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Development of Low and High Chromium Alloyed Creep Resistance Steels for Power Plants and Related Applications

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Abstract. The development of power plant technology towards larger and more efficient units is linked to the development of Cr alloyed creep resistant steels. These steels that are mainly used in power generating and petrochemical plants, have improved successively by introducing new alloying elements and new microstructures. Around the 1940s, molybdenum was added to low chromium steels such as 2.25 Cr 1Mo to improve their application temperature to about 560 ºC. Niobium that is contained in all the latest high strength steels, which belongs to the group of 9-12% Cr steels, has been one of the most successful new elements. The use of these steels allows the design of power plants with steam temperatures up to 625 °C. Furthermore, ferritic steels are currently under development for steam temperatures of 650°C and more.

Another recent development of the creep strength of creep resistant martensitic steels at higher temperatures was introduced by partial replacement of molybdenum by tungsten such as grade T23, NF616 (T92) and HCM12A (T122). This improvement in creep strength led to the raising of the operating temperatures of power plants using these new grades of steels, resulting in energy savings and reduction of the environmental impact. In addition to high creep strength other material properties are also important, e.g. hardenability, corrosion resistance, and weldability. All product forms of these steel grades such as large forgings and castings are used to build turbines, whereas tubes, pipes, plates and fittings are the typical products for application in pressure vessels, boilers and piping systems.

Keywords: Creep resistant steels, creep strength, oxidation resistance, piping, turbine rotors.

INTRODUCTION

For decades scientific researches into fossil-fired power plants have been carried out through a lot of scientific researches in many countries. These researches have indicated that due to the use of carbon steel as a construction material by the 1920's, the maximum operation limits on steam were at 4 MPa and 370°C. When Mo was added to the steel, the operational conditions were raised to 10 MPa and 480 °C. In the 1940's, the use of Cr-Mo steels allowed operational conditions of 17 MPa and 566°C[1]. Around that time, 2.25Cr-1Mo (T22) and 9Cr-1Mo (T9) steels were introduced for power plant applications, and T22 is still used extensively up to about 538ºC. Over the years, 2.25-3Cr steels with improved properties compared to T22 have been developed. The most recent developments occurred in the 1990s and involved 2.25Cr steels in which the replacement of molybdenum by tungsten was used to develop the steel grade T23 with a nominal composition of (Fe-2.25Cr-1.6W-0.1Mo-0.25V-0.05Nb-0.45Mn-0.20Si-0.003B-0.06C).

Another development was a 2.25Cr-1Mo-0.25V-0.3Si-0.50Mn-0.07Ti-0.005B-0.08C steel (T24) with strength somewhat inferior to that of T23. There has been continued emphasis on higher-operating temperatures for improved efficiency, since increased efficiency generates energy savings and reduces environmental impact. For some applications, this has meant switching to steels with better high temperature performance, such as modified 9Cr-1Mo (T91) developed in the 1970s as an improvement of T9 by the addition of V, Nb, and N to induce the formation of stable carbides, nitrides, and carbonitrides. More recently, steels such as NF616 (T92) and HCM12A (T122) have been developed; these are modifications

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of T91 that involve the replacement of some of the molybdenum by tungsten. For applications at temperatures 600 ºC, the advantages of low-chromium bainitic steels, especially in welding, have made them the continued choice[2].

Table 1 presents an overview on the creep resistant ferritic steels which are used in power plants for tubing and piping. The list of steels can be subdivided into C-Mn steels (No. 1and2), Mo steels (No. 3 and 4), low alloyed Cr-Mo steels (No. 5-9), and 9-12 % Cr steels (No. 10-15). Because of the large number of different steel grades, only a few typical representatives of each group could be included in the Table. The steel grades have been listed according to increasing content of alloying elements where the chemical composition becomes increasingly complex.

As can be seen from Table 1, niobium has been an important element and niobium bearing steels are found in each group. The complexity of chemical composition is reflected by a complexity in microstructure. Different hardening mechanisms have been used to achieve an optimized product. As a result, the creep rupture strength has been raised by a factor of about 10 as shown in Figure 1[3].

The aim of this paper is to overview the historical improvements of the mechanical properties (mainly creep strength) of creep resistant martensitic steels at elevated temperatures and the effect of these developments on the application of these steels in the power and petrochemical plants.

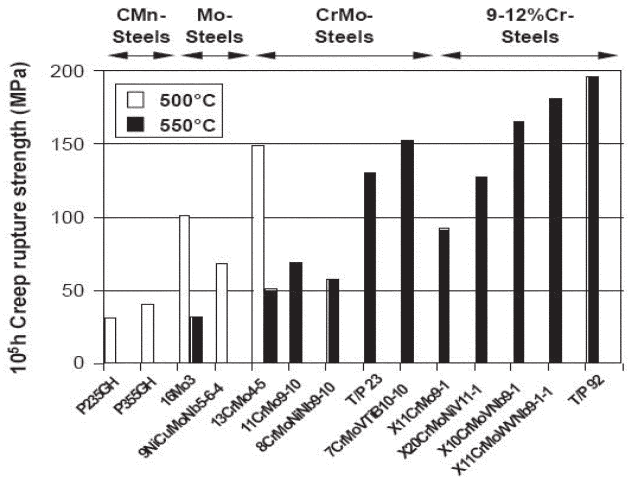

Fig. 1. Creep rupture strength of heat resistant steels for tubes and pipes.

OVERVIEW ON CREEP RESISTANT FERRITIC STEELS

C - Mn Steels

Steel grade P235 can be regarded as typical C-Mn steel having a ferrite pearlite microstructure. C and Mn contents are the major factors influencing the strength properties. Figure 2 shows a plot of the minimum 0.2% proof strength values together with the average 10^5 h creep rupture strength as function of temperature. The European design codes are based on minimum proof strength values at low and creep rupture strength values at high temperatures. Both regimes are separated by

Table1. Chemical composition of Cr-alloyed steels[3].

Steel	Chemical composition (wt. %)									
Designation	C	Si	Mn	Al	Cr	Ni	Mo	V	Nb	B	Others
13CrMo-4-5 (T/P11)	0.1-0.17	0.1-0.35	0.4-0.7	max 0.04	0.7-1.1		0.45-0.65				
11CrMo-9-10 (T/P22)	0.08-0.15	0.15 -0.4	0.3-0.7	max 0.04	2.0-2.5		0.9-1.2				
8CrMoNiNb-9-10	max 0.1	0.15 -0.5	0.4-0.8	max 0.05	2.0-2.5	0.3-0.8	0.9-1.1		min 10×%C		
7CrMoVTiB-10-10 (T/P24)	0.05-0.1	0.15-0.45	0.3-0.7	max 0.02	2.0-2.6		0.9-1.1	0.2-0.3		0.0015 -0.007	0.01N 0.07Ti
7CrWVMoNb-9-6 (T/P23)	0.04-0.1	max 0.5	0.1-0.6	max 0.3	1.9-2.6		0.05-0.3	0.2-0.3	0.02-0.08	0.0005 -0.006	0.03N 1.6W
X11CrMo-9-1 (T/P9)	0.08-0.15	0.25-1.0	0.3-0.6	max 0.04	8.0-10.0		0.9-1.0				
X20CrMoNiV-11-1	0.17-.0.23	0.15-0.5	max 1.0	max 0.04	10.0-12.5	0.3-0.8	0.8-1.2	0.23-0.35			
X10CrMoVNb-9-1 (T/P91)	0.08-0.12	0.2-0.5	0.3-0.6	max 0.04	8.0-9.5	max 0.4	0.85-1.05	0.18-0.25	0.06 -0.1		0.05N
X11CrMoWVNb-9-1-1	0.08-0.13	0.1-0.5	0.3-0.6	max 0.04	8.5-9.5	0.1-0.4	0.9-1.1	0.18-0.25	0.06 -0.1	0.0005 -0.005	0.07N 1.0W

the intersection of the proof strength with the creep rupture strength curve. In the case of P235 the intersection point is around 420°C.

