3 Fracture toughness of turbine rotor steels<sup>[5]</sup>



Fig. 4 Stress rupture properties of candidate superalloys for bucket (based on Ref 15)

Currently, there are about ten rotors in 565 °C steam turbine service.<sup>[4]</sup> About five pilot rotors containing variants of similar steels such as X12CrMoVWNbN1011 have been introduced in service in the late 1990s in Europe.<sup>[5,10]</sup> Creep rupture data up to 80,000 h have been collected. Numerous gas turbine disks of the alloy X12CrMoVWNbN 101 alloy also known as COST 501 E-type alloy have been placed in operation.<sup>[5]</sup>

Trial rotor forging manufacture has been reported on alloy X18CrMoNbB91,<sup>[11]</sup> X12CrMoVWNbN1011,<sup>[10]</sup> TOS 110,<sup>[4]</sup> and HR 1200.<sup>[9]</sup> While Larson-Miller extrapolations suggest that these steels can be used at 620, 630, and 650 °C, respectively, the extent of long-time creep data available is not clear. This is often a problem, because long-time data are not obtained or not published due to commercial reasons and the validity of the parametric extrapolations cannot be independently verified. Furthermore, very few publications report creep rupture ductility values. Susceptibility to notch sensitivity is therefore not clear.

Fracture toughness data on various rotor steels have not

 Table 3 Nominal chemical compositions of candidate alloys for buckets (wt.%)

Alloys	Fe	Ni	Со	Cr	Al	Ti	Мо	W	Nb	В	Zr	С	Mn	Si	Others
M-252		Bal	10.0	20.0	1.0	2.6	10.0			0.005		0.15	0.5	0.5	
Inconel 718	18.5	Bal		18.6	0.4	0.9	3.1	•••	5.0			0.04	0.2	0.3	
Refractaloy 26	16.0	Bal	20.0	18.0	0.2	2.6	3.2	•••				0.03	0.8	1.0	
Nimonic 90		Bal	16.5	19.5	1.45	2.45		•••		0.003	0.06	0.07	0.3	0.3	
HR 1200 (FN5) <sup>[5]</sup> Alloy C <sup>[14]</sup>	Bal	0.5	2.7	11.0			0.23	2.7	0.07	0.02		0.10	0.55	0.06	V 0.22
Alloy D <sup>[14]</sup> (T0S203) <sup>[4]</sup>		0.6	1.0	10.5			0.10	2.5	0.10	0.01		0.11	0.5	0.05	V 0.2 N 0.03 Re 0.2

been reported in detail. It has generally been asserted that the toughness of the new steels is at least as good or better than that of the 1CrMoV steels. An example of the type of comparisons offered is shown in Fig. 3.<sup>[5]</sup> Earlier results published in Ref 12 also confirm that the fracture toughness of the 12Cr steels are invariably better than that of conventional CrMoV steel.

In conventional plants, the steam inlet temperature to the low pressure turbine is currently limited to 360 to 360 °C (680 to 700 °F, primarily for fear of long-term temper embrittlement at higher temperatures). Development of superclean NiCrMoV rotor steels containing very low amounts of As, P, Sb, Sn, Mn, Si, and S in recent years would enable use of crossover temperature up to 427 °C (800 °F). The superclean steels not only have extraordinary resistance to embrittlement, but also have reduced susceptibility to stress corrosion cracking, which is the main problem in the LP turbines.<sup>[13]</sup>

## 2.2 Blade/Bucket Materials

Turbines designed to operate at the advanced steam conditions require advanced blade material for the control stage and first stages of the reheat sections. Type 422 stainless steel has been successfully used up to 550 °C (1025 °F) in the past. Higher-strength alloys are needed at higher temperature applications.

Ferritic 9–12%Cr alloys offer the major advantage that their thermal expansion coefficients closely match those of the 9–12%Cr rotors, so that no design modifications are needed to allow for differential expansion, such as may occur with the use of superalloy buckets. Many of the rotor alloys listed in Table 2 may meet the requirements for the advanced steam conditions, but there is little published data relating to their evaluations for use in blades. Muramatsu has suggested two ferritic alloys, alloy C and alloy D, as candidate steels for use up to 630 °C (1166 °F).<sup>[14]</sup> Alloy C very closely resembles HR 1200 (also FN5 of Ref 5) listed in Table 2. Candidate alloy D contains less Co, but has a rhenium addition of 0.2%. Alloy D is nearly identical with what Toshiba refers to as TOS203.<sup>[4]</sup> The compositions of these ferritic steels are listed in Table 3.

