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Heat-Resistant Steels, Microstructure Evolution and Life Assessment in Power Plants

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1. Introduction

Most parts of the electricity generating equipments in power plants work at elevated temperature and high steam pressure, including boiler, turbine and connected system of tubing and piping. The generating equipments operate with steam pressures in the range of 20MPa or even more and the steam temperature is also high in the range of 600 °C. This will be the condition of water and steam inside the circulates through generating system. On the furnace side in boiler, the gas temperatures outside of the tubes can be as high as 1400 °C. The water or steam carrying tubes, the drum and other connected parts have to be strong enough to withstand these temperatures and pressures. In power plant, great efficiency means a saving in fuel and less emission of carbon dioxide in a given electricity output, which consequentially reduces the rate at which damage is done to the globe environment. The efficiency of steam turbines can be obviously improved by increasing the maximum operating pressure and temperature. That is why there is a tendency that operating parameters become much higher to promote efficiency.

We can imagine what will happen if the tubes or pipes burst open at such high pressure and temperature, which will be a catastrophic accident and lead to fatalities. To prevent such failures every detail should be subject to strict adherence to code compliances, from the metallurgy of the steel used, strength calculations for each part to manufacturing and welding procedures. Every part is tested and results documented to ensure compatibility with the codes. At the end of the construction phase, Hydro tests at pressure of 1.5 to 2 times the operating pressure were carried to ensure that all parts can withstand the high pressure conditions. Under normal operating conditions, the pressure parts can withstand these high temperatures and pressures for years. If there is an abnormal increase in pressure, the safety valves will automatically open and let out the steam to the atmosphere.

Although safe design and careful condition monitoring have always been of great concern for the power industry, high temperature components loaded with steam pressure in power plants have a high damage potential during long-term service. Today this issue becomes more and more important with the higher and higher steam parameters. So a great number of standards, rules and guidelines exist worldwide to avoid catastrophic failures and to deliver the right basis for condition based inspection. Furthermore, technical advances in

design, instrumentation, condition monitoring and materials are driving forces for the enhancement of life prediction and assessment procedures. However, well understanding of material degradation in service is the basis for improved inspection and scheduling maintenance to keep the plants in reliability, availability and profitability.

With the development of power technology and heat resistant steels, the later the power plant was constructed, the higher the operating parameters (temperature and steam pressure and gross generation). For the reason of developing history, today many different level power plants operate at different parameters around the world, and the generating components were manufactured from various alloys using a wide range of fabrication techniques. Because the design conditions of boilers vary within a broad power generating system, there are many different alloys being used in various product forms. New alloys with complex metallurgy have being introduced for decades, and the information base for well established alloys continues to grow.

It is believed that creep and material structure evolution are tightly related. Components subjected to creep stress have a limited lifetime. In fact, a large number of studies have been performed in order to relate microstructural investigation and service exposure or residual life. Many reports have involved this issue [1,2,3].

This chapter is intended to give an overview of the heat resistant steels used in power plant, including development of these materials, their application, techniques applied for microstructural investigation in order to assess residual life.

2. Heat resistant steels and application

Here it is presented a general idea of heat-resistant steels and a brief review of its current status for power generation applications. And some information on microstructural characteristics, appropriate for the application, data of critical properties are given for selected materials. We attempt to give an overall impression of the advantages and limitations of the various classes of steels with the emphasis on applications.

2.1 Profile of heat resistant steels

Generally, there are two fundamental classes of heat resistant steels used in power plants, the "ferritic/martensitic" and the "austenitic". The ferritic/martensitic steels have the same body-centered cubic crystal structure as iron. They are simply iron containing with relatively small addition alloy elements, such as the main element chromium added from 2% to about 13%. These ferritic/martensitic grades also have a little manganese, molybdenum, silicon, carbon and nitrogen, mostly included for their benefits in precipitation strengthening and prompting high temperature behavior. Ferritic grades are used broadly because they are much economic for their low content of alloy additions. They also have some resistance to oxidization at red heat, and which is in direct proportion to chromium content.

Ferritic/martensitic steels used in high temperature can be divided in two classes by microstructure and content of additions. One class are usually named low alloy steels, which contain 1-3%Cr and total alloy elements less than 5%; another are called 9-12Cr martensitic steels and commonly contain alloy elements in the range 10-20%. With the operating parameters increasing in power plants, more and more components fabricated with martensitic steels, and pearlitic steels have a tendency to be replaced partly. In recent

years, worldwide efforts to increase efficiency in power plants have created a demand for steels that can withstand higher pressure and higher service temperatures. The representative developments are grade P/T91 - X10CrMoVNb9-1, T/P92, and so on, which are modification of the existing 9-12Cr% grade with additions of vanadium, niobium, nitrogen et al. Till today, the most advanced martensitic steels exposes at the steam temperature less than 650 °C.