Above this temperature, a design becomes time dependent because the lifetime of a component is limited by the creep process. An interesting modification of P235 is the Nb- bearing grade P355. The proof strength values could be raised considerably as a result of Nb- addition due to grain refinement. However, the increase of creep rupture strength is rather small. This increase can be attributed mainly to the increase of Mn, which is a solution hardening element. Since proof and creep rupture strength have not increased by equal amounts, the intersection point between the creep and proof strength regime is shifted to 400°C. The advantage of P355 clearly lies in the application below this temperature.

Mo Steels

A similar effect can also be seen for the Mo-steels, which are also represented in Figure 2. These steels are basically of the same type with about 0.3% Mo, which is a strong solution hardening element. The solution hardening effect is the main cause for the increase of creep rupture strength, which is similar for both steels. Grade 9NiCuMoNb5-6-4, also well known as WB 36, shows a dramatic increase of proof strength, which again is partly caused by the grain-refining effect of Nb[3]. In addition, hardening by copper precipitation increases the proof strength.

Cr-Mo Steels

It has been found that the strengthening effect of Mo cannot fully be used, since creep ductility strongly decreases with increasing Mo content. Another limitation in the application of Mo-steels is the observed decomposition of iron carbides above 500°C (graphitization). A solution to both problems was the use of chromium as an alloying element in combination with molybdenum. In fact Cr-Mo steels were the first ones that allowed power stations to be operated at steam temperatures above 500°C.

The classical Cr-Mo steels are 13CrMo4-5 (T/P11) and 11CrMo9-10 (T/P22). Their creep rupture strengths are distinctly higher than the simple Mo-steels (Fig. 3), which is mainly a result of higher Mo-content. Cr-Mo steels form chromium carbides which are stable above 500°C. Therefore, graphitization is no longer a problem. Chromium also promotes the use at higher temperatures due to its positive influence on oxidation resistance.

The steels 7CrMoVTiB10-10 (T/P24) and T/P23, also represented in Figure 3, reveal extremely high strength properties. These are newly developed steels on the basis of T/P22. Having a similar microstructure as T/P22, their strengths properties have been raised considerably by additional alloying with Ti, V and B in the case of T/P24 as well as W, V, Nb and B in T/P23[3].

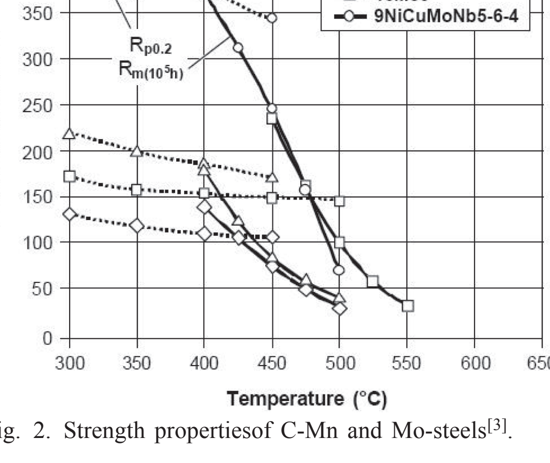

Fig. 2. Strength propertiesof C-Mn and Mo-steels[3].

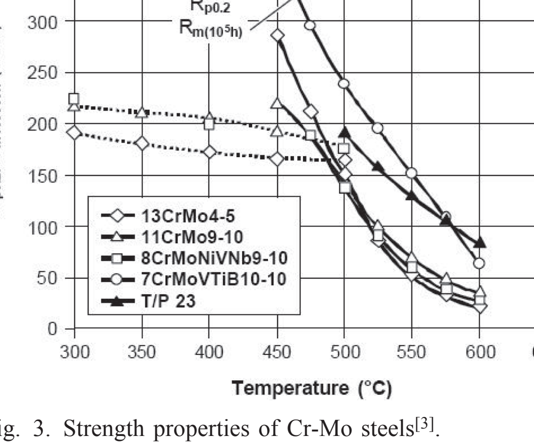

Fig. 3. Strength properties of Cr-Mo steels[3].

9-12 % Cr Steels

The increase of chromium in Cr-Mo steels above 7 % leads to a group of steels which have a martensitic microstructure as a common feature. This microstructure introduces a new element of structural hardening. It is characterized by a high dislocation density and a fine martensite lath structure which is stabilized by $M_{23}C_6$ precipitates. Thus structural hardening is responsible for the large increase in strength of X11CrMo9-1, as compared to 11CrMo9-10 (Fig. 4). Further improvements of the creep strength have been achieved by alloying with V, Nb, W and B.

The introduction of X20CrMoNiV11-1 at the beginning of the sixties has been a major step to increase power plant efficiency. Its creep rupture strength at a temperature of 540°C is nearly twice that of the low-alloy ferritic steels available at that time (*e.g.* 10CrMo9-10 with 10^5 h- creep rupture strength of 78 MPa compared to 147 MPa for X20CrMoNiV11-1). Transformation behavior and microstructure is comparable to X11CrMo9-1. The higher creep rupture strength of X20CrMoNiV11-1 is mainly caused by the higher amount of $M_{23}C_6$ carbides as result of high carbon content.

After a period of standstill, the material development was reactivated by work carried out in the USA and Japan in the mid seventies. The prototype of the new steels from this development work is the modified 9% Cr steel T/P91 (EN designation: X10CrMoVNb9-1) invented in the USA. Meanwhile, this steel is well known and applied in power plants all over the world. It is used in new plants as well as in refurbishment work of high pressure/high temperature piping systems.

Although the carbon content is lower, the creep rupture strength of T/P91 is distinctly higher than that of X20CrMoNiV11-1. This has been achieved by alloying with V and Nb. T/P91 uses the precipitation of finely dispersed Nb/V carbonitrides of type MX as an additional strengthening effect. It was essential to balance the composition because an optimum

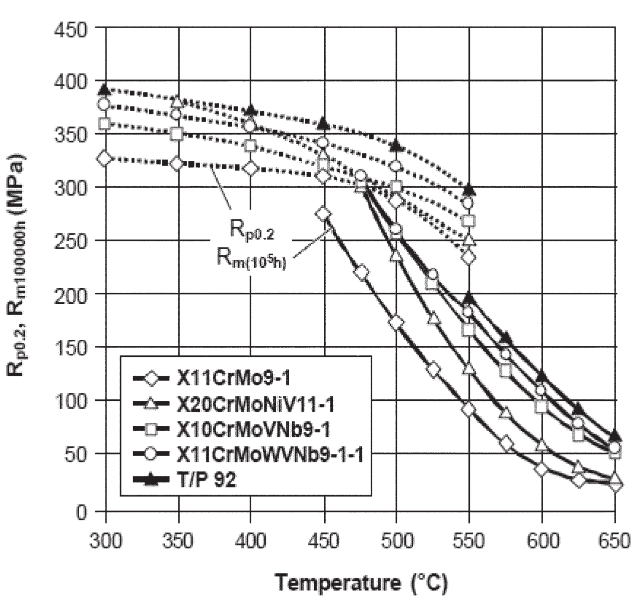

Fig. 4. Strength properties of 9-12% Cr- steels[3].

dispersion and particle size of MX can only be achieved by an optimized Nb/V-ratio and N content. Subsequently new steel grades have been developed on the basis of T/P91 such as X11CrMoWVNb9-1-1 (T/P911), T/P92 and T/P122. These steel grades represent the current state of development for creep resistant ferritic steels[3].