Superalloy materials offer an alternative to the advanced 12Cr material for application to the blades for the control stage and first reheat stages. Although superalloys have been used extensively in gas turbine applications, the adequacy of these alloys for steam turbine application needs to be evaluated.

In the early 1990s, an EPRI project was undertaken to review available data on superalloy materials, and to select the most 
 Table 4 Features and problems of four candidate alloys for blades<sup>[15]</sup>

Alloy	Features and problems							
M-252	Extensive service history as gas turbine buckets							
	Good balance of strength and ductility							
	Lower thermal expansion coefficient							
	No tenon peening experience							
Refractaloy 26	Experiences as advanced steam turbine buckets							
-	Good balance of strength and ductility							
	Tenon peening experience							
Nimonic 90	Good balance of strength and ductility							
	Tenon peening is hopeful (no experience)							
	Notch ductility behavior is not clear							
Inconel 718	Extensive service history as gas turbine parts							
	No tenon peening experience							

promising alloy for application to steam turbine blades.<sup>[15]</sup> Material data and other information obtained was documented to support the selection of the material. A tenon peening procedure was then developed for the selected superalloy.<sup>3</sup>

The first step in the selection process was to investigate the most important material properties for blades designed for application at high temperatures. These properties were creep rupture strength, thermal expansion coefficient, and ductility.

Most of the Ni-based superalloys have creep rupture strengths superior to the 12%Cr alloys. Ideally, the thermal expansion coefficient of the bucket alloy should be the same as that of the 12Cr turbine rotor. However, the thermal expansion coefficients of superalloys are generally greater than that of 12Cr steel. Therefore, as a first-step selection, candidate superalloys were limited to those having thermal expansion coefficients close to that of 12Cr. This criterion limited candidate superalloys to those having mean thermal expansion coefficients less than  $15 \times 10^{-6/\circ}$ C ( $8.3 \times 10^{-6/\circ}$ F), which resulted in a thermal expansion coefficient ratio between the bucket and rotor of less than 1.2.

A total of 16 superalloys were initially identified as potential candidates. The alloys were compared and rated in terms of acceptability on the basis of tensile strength, creep strength,

<sup>&</sup>lt;sup>3</sup>For each row of blades, a circular cover serves as the sealing surface for the radial steam seals and structurally couples the blades together. The tenons, which protrude through holes in the covers, are peened to form heads, serving the function of attaching the blades to the cover.

 Table 5 Chemical composition of superalloy bolt materials in steam turbines<sup>[3]</sup>

	Chemical composition in %												
Alloy	С	Cr	Ni	Со	Мо	Ti	Al	В	Fe				
Incoloy 901(a)	Max 0.10	11-14	40-45	Max. 1.0	5.0-7.0	2.0-3.0	Max 0.35	0.010-0.020	Bal				
Refractaloy 26	Max 0.08	16 - 20	35-39	18 - 22	2.5 - 3.5	2.5 - 3.5	Max 0.25	0.001 - 0.01	Bal				
Inconel X750(a)	Max 0.08	14 - 17	Bal			2.25 - 2.75	0.4 - 1.0	(0.7–1.2Nb)	5-9				
PER 2B(b)	Max 0.15	19-23	Bal	13 - 20		1.6-3	1 - 2	••••	Max 10.0				
Nimonic 80A(c)	Max 0.10	18-21	Bal	Max 2.0		1.8–2.7	1.0 - 1.8	Max 0.008	Max 3.0				

(a) Tradename of INCO Alloys International, Huntington, WV

(b) Tradename of Aubert & Duval

(c) Tradename of Wiggins Alloys

Table 6 Failure of superalloy bolt materials in steam turbines  $[^{3,16]}$ 

Bolt material	Number of units	Number of bolts	Number of failure cases	Percentage of failed bolts
Incoloy 901	49	434	15	14.9
Refractaloy 26	26	$\sim$ 50,000	?	$\sim 0.03$
PER 2B	6	1470	0	0
Nimonic 80A	231	20,291	24	0.37
Inconel X750	3	28	1	3.5

notchbar creep strength, thermal expansion, and peening capability. Based on the comparison, the selection was narrowed to four materials, *i.e.*, M-252, Refractalloy 26, Nimonic 90, and Inconel 718. The composition of these alloys is provided in Table 3. A comparison of the stress rupture properties is shown in Fig. 3.