When enough nickel is added to the iron–chromium mix, the alloy becomes austenitic which has a face-centered cubic crystal structure. Austenitic steels have much higher strength and ductility and also have much greater creep-rupture strength than the ferritic/martensitic steels. At room temperature the austenitics are more ductile and generally easier to fabricate. Austenitic steels are much expensive for their high contents of alloy element additions, which are usually used at the steam temperature over 650°C.

2.2 Effects of alloy elements

Heat Resistant steels are those solid solution strengthened alloy steels for use at temperatures over 500°C and limited in the extreme to 750°C. As they are used over a certain broad temperature ranges, these steels usually were strengthened by hard mechanism of heat treatment, solid solution and precipitation. In order to achieve the desired properties, all those heat-resistant steels are composed with several alloy elements except one or two basis elements. Their complicated compositions achieve the outstanding high temperature properties. Many efforts have been dedicated to this goal for decades [4,5,6,7].

In heat resistant steels, the most important alloying elements are chromium (Cr) for oxidation resistance and nickel (Ni) for strength and ductility. Other elements are added to improve these high temperature properties. Their effects are given generally as follows:

Chromium (Cr) is the one element present in all heat resistant steels. Oxidation resistance comes mostly from the chromium content. Chromium also adds to high temperature strength and carburization resistance. Chromium tends to make the atomic structure “ferritic”. Both chromium and iron have the tendency to form ferrite, and which is counteracted by nickel. High chromium also contributes to sigma formation.

Nickel (Ni) added to a mix of iron and chromium increases ductility, high temperature strength, and resistance to both carburization and nitriding. Nickel tends to make the atomic structure “austenitic”. Iron base alloys become austenitic when a certain amount of nickel added, so it is the most important element in austenite. Nickel decreases the solubility of both carbon and nitrogen in austenite. The austenitic heat resistant steels content at least 8%Ni.

There are some other metallic alloying elements, such as manganese (Mn), molybdenum (Mo), titanium (Ti), vanadium (V), tungsten (W), aluminum (Al), cobalt (Co), niobium (Nb), zirconium (Zr), Copper (Cu) and the rare earth elements such as boron (B), cerium (Ce), lanthanum (La) and yttrium (Y). These elements added well improve the steels integrative properties at elevated temperature. Some of them for strength, others are largely for oxidation resistance, process workability and microstructure stability.

As to the nonmetallic elements, Carbon (C) is the most important strengthening element, even a few hundredths of a percent. When the carbon level increases, the steel becomes stronger, but it also becomes less ductile. Carbon is controlled within certain limits in heat resistant steels and the limits are related to the processing methods. Most wrought heat resistant steels contain around 0.05 to 0.10% carbon, while cast heat resistant steels usually have from 0.35% up to 0.75% carbon. Carbon dissolves in the alloy and induces solution

strength. It is also present as small, hard particles called carbides. These are chemical compounds of carbon with metallic elements, such as chromium, molybdenum, titanium and niobium et al. Nitrogen (N) is a small amount in heat resistant steels, and serves to strengthen both martensitic austenitic alloys. Silicon (Si) decreases the solubility of carbon in the metal (metallurgically it increases the chemical "activity" of carbon in the steels), which is an important variable in the steelmaking process, as a strengthening element, normally above 0.04%. Silicon improves both oxidation and carburization resistance, as well as resistance to absorbing nitrogen for heat resistant steels at high temperature. A silicon oxide layer formed just under the chromium oxide scale on the steels is what helps the alloy resist carburization and nitrogen absorbing. Sulphur (S) is normally regarded as an impurity, and commonly limited below 0.010% in most steels. Sulphur is also detrimental to weldability. But it has the benefit of improving machinability, so it is kept up around 0.02% for 304 and 316 steels. Phosphorus (P) is generally undesirable element in heat resistant steels for brittle effect when it segregates at grain boundary. It is also harmful to nickel alloy weldability. It is normally specified an upper limit for most steels, even as the nickel weld fillers are specified to have no more than 0.015% phosphorus.

2.3 Precipitates

As mentioned above, to great extent, all the heat resistant steels are strengthened by precipitation. Generally, complex alloy steels are more advantageous than those simply alloyed, because they have a predominant characteristic of precipitate reaction. However, the more complex the steel is, the more complicated precipitation reactions.

Most of these precipitates are nitrocarbides, and few of them are inter-metallic compounds, including the intergranular and boundary precipitation as well as variable carbide reactions. The morphology, size and distribution of these precipitating particles are modified by complex alloy elements and which enhance the properties obviously because of carbide reactions accompanied by microstructural and microchemical changes. As to what kinds of precipitates present in a specified steel is bound with its compositions and heat-treatment states.