STEELS FOR PIPING AND TUBING APPLICATIONS

Low Alloyed Cr-Steels

Low-alloy ferritic 2.25Cr-1Mo steel and its recent modified grades are used extensively as structural material in the steam-generating systems of power plants and petrochemical industries. Service conditions in these plants demand the use of a various materials in different sections of components. A modification of this type (2.25%Cr-Nb-V contained W) is also introduced for similar applications due to its improved tensile properties at elevated temperatures to a level equivalent to those of 9Cr-1Mo-Nb-V steels. A unique chemical composition patent for this steel was obtained in the 1980s by JFE Steel Corporation and has realized the follow-ing advantages:

(1) Low C and N contents result in good weldability.

(2) Preheating and post weld heat treatment are unnecessary.

(3) The crack resistance of the heat affected zone (HAZ) was improved.

(4) The low Al content, which was reduced to the mini-mum possible limit, results in good creep properties[4].

The modified steel grade (3Cr-3WVTa) was also developed for elevated-temperature service in the power-generation and petrochemical industries. Creep-rupture strength of this new steel at 600 ºC exceeded those of the two advanced commercial 2.25Cr steels T23 (Fe-2.25Cr-1.6W-0.25V-0.05Nb-0.07C) and T24 (Fe-2.25Cr-1.0Mo-0.25V-0.07Ti-0.005B-0.07C) as it is shown in Figure 5. Moreover, the strength of 3Cr-3WVTa approached that of modified 9Cr-1Mo (T91) at 650 ºC. Elevated-temperature strength in this new steel is obtained from a bainitic microstructure with a high density number of fine needle-like MX precipitates in the matrix.

The presence of tantalum promotes a finer MX precipitate in the 3Cr-3WVTa than in the 3Cr-3WV

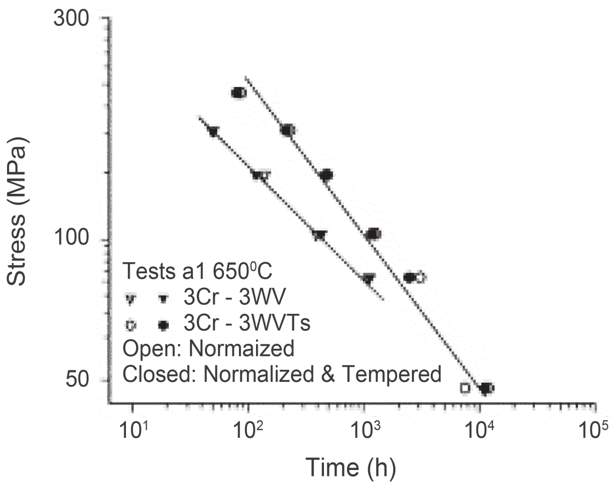

Fig. 5. Creep-rupture curves for 3Cr-3WV and 3Cr-3WVTa at 650ºC[2].

(Figs. 6a and 6b), and it suppresses the coarsening of these fine precipitates during creep.

At Oak Ridge National Laboratory (ORNL), reduced-activation bainitic steels with a base composition of nominally Fe-2.25Cr-2W-0.25V-0.1C (2.25Cr-2WV) were developed. This base composition with H" 0.1% Ta (2.25Cr-2WVTa) showed improved strength relative to even some 9Cr steels, but it suffered from inferior toughness. Prior to work on reduced-activation steels, work at ORNL demonstrated that quenched-and-tempered plates of a Fe-3Cr-1.5Mo-0.25V-0.1C steel had, unexpectedly, better toughness than normalized (air-cooled)-and-tempered plates[2].

P91 Steel

In the 1970s, there was considerable interest in the 9 % Cr steels for components of the fast breeder nuclear reactor. On the basis of the familiar Fe9Cr1Mo steel used since the 1950s in petrochemical plant, improved steel was developed by the Oak Ridge National Laboratory and subsequently incorporated into the ASTM specifications under the designation P91. A remarkable increase in the stress rupture strength was achieved by the addition of 0.2 % V, 0.06 % Nb and 0.05 % N[5]. The heat resistant martensitic steel P91 is being utilized in conventional power plants for piping systems with operating temperatures of 560 – 600ºC and high pressures in the range of 270 bars. These high operating temperatures and pressures require high quality welds to ensure safety of equipment and personnel[6] .

In the early 1980's, tubing of 9Cr-1Mo-V (P91) steel was introduced into the superheaters of power boilers. Because P91 steel is an air-hardenable martensitic high-strength alloy, the specifications of preheating and post weld heat treating conditions are critically important. However, maintaining preheat temperature before post weld heat treatment is essential for minimizing the probability of hydrogen cracking in weld heat-affected zones[7].

P92 Steel

P92 is a development of the now well established steel grade P91, which is modified by reducing the Mo content to about 0.5 % (In order to avoid the formation of delta-ferrite in the microstructure), and adding about 1.7% W plus a few parts per million of B. Controlled microalloying in the form of Nb, V and N is retained. This composition modification gives rise to very stable carbides and carbo-nitrides which improve long term creep strength. This steel is designed to operate at temperatures up to 625°C and it is claimed that high temperature rupture strengths are up to 30 % greater than for P91. For example at 600 °C the 100,000 hour creep rupture strength of P91 base material is about 95 MPa whereas P92 is about 123 MPa. Exploitation of P92 is relatively limited and further confidence and experience in the fabrication and use of the alloy still has to be

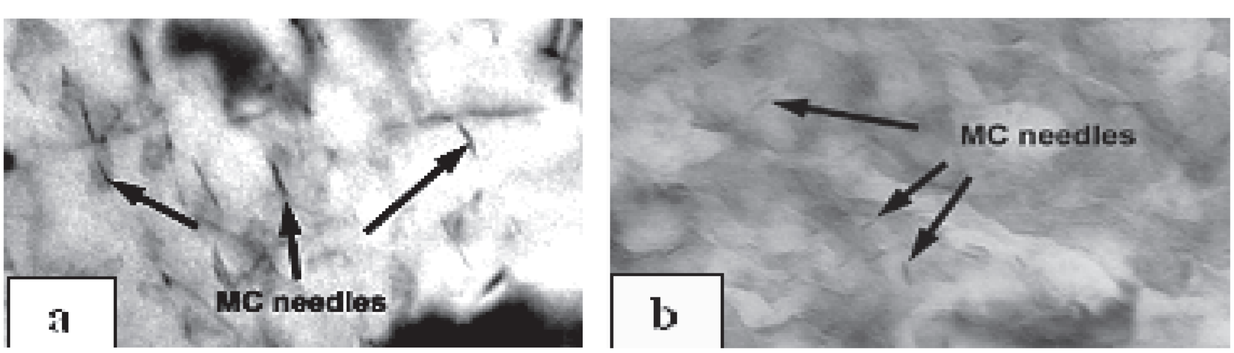

Fig. 6. Ultra-fine precipitate needles in the matrix of(a) 3Cr-3WV and (b) 3Cr-3WVTa steels[2].

developed. However, a number of installations were completed in the late 1990s and more are under construction or being planned[8]. Figure 7 shows the TEM micrographs of austenitised and tempered P92 steel.