Alloy M-252 has had considerable favorable gas turbine experience in both manufacture and service exposure, and numerous blade sets have been in satisfactory service for 100,000 h or more. This alloy has a low thermal expansion coefficient and shows a good balance of strength, ductility, and creep rupture strength. However, because there is structurally no requirement for tenon peening in gas turbine designs, there is no experience with peening operations concerning M-252.

Refractalloy 26 shows a good balance between strength and ductility, and good results were obtained in a preliminary test on tenon peening capability. Furthermore, Refractalloy 26 has been applied with good results in steam turbine blades in the research and development of an advanced steam turbine plant in Japan.

Nimonic 90 shows a relatively good balance in the investigated physical and mechanical properties. The manufacturing experience and the tenon peening capability are not clear. However, because the ductility of Nimonic 90 at room temperature is superior to that of Nimonic 80A, which has good tenon peening capability, tenon peening of Nimonic 90 may be successfully accomplished.

Inconel 718 exhibits very high tensile and yield strengths at room temperature, and there remains a high uncertainty concerning its tenon peening capability. Nevertheless, because this alloy has been utilized extensively in gas turbines for a variety of applications, it is difficult to exclude this alloy from the candidate alloys. Table 4 summarizes the features and problems for the application of the four alloys (M-252, Refractalloy 26, Nimonic 90, and Inconel 718) selected above from the total candidate list of 16. These four alloys are potentially suitable for the blade application based upon the above results. Alloys M-252 and Refractalloy 26 are particularly favorable and are the selected candidates for the prime alloy and backup alloy, respectively.

The primary reason for the selection of M-252 as the prime alloy is because of the vast amount of favorable gas turbine experience. Its peening capability, however, was found to be much lower compared to Refractalloy 26. The reasons for the selection of Refractalloy 26 as the backup alloy are as follows: (1) it contains an alloy addition of iron and, therefore, represents an alternate choice to the exclusively nickel-based superalloys; (2) it shows a good balance of material properties; (3) it has a confirmed good peening capability; and (4) although it does not have extensive service history, it has performed well in the steam turbine blades in the research and development of an advanced steam turbine plant in Japan, which operated for about one year at 649 °C (1200 °F).

Refractalloy 26 has been used extensively and successfully in steam turbines for over 30 years. Refractalloy 26 has been used not only for blades, but also for bolts and occasionally for rotors. The excellent properties of this alloy cited by Yamada *et al.*<sup>[15]</sup> and its vast operating experience make it a most desirable high-temperature material.

# 2.3 Bolting Materials

Considerations affecting the selection of high-temperature bolting materials are nearly identical to those applicable to bucket materials. Bolting material must possess high-temperature mechanical strength, creep strength, freedom from notch sensibility, resistance to stress relaxation (*i.e.*, high creep resistance), and a coefficient of thermal expansion compatible with the 9-12%Cr ferritic steel casings. A major design consideration is to ensure that the bolt will remain tight between scheduled outages, ranging from 20,000 to 50,000 h.

In an EPRI-sponsored project, Mayer investigated worldwide experience on steam turbine bolt materials.<sup>[16]</sup> The chemical composition and service experience of four superalloys are shown in Tables 5 and 6. From Table 6, the failure rate of Incoloy 901 seems to be unacceptably high and the experience base with INCO X 750 seems too small. From among the other three promising alloys, Mayer chose Nimonic 80 and Refractalloy 26 for more detailed investigations.<sup>[17]</sup> They concluded that Nimonic 80A with some bolt design modifications was the best course to take. Seth, however, concludes that Refractalloy 26 should be preferred in the light of extensive service experience with the alloy.<sup>[3]</sup>

# 3. Conclusions

- The materials technology needed to construct ultrasupercritical plants with steam temperatures up to 625 °C and pressure up to 34 MPa is mostly available, largely in the form of commercial steels. It is anticipated that the capability to operate at 650 °C can be achieved in the very near future.
- For HP/IP steam turbine rotors, several alloys, TMK1, TR1100, TOS107, and a modified GE alloy, can operate up to 593 °C. Some European alloys and Japanese alloys (TOS110, EPDC alloy B) have been tested as trial rotors and can be used up to 620 °C. For 650 °C application alloys, HR1200 and a European alloy designated FN5 seem to be promising candidates, but have not yet been fully qualified. A low Al, low Ni modified version of HR1200 also seems promising.
- Many of the rotor-type ferritic alloys also appear suitable for control stage blading up to 620 °C. Superalloys M-252 and Refractalloy 26 seem to be the leading candidates for use up to 650 °C.
- For high-temperature bolting, Nimonic 80A and Refractalloy 26 seem to be the most promising.

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