The kinds of precipitate usually form in ferritic heat-resistant steels are $M_{23}C_6$, M_3C , M_2C , M_6C , MX , Laves and Z-phase. Some extra phases, such as θ , χ and G-phase, may form in austenites. The various precipitates frequently reported in heat resistant steels are given in the following table 1[8,9,10,11].

Precipitate	Structure	Parameter (Å)	Composition
NbC	fcc	a=4.47	NbC
NbN	fcc	a=4.40	NbN
TiC	fcc	a=4.33	TiC
TiN	fcc	a=4.24	TiN
Z-phase	tetragonal	a=3.037 c=7.391	CrNbN
$M_{23}C_6$	fcc	a=10.57-10.68	$Cr_{16}Fe_5Mo_2C$ (e.g.)
M_6C	diamond cubic	a=10.62-11.28	$(FeCr)_{21}Mo_3C$; Fe_3Nb_3C ; M_5SiC
Sigma	tetragonal	a=8.80 c=4.54	Fe,Ni,Cr,Mo
Laves phase	hexagonal	a=4.73 c=7.72	Fe_2Mo , Fe_2Nb
χ -phase	bcc	a=8.807-8.878	$Fe_{36}Cr_{12}Mo_{10}$
G-phase	fcc	a=11.2	$Ni_{16}Nb_6Si_7$, $Ni_{16}Ti_6Si_7$

Table 1. The main precipitates in heat-resistant steels

There is a simple relationship between carbide structure and the metallic element in the periodic table. It is shown in table 2.




Group \ Row	IV	V	VI	VII	VIII			
3	TiC	VC	V_2C	$Cr_{23}C_6$ Cr_7C_3 Cr_3C_7	$Mn_{23}C_6$ Mn_7C_3 Mn_3C	$\xi-Fe_3C$ Fe_3C Fe_2C	Co_3C Co_2C	Ni_3C
4	ZrC	NbC	Nb_2C	Mo_2C MoC				
5	HfC	TaC	Ta_2C	W_2C WC				
								
					Cubic	Hexagonal	Orthorhombic	

Table 2. Relationship between carbide structure and the position of metallic elements.

Table 2 Relationship between carbide structure and the position of metallic elements in the periodic table [12]. At service condition, The most common populations of secondary phases in heat resistant steels are $M_{23}X_6$ carbides, MX carbonitrides, Laves phase and Z phase [13]. So a lot of attention has been paid to these precipitates of $M_{23}C_6$, MX, Laves and Z-phase for their notable effects on creep behavior. Much more details about them are given as follow: $M_{23}C_6$ is the main precipitates in most heat resistant steels. It is believed that the amount of $M_{23}C_6$ and its size and distribution strong affect the creep strength of creep-resistant steels. Generally this carbide is chromium rich, with Fe, Ni, Mn and Mo substitute for Cr partially, and the fraction of these substitute atoms can be up to forty percent [14]. The crystal structure of $M_{23}C_6$ is a complex face centered cubic (fcc) with a parameter about 1.06nm, which changes slightly for metallic elements variation.

As the main carbides in heat resistant steels, $M_{23}C_6$ precipitates mostly precipitate along grain boundaries during tempering treatment, and some particles might form in the process stage. Even though $M_{23}C_6$ is a very stable precipitation in structure, but they coarsen obviously during creep exposure at elevated temperature. Their average size increases while density decreases with exposure time prolonged. The large particles are growing and the fines dissolving but volume fraction remains constant. Measurement the size distribution and the content change of metallic element were made by researches [15,16] to characterize the microstructure evolution. Investigations [17,18] indicate that B addition has an obvious effect to improve creep strength.

Another typical kind of carbide/nitride nominated as MX is with cubic NaCl-type structure. Its crystal parameter is 0.43 ± 0.017 nm for composition variety. Much fine and dispersive MX particles precipitate intergranular and ingranular during tempering and exposure at elevated temperature when the strong forming elements of V, Ti, Nb and W added in alloys. MX carbonitrides usually form on dislocations in the matrix, so they increase creep strength for their dislocation pinning action. Even though MX precipitates are stable and do not coarsens heavily during creep exposure [19,20]. However, it is found that they might dissolve and form complex nitride Z-phase under long-term creep exposure [21].

Z-phase, $Cr(V,Nb)N$, is another nitride precipitate with similar elements as the MX. Its crystal structure is tetragonal and lattice parameters are $a=0.30$ nm and $c=0.74$ nm. In high chromium ferritic steels, a Z phase was found after long-term creep [8]. Additionally, it has

been observed that the Z phase precipitates after creep in both weld metals and the heat-affected zone.