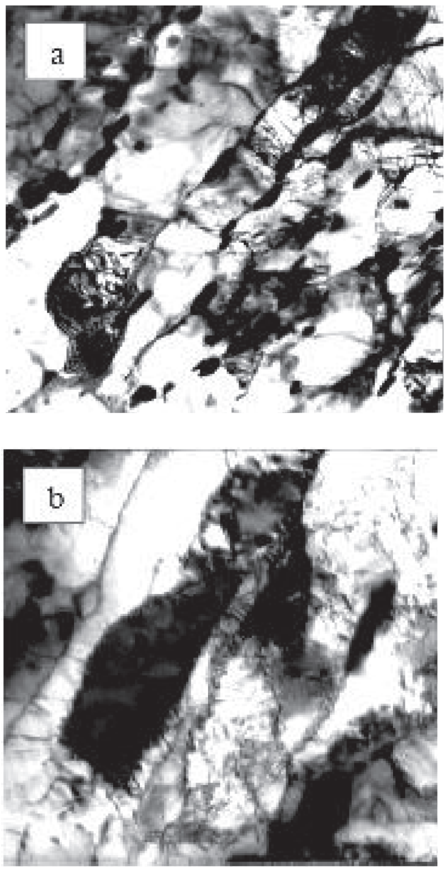

Fig. 7. TEM micrographs of P92 austenitised for 2 h at (a) 970 °C, (b) 1145 °C, followed by tempering for 2 h / 775 °C[5].

E911 Steel

E911 steel (X11CrMoWVNb9-1-1) has been developed by the work carried out in Europe as part of the COST 501 WP11 project, entitled "Advanced Materials for Power Engineering Components - High Efficiency, Low Emission Systems". Its chemical composition is essentially the same as the P91, except it contains 1 % W additionally and also some B. The benefit of B is believed to decrease the coarsening rate of carbides. E911 and P92 are intended for use in main steam lines. E911 and P92 differ only in their Mo and W contents, while the molybdenum equivalent (Mo + 1/2 W) of both steels is nearly the same. The Continuous Cooling Transformation (CCT) diagram of E911, shown in Figure 8 is essentially the same as that of P91 and P92. The M_S and A_{C1b} temperatures as well as martensite hardness are more or less the same for the three steels, and also the location of the ferrite-carbide transformation nose is comparable to that of P91 steel grade[3].

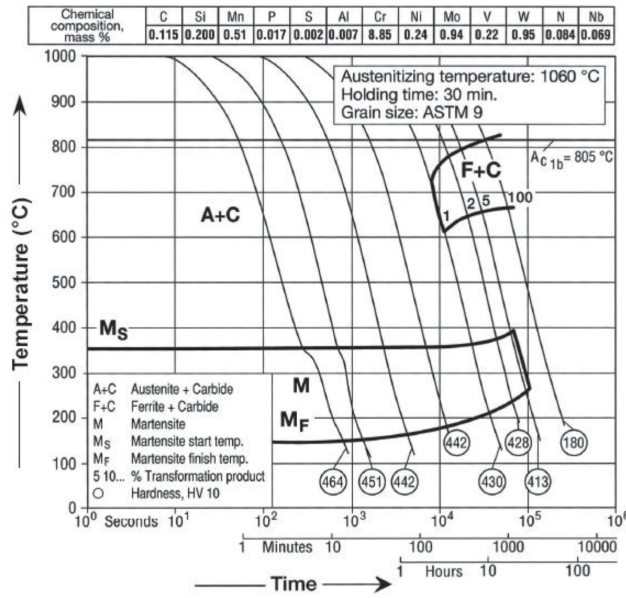

Fig. 8. The CCT-diagram for X11CrMoWVNb9-1 (T/P911)[3].

The optimization of the E911 composition has improved the creep properties at 600 ºC and 625 ºC; however, the most important improvements are to the oxidation performance. At temperatures above approximately 600ºC, it is not the creep strength that limits the high temperature operation of 9 % Cr materials such as E911, but the oxidation rate [9]. The tensile properties of P911 are improved compared with the well established steel P91 as it is indicated in Figure 9[10].

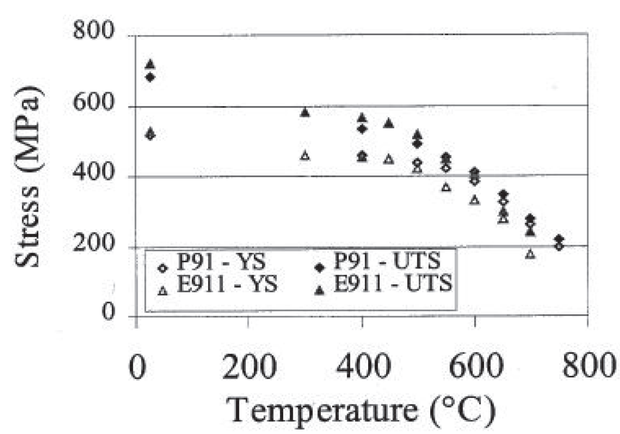

Fig. 9. Comparison of tensile properties versus temperature of the P91 and E911 steel-pipes[10].

Comparison of the Microstructure of P91, P92 and E911 Steels

Ennis and his co-author[5] carried out an experimental work in which a standard heat treatment for three investigated steels (given in Table 2). They found that the three steels exhibited similar microstructures, as shown in Figure 10. Austenitizing produced a martensitic structure with a high dislocation density within the martensite laths. During tempering recovery caused the formation of sub-grains and dislocation networks.

The creep strength of 9-12 % Cr steels, is correlated inversely with the martensite lath width and therefore with the sub-grain size. Measurements of the average sub-grain width and of the dislocation density within the subgrains, performed by means of quantitative TEM, are presented in Table 3.

Table 2. Standard heat treatment of P91, P92 and E911 steels[5].

P91 Steel	P92 Steel	P911 Steel
1h/1050 °C + 1h/750 °C, air cooled	2h/1070 °C + 2h/775 °C, air cooled	1h/1050 °C + 1h/750 °C, air cooled

Table 3. Dislocation density and mean sub-grain size as received of P91, P92, E911 steels[5].

Steel	Dislocation density $\times 10^{-14}$, m^{-2}	Mean sub grain size, µm
P91	7.5 ± 0.8	0.4 ± 0.06
P92	7.9 ± 0.8	0.4 ± 0.09
E911	6.5 ± 0.6	0.5 ± 0.05

It can be seen that sub-grain size is fairly similar in all investigated steels. The small differences can be attributed to the different prior austenite grain size. Dislocation densities in P91 and P92 steels were similar and little higher than in E911 steel.

Besides recovery processes the precipitation of carbides, carbonitrides and nitrides occurred during tempering of the three steels examined by Ennis and his co-author. They also observed that $M_{23}C_6$ carbides containing Cr, Fe, Mo and W, precipitated preferentially on the prior austenite grain boundaries and on the martensite lath boundaries. These precipitates retard the sub-graingrowth and therefore increase the strength of the materials.

Comparison of the Rupture Strengths of P91, P92 and E911 Steels

From Figure 11, it is clear that the stress rupture strengths of the currently used and the new power station steels are compared on the basis of the maximum service temperature for 10^5 h stress rupture strength of 100 MPa. It may be seen that the maximum service temperature increases with increasing complexity of the steel composition, and the more highly alloyed steels have sufficient stress rupture strength to be considered for application at temperatures in excess of 600°C.

Figure12 shows the secondary creep rates of P91, P92 and E911 at 600 and 650°C plotted against the applied stress. Data taken from the published literature for the same heat are included where available. It can be seen that at high stresses the differences in the secondary creep rates of the three steels are relatively small. In the low stress region, however, the differences between the steels become more pronounced.

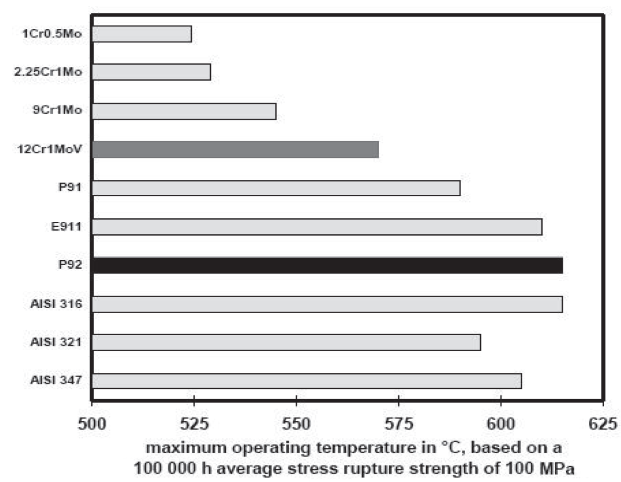

Fig. 11. Stress rupture strengths of the currently usedand newly developed power station steels[5].

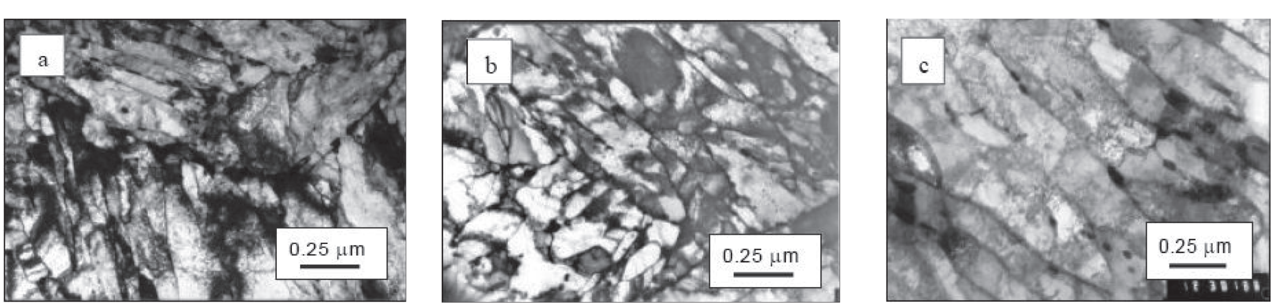

Fig. 10. TEM Micrographs of the as received steels (a) P91, (b) P92 and (c) E911, showing the elongated sub-grains of tempered martensite[5].

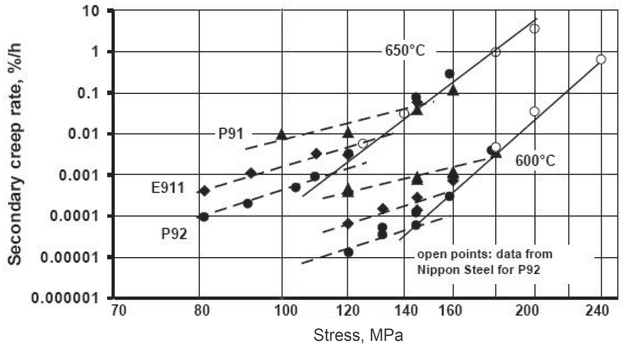

Fig. 12. Secondary creep rates for P91, P92 and E911[5].

The Role of Stress on the Creep Rupture Strength of 9-12 % Cr Steels

The creep deformation characteristics may be described by the Norton equation (minimum creep rate is proportional to the applied stress to the power n) with two different values for the Norton stress exponent n.

$$\dot{\varepsilon} = K \sigma^n$$

Where K and n are experimentally derived material constants.

At high stresses, the value of n is around 16 while at lower stresses, the data conform to an n value of 6. The change in n is indicative of a change in the creep characteristics. Figure 12 also shows that at high stresses the differences in the secondary creep rates of the three steels were relatively small and the high dislocation densities resulting from the martensite transformation dominate the deformation.

In the low stress region, however, the differences between the steels became more pronounced. The results of long-term (200000 h) creep rupture strength of different 9-11 % Cr steels are shown in Figure 13. It can be observed that at the usual levels of service temperatures, the relative improvement from X20 to P91 is roughly similar to the improvement observed for the traditional low-alloy steels (10CrMo9-10 and 14MoV6-3) to X20. However, the relative improvement from P91 to newer steels (E911 and P92) is less impressive. Particularly,a small difference seems to now exist between P91 and E911[11]. From the above equation, the time to rupture for the steels exposed to elevated temperatures decreases with the increasing of the applied steel, as shown in Figure 14[12].

NF616 Steel

The use of NF616 (P92), for example, may allow about 35 % increase in the allowable stress at 600°C. This in turn permits a decrease in section thickness (Fig.15), and thereby a reduction in weight, as well as lower welding costs. Consequently, the through-wall temperature gradients will be reduced resulting in a reduction in the thermal fatigue loading experienced[13]. This type of steel has been developed and shown to be capable of operation up to 620 °C[14].

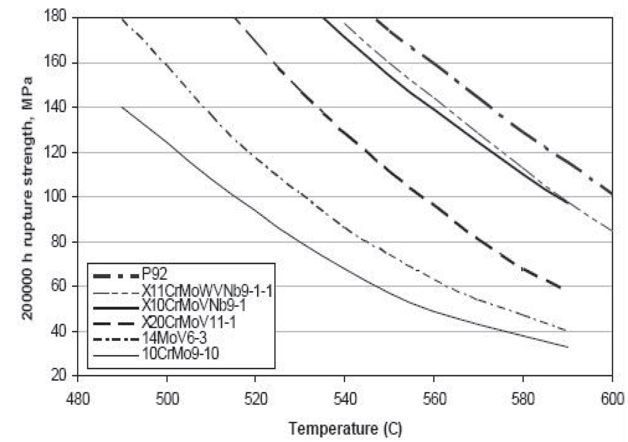

Fig. 13. Comparison of the 200,000 h creep rupture strength of selected 9-11 % Cr steels and the low-alloy steels 14MoV6-3 and 10 CrMo9-10 according to EN 10216-2 and ECCC data sheets[11].

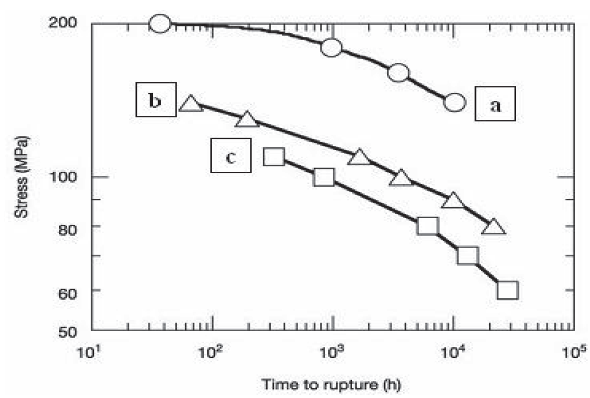

Fig. 14. The stress-time to rupture relationship for (a) New 9% Cr nanostructure carbonitride dispersion steel, (b) P92 steel grade and (c) P91 steel[12].

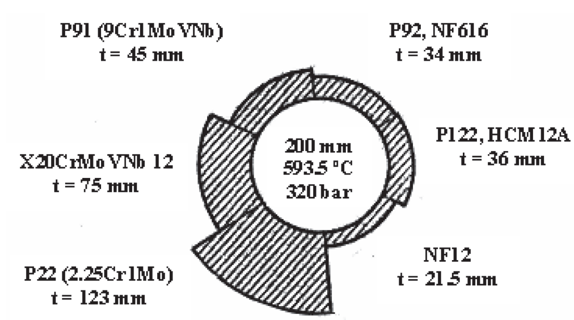

Fig. 15. Variation in wall thickness (t) with material grade (with an internal diameter of 200 mm) for service at 593.3 °C and 320 bar [13].

P122 Steel

In recent years, several new high creep strength ferritic steels have been developed for boiler pressure parts, with 11Cr–0.4Mo–2W–V–Nb–Cu steel (P122) having excellent corrosion resistance and approximately 1.3 times higher creep strength than Modified 9Cr–1Mo steel (P91). This steel has already been used for main steam pipes, high-temperature reheats pipes and headers, as well as SH/RH tubes in modern large capacity fossil power plants.

This steel consists of a tempered martensitic structure that is the same as for P91. The microstructure of the heat affected zone (HAZ) in welds is quite complicated because of the transformation and recovery caused by repeated heat cycles through welding processes[15]. It is well known that welds are weaker in creep strength than base metal under higher temperature and lower stress conditions. Welds usually fracture at the intercritical HAZ adjacent to base metal, known as type IV failure, although the failure mechanism has yet to be elucidated. This type of failure is indicated in Figure 16.

For P122, the chromium content has been raised to about 12 % in order to improve the oxidation resistance. The increased chromium content influences the phase stability and therefore 0.9 % Cu was added to obtain on fully martensitic microstructure. This is because P122 type of ferritic steel is preferred boiler material owing to its higher oxidation resistance. The disadvantages of P122 are mainly found in the area of fabricability. This can be attributed mainly to the high copper content. Low A_{C1} temperature entails longer tempering times at lower temperatures when the steel has to be tempered after hot working and welding[3].

Fig. 16. Microstructure of creep damaged HAZ observed by replica[15].

Reduced Activation (RA) Steels

For martensitic/ferritic steels, the main alloying elements such as molybdenum, niobium and nickel present in ordinary commercial steels are substituted by elements such as tungsten, vanadium and tantalum. These elements have a similar influence on the processing and the structure, but exhibit a lower radiological impact. The development process for the RA alloys can benefit from the many years of experience on power plant materials even though the use of boron or cobalt is not permitted in fusion reactors. The used design procedure is based essentially on the following rules and assumptions:

1. B, Co, Nb and Mo which are present in conventional creep-resistant steels are eliminated.
2. The amount of W is increased as much as possible for solid solution strengthening.
3. The creep resistance of martensitic steels is enhanced by a fine dispersion of non-shearable particles which are resistant to coarsening. V nitrides are good in this context.
4. A fine dispersion of V nitride particles can only be achieved if they all dissolve at the austenitization temperature, which in the industrial context must be 1200 °C or lower.
5. The balance between austenite and ferrite stabilizing elements has to be controlled to avoid the formation of ä ferrite at the solutionizing temperature 1200°C-1250°C. With these criteria, the list of solutes permitted becomes limited to the following elements: Cr, W, V, Ni, Si, Mn, N and C[16]. Table 4 shows the nominal composition of reduced-activation steels in Japan, Europe and USA[17].

T23 and T24 Steels

As shown in Figure 17, the new steels T23 and

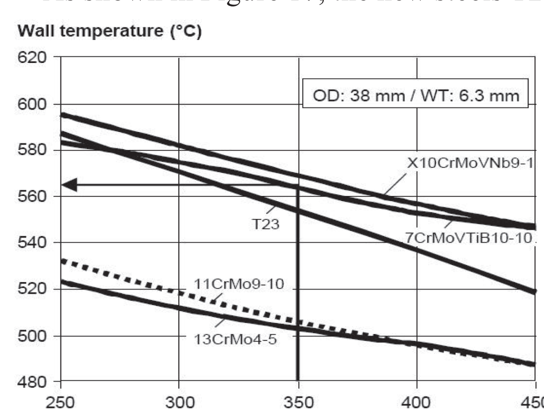

Fig. 17. Allowable temperaturesfor different waterwall materials[3].

7CrMoVTiB10-10 (T24) allow high enough wall temperatures. The steels have been developed in Japan (T23) and Germany (T24). They are both based on 11CrMo9-10. Thanks to their lower carbon content where the maximum hardness at the HAZ lies at 350-360 HV10. The steels are micro-alloyed with V, Nb, Ti and B to achieve high creep rupture strength (see Figure 3). T23 also contains W, while its Mo content is considerably reduced (see Table I). The applied hardening mechanisms are basically the same as have been used for the new 9-12 % Cr steels.

Due to their origin, however, most of the other properties of T23 and T24 are similar to T22 (11CrMo9-10). They belong to the group of Cr-Mo steels with a predominantly bainitic microstructure. As an example, Figure 18 shows the transformation behavior of T24. The main difference to the transformation behavior of T22 is the retardation of ferrite formation, which is caused by the micro-alloying additions. Because of high cooling rate, the thin-wall tubes used as membrane walls exhibit a bainitic martensitic structure. Both steels are used in a normalized and tempered condition[3].

STEELS FOR STEAM TURBINES

Steels for Rotors, Discs and Blades

The most commonly used alloys for steam turbine rotors and/or discs are the CrMoVWNbN steels, which can vary in chromium content from 1 to 13 % depending on the preference of individual manufacturers. These alloys (Table 5) are widely used up to a temperature limit of about 566°C. However, the higher-W, lower-Nb and C versions are capable to be used up to 593°C. The issues for alloys for higher-temperature use are similar to those for materials of steam piping. Versions of these ferritic steels, based on the advanced 9-12% Cr compositions, are already in service at steam temperatures of 600°C, and it is expected to be usable to approximately 620°C (and possibly 650°C). The main manufacturing concern is how rotors, discs and other large castings and forgings components can be made. Very large rotors now can be produced, but experience is related mostly to Cr-Mo-V alloys (used in current 541-566°C plants), and for 12 Cr alloys (needed for advanced steam cycles to 620°C)[18].

For turbine blades, the steel grade 422 which is a

Table 4. Nominal composition of reduced-activation steels (wt %)[17].

Program	Steel	C	Si	Mn	Cr	W	V	Ta	N	B	Others
Japan	F82H	0.1	0.2	0.5	8.0	2.0	0.2	0.04	<0.01	0.003	-
	JLF-1	0.1	0.08	0.45	9.0	2.0	0.2	0.07	0.05	-	-
Europe	OPTIFER Ia	0.1	0.06	0.5	9.3	1.0	0.25	0.07	0.015	0.006	-
	OPTIFER II	0.125	0.04	0.5	9.4	-	0.25	-	0.015	0.006	1.1 Ge
	EUROFER	0.11	0.05	0.5	8.5	1.0	0.25	0.08	0.03	0.005	
USA	ORNL 9Cr2WVTa	0.1	0.3	0.4	9.0	2.0	0.25	0.07	-	-	-

Table 5. Samples of rotor steels[20].

Rotor type	Steel grade	$R_{p0.2}$ (N/mm^2)	R_m (N/mm^2)	A_5 (%)	Impact Energy at 20 °C (J)	Service Temperature (°C)
HP, IP	30CrMoNiV 5 11 21CrMoNiV 5 9	≥550	≤850	15	≥24	≤560
	X22CrMoV 12 1	≥590	≤930	13	≥24	≤600
	X12CrMoWVNbN 10 1 1	≥700	≤1000	13	≥24	≤630
HP-LP	23CrMoNiWV 8 8	≥550	≤850	13	≥80	≤530
S-Rotor	26NiCrMoV 10 10	≥580	≤820	16	≥100	≤350
LP, Ge	26NiCrMoV 11 5	≥610 / ≥650	≤850 / ≤900	15	≥100	≤350
	26NiCrMoV 14 5	≥705	≤980	15	≥100	≤350
LP Disk	26NiCrMoV 14 5	≥750 / ≥820	≤970	15	≥100	≤350

HP = High pressure IP = Intermediate pressure LP = Low pressure S = Saturated steam
Ge = Generator $R_{p0.2}$ = Yield strength R_m = Tensile strength A_5 = Elongation

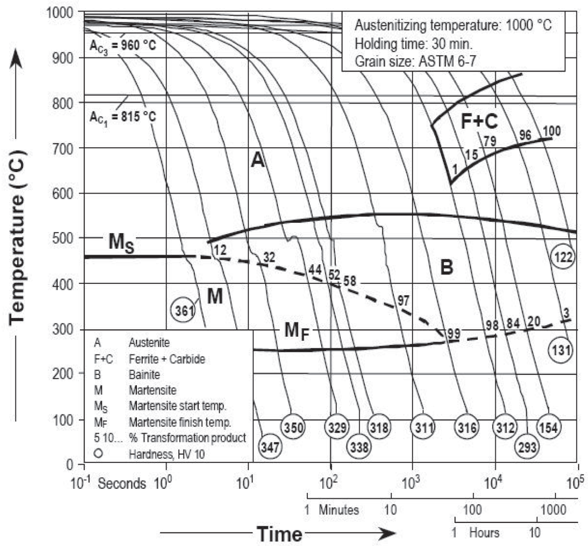

Fig. 18. The CCT diagram for7CrMoVTiB10-10 (T/P24)[3].

modified AISI 420 martensitic stainless steel with Mo and W additions is designed for service temperatures up to 650°C with a satisfactory combination of strength and toughness. This steel can also be used for high-strength fasteners, valves, as well as structural components for aircraft applications. Turbine blades made of martensitic stainless steels, *e.g.* 403 and 422 stainless steels, are used frequently in modern fossil power plants. Type 422 can be heat treated to obtain a wide range of mechanical properties to meet the requirements of a specific application[19].

Steels of Casings/Shells

The casings of steam turbines are typically large structures with complex shapes that must provide the pressure containment for the steam turbine. Depending on the design of the turbine, an inner casing or cylinder may be employed to enclose the hot gas path, so that the main steam from the steam generator first flows into the steam chest, through the inner cylinder, over the vanes and blades, and then returns through the annulus between the inner cylinder and the outer casing before being sent to the reheater.

Because of the size of these components, their cost has a strong impact on the overall cost of the turbine. The materials used currently for inner and outer casings are the 1-2CrMo steels, usually as castings products. The temperature limit of these alloys in this application is approximately 566°C, and is set by their resistance to oxidation in steam. For higher temperatures, cast 9CrMoVNb alloys are considered to be adequate in terms of strength capabilities to 593°C, while the 12Cr steels in either cast or forged form currently appear to be limited to 620 °C, assuming that their steam oxidation resistance is acceptable[18].

STEELS FOR WATER WALLS AND BOILER TUBES/PIPES

Bainitic-ferritic steels, such as 10CrMo4-5 (T12) and 11CrMo9-10 (T22), which have been used so far, do not have adequate creep rupture strengths for use in water walls under the conditions of advanced power plants (Figure 17). From the viewpoint of creep strength T91 (X10CrMoVNb9-1) seems to be a suitable solution. As a requirement of manufacturing, water walls cannot be subjected to a post-weld heat treatment after welding. However, martensitic 9-12% Cr steels attain a maximum hardness between 450 HV_{10} (*e.g.* T91) and 650 HV_{10} (*e.g.* X20CrMoNiV11-1) in the as-welded HAZ, depending mainly upon the carbon content. A reduction of carbon content in these steels is only possible to a limited extent for reasons of microstructural stability. Such high hardness levels are not acceptable, mainly because of the risk of stress corrosion cracking. Therefore, the high strength 9-12% Cr steels are not suitable for use in waterwalls. The aspect of hardness had to be taken into account when developing new steels. As shown in Figure 17, the new steels 7CrWVMoNb9-6 (T23) and 7CrMoVTiB10-10 (T24) allow high enough wall temperatures. Thanks to their lower carbon content, that makes the maximum hardness in the HAZ of their weld joints lies at 350- 360 HV_{10}.

Outside of Europe, T23 is used as tube material for reheaters and superheaters. Due to the low chromium content, however, this application is limited by oxidation and flue gas corrosion. The steel grade 7CrMoVTiB10-10 (T24) could be an interesting alternative to P91 for use in conventional plants with steam temperatures up to about 545°C. With increasing steam temperature the lifetime of components will not only be limited by creep strength but also by oxidation and high temperature corrosion. Service tests have shown that the newly developed steels T/P911 and T/P92 are not suitable for use as boiler tubes with a steam temperature of 600°C. In general 9 % Cr steels have a distinctly lower oxidation resistance than 12 % Cr steels, like X20CrMoNiV11-1. The difference becomes most severe at temperatures above 600°C. Figure 19 illustrates the

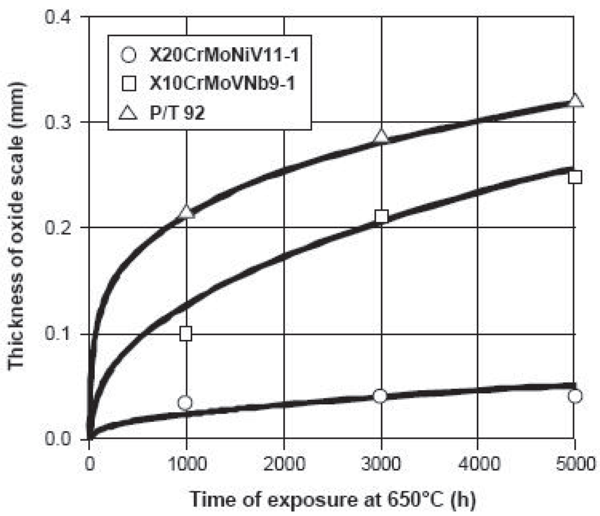

Fig. 19. Steam oxidation of 9-12 % chromium - steels at 650°C[3].

comparison by steam oxiation for the steel grades, X20CrMONiVII-1, X10CrMoVNb9-1 (T/P91) and T/P92. It shows that 9% Cr steels can not be used in steam lines outside the boiler, if the steam temperature is 650°C or over[3]. In recent years, 9-11%Cr ferritic heat resistant steels were developed by addition of Co and/or W, such as NF616 (9Cr-1.8W-0.5Mo), HCM12A(11Cr-2W-0.4Mo-Cu), NF12 (11Cr-2.6W-Mo-Co-V-Nb) and E911(9Cr-1W-1Mo), for thermal power boilers. Due to the high creep rupture strength of these steels, the Ultra Super Critical (USC) boilers with the high steam condition of 25MPa/600°C can be used, and now several USC power plants of 1,000 MW class have been operated in Japan. To achieve higher plant efficiency, a still higher steam condition is expected; therefore further research have been continued in Japan and Europe to increase the creep rupture strength of ferritic steels. The final target of rupture strength of these ferritic steels seems to be MPa at 100,000 hours/650°C.

For example, Takashi Sato and his co-authors in Japan[21], carried out a practical research on the ferritic heat resistant steel 9%Cr-W-Co, and they proposed that this ferritic steel can be used as a candidate material for boiler tube and pipe for up to 650°C application. They confirmed the improvement of creep resistance and formability of the proposed steel by applying both long-term creep rupture and boiler tube manufacturing tests The contents of Al and Ni of the investigated steel were reduced to 0.001% and 0.035% respectively because some researchers believe in their contribution to the reduction of the long term creep rupture strength of the ferritic steels[21].

FERRITIC/MARTENSITIC STEELS FOR HIGH TEMPERATURE APPLICATION

Several investigators have looked beyond the typical Cr-Mo-W-V steels for novel compositions and processing routes to develop new ferritic and martensitic steels for service to 650ºC and higher. One such composition was 9Cr-3.3W-0.2V-0.05Nb-0.05N-0.08C steel containing 1–3% Pd. In another study, 15% Cr ferritic steel with a base composition of Fe-0.1C-15Cr-1Mo-3W-0.2V-0.05Nb-0.07N-0.003B was alloyed with up to an additional 3% W and 3% Co. A combination of 6 % W and 3% Co in this steel provided the best strength properties due to the resulted precipitates (not identified). For nuclear considerations and subsequent activation, the cobalt alloys are probably not an option, although the class of steel may offer other non-cobalt-containing options.

Information on the development of low-carbon (0.002 %) 9Cr-3W-3Co-VNb steel with 0.05 % N has recently been published. Improved creep strength was attributed to nano-sized MX carbonitrides along prior-austenite grain boundaries and lath boundaries. Another recent experimental steel development is a carbon-free martensitic alloy. The steel composition is Fe-11.0Ni-5.0Cr-10.0Mo-0.20Ti-0.12Al-0.005B and has an excellent properties at 700ºC.

Oxide dispersion-strengthened (ODS) ferritic steels are another alternative with the potential of having the advantage of ferritic steels, but being able to push operating temperatures to 650ºC and beyond. These steels are presently receiving an ever increasing amount of attention as possible candidate materials for first wall and blanket structural materials for future fusion reactors and for fuel cladding for fast fission reactors. They have also been considered in the planning for generation IV reactors, as well as for the conventional power-generation industry, as they push for operating temperatures beyond 650ºC. The first ODS steels consisted of a low-carbon, high-chromium (12–17 % Cr) non-transformable ferrite matrix with a high number density of small Titania (TiO_2) and/or Yttria (Y_2O_3) particles as the strengthening dispersion.

Two early compositions studied extensively were: Fe-13Cr-1.5Mo-2.9Ti-1.8Ti_2O_3 (DT2906) and Fe-13Cr-1.5Mo-2.2Ti-0.9Ti_2O_3-0.5Y_2O_3 (DT2203Y05). Elevated-temperature strength is provided by a dispersion of fine Titania and Yttria particles and by ÷-phase (70% Fe, 15% Cr, 7% Ti, and 6% Mo) that forms at grain boundaries. The development programs seek to process the presently available steels (e.g., commercial MA957 (Fe-14Cr-1Ti-0.3Mo-0.25Y_2O_3) to produce an equiaxed structure and explore new alloy compositions. Many of the new alloys use tungsten instead of molybdenum, and they usually use Y_2O_3 dispersions with lower titanium concentrations than were used for the earlier versions.

The Central Research Institute of the Electric Power Industry of Japan and Kobe Steel Ltd have presented information on 12Cr-8Mo and 12Cr-8Mo-0.1Y_2O_3 steels fabricated for cladding of metallic fuel for fast breeder reactors. The steels, fabricated by mechanical alloying/powder metallurgy techniques, were shown to have two-to-three times the creep-rupture strength of a conventional 12Cr (HT9) steel. Two attempts have been made to produce dispersion-strengthened steels by more conventional techniques than mechanical alloying/power metallurgy techniques. The first has good creep strength to 650–700°C, and it achieves its excellent elevated temperature properties by dispersion strengthening. The steel, designated A-21 has a nominal composition of Fe-9.5Cr-3Co-1Ni-0.6Mo-0.3Ti-0.07C that is strengthened by a fine dispersion of tiny titanium carbides produced by austenitizing to dissolve all precipitates and then hot working the austenite (ausforming) prior to cooling to form martensite. A some-what similar approach to the A-21 but without the hot working is the development of a steel designed to use precipitation strengthening with vanadium nitrides and carbonitrides. In this case, the steel with the complicated nominal composition of Fe-12Cr-0.5Ni-2Mn-10Co-1.5Mo-0.7V-0.06Nb-0.04Ta-0.04Ti-0.15N-0.03C was austenitized at 1180ºC for 1 h and then ausaged at 700ºC for 120 h, after which it was cooled to room temperature, and finally tempered at 700ºC for 4 h. The objective was to form a high number density of fine precipitates. The properties of the steels produced by the initial attempts at this process were less-than desired, and further work is required[17].

CONCLUDING REMARKS

1- Concerning the steel P92, it is modified from the well established alloy P91, by reducing the Mo-content to about 0.5% (In order to avoid the formation of delta-ferrite in the microstructure), and adding about 1.7% W plus a few parts per million of B, with retained controlled microalloying of Nb, V, and N. This composition modification gives rise to very stable carbides and carbo-nitrides which improve long term creep strength. This steel is designed to operate at temperatures up to 625°C and it is claimed that high temperature rupture strengths are up to 30% greater than for P91.

2- Maximum service temperature increases with increasing complexity of the steel composition, and the more highly alloyed steels have sufficient stress rupture strength to be considered for application at temperatures in excess of 600°C.

3- Creep strength of 9-12% Cr steels is correlated inversely with the martensite lath width and therefore with the sub-grain size.

4- Comparing the long-term (200000 h) creep rupture strength of different 9-11% Cr steels at the usual levels of service temperatures and the relative improvement from X20 to P91 is roughly similar to that observed for the traditional low-alloy steels (10CrMo9-10 and 14MoV6-3) to X20. However, the relative improvement from P91 to newer steels (E911 and P92) is less impressive, where small difference seems to now exist between P91 and E911.

5- Although P122 steel has an excellent corrosion resistance and approximately 1.3 times higher creep strength than P91, the microstructure of its HAZ in welds is quite complicated because of the transformation and recovery caused by repeated heat cycles through welding processes. It was pointed out that such welds are weaker in creep strength than base metal under higher temperature and lower stress conditions. Due to this, P122 is preferred to be used as boiler components because of its higher oxidation resistance. However, it is not favored to be used for thick section components

6- Oxide dispersion-strengthened (ODS) ferritic steels are another alternative that were studied extensively to push operating temperatures up to 650ºC and beyond. Steels such as (DT2906) Fe-13Cr-1.5Mo-2.9Ti-1.8Ti_2O_3, and (DT2203Y05) Fe-13Cr-1.5Mo-2.2Ti-0.9Ti_2O_3-0.5Y2O3 are examples of this. Their elevated-temperature strength is provided by a dispersion of fine Titania and Yttria particles and by ÷-phase (70% Fe, 15% Cr, 7% Ti, 6% Mo) that forms at the grain boundaries.

7- Other improved creep rupture steels (12Cr-8Mo and 12Cr-8Mo-0.1Y_2O_3) were presented by The Central Research Institute of the Electric Power Industry of Japan and Kobe Steel Ltd. These steels were fabricated by mechanical alloying/powder metallurgy techniques and shown to have two-to-three times the creep-rupture strength of the conventional 12Cr (HT9) steel at 650–700°C.

8- Improvement was made on steels with high service temperature of 700ºC, low-carbon steel (Fe-0.002C-9Cr-3W-3Co-VNb-0.05N) and carbon free steel (Fe-11.0Ni-5.0Cr-10.0Mo-0.20Ti-0.12Al-0.005B) have been publicized and still under investigation.

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