The discovery of Z phase precipitation in a 9–12%Cr steels actually used in power plants raised serious questions about the long term stability. Very little is known about the behavior of Z phase in 9–12%Cr steels, since it has been observed to precipitate only after long times of exposure in plants or after long term creep testing. Z-phase formation has been recently recognized to decrease the long-term creep strength, because the formation of Z-phase consumes fine MX carbonitride particles that are the main strengthening species in 9 – 12% chromium ferritic steels[22]. The Z phase precipitates as large particles, which do not contribute to precipitate strengthening, and thus the creep strength of the steel is considerably lowered. The additions of W and Mo in alloys improve their creep behavior obviously; However, these elements are apt to form intermetallic phase Laves phase $(Fe,Cr)_2(Mo,W)$. Laves phase particles usually precipitate in grain boundaries close to $M_{23}C_6$ carbides in equiaxed shape during creep exposure [23,24]. The crystal structure of Laves phase is hexagonal with $a=0.47$, $b=0.78$ nm with a small range variety for composition change. It is found that the size of Laves phase particles increase rapidly in higher exposure temperature. There is an argument about the effects of Laves phase on creep property. The precipitation of Laves phase leads to a depletion of these two elements Mo and W in the matrix and to a reduction of the solid solution hardening effect in alloys. On the other hand, Laves phase precipitation can increase the creep strength by precipitation hardening before it coarsens obviously. It believes that the Laves phase has a negative effect when its size becomes as one of the largest precipitates in alloys.

As to what kinds of precipitation present in a specified steel is related to its chemical compositions, heat-treatment parameters. In fact, the heat-resistant steels have shown very complicated metallurgy physics factors, e.g. investigations indicate that the same steel in different heats or the same steel exposed in different conditions and experiences may contain different carbides with dissimilar precipitation, morphology or distribution. That is why the metallurgists face a challenge when they try to evaluate the residual life from the appearance of precipitation and microstructure evolution.

3. Classes of heat-resistant steels and applications

Heat-resistant steels have chemical stability, enough strength and gas corrosion-resistance. They can be divided into low alloy steels, martensitic steels, and austenitic steels according to their chemical composition and microstructure.

3.1 Low alloy steels

Due to good mechanical properties at elevated temperatures and sufficient corrosion resistance, low alloy steels are widely used in pressure part applications in boilers for thermal power plants. This type steels are especially used in thick-section components such as headers and steam pipes. Particularly these are tubing steels for the cooler sections of superheaters and reheaters and also for the waterwalls.

Traditionally, in power generation industry, this class alloy steels Grades 11 and 22 have been used for waterwalls, superheaters and thick-section parts in boilers; and 1CrMoV for rotors for many years[25,26]. grade 22 (2.25Cr1Mo) developed in 1960' and applied in worldwide power plants for large amount of components: tubes, pipes, cast, forged.

With the increased steam pressures and temperatures, the rising of operating parameter in power plants also have an impact on the conditions for operating water walls. Therefore, the former standard materials used for water walls like T/P12 (13CrMo4-4) do no longer meet the requirements of advanced boilers. Since steels used in water wall panel should allow welding without post weld heat treatment (PWHT), the water wall panel is too large to perform a heat treatment. This demand also excludes high-strength steels martensitic steels. Two new steel grades present and satisfy all requirements. They are T/P23 originated in Japan and T/P24 (7CrMoVTiB10-10) developed by Vallourec and Mannesmann (V&M) in Germany. W. Bendick et al [27] pointed out that the characteristics of both steel grades have potential application.

In the years '80-90 many efforts have been devoted to increase the plants performances and therefore materials with enhanced performances were requested. The metallurgists and the material researchers started to develop new chemical compositions on the base of existing steels with the addition of elements (V, W, Nb, Ti) able to give strengthening by precipitation [3]. The new advanced low alloy Grades 23 and 24 steels, improved based on Grades 22, are strong candidates for new power and petrochemical plant construction and for the eventual large-scale replacement of steam pipework on existing power plant. Grade 23 is a modified 2Cr1Mo steel and it is claimed that does not require post-weld heat treatment. The improvements have been achieved through the addition of tungsten and boron whilst reducing the carbon content. A further recent development has been Grade 24, where the microstructure has been further refined by modification of the vanadium, niobium, titanium, boron, tungsten and molybdenum levels. This steel has superior long-term creep properties to Grade 23 at 500 °C; is equivalent to Grade 23 at 550 °C, and is intermediate between Grade 22 and 23 at 600 °C.

The main differences in compositions are described in the following table 3 based on ASTM A213 Standard.

Grade		C	Mn	P	S	Si	Cr	Mo	W	Nb	V	B	Other
22	min	0.05	0.30	-	-	-	1.90	0.87	-	-	-	-	-
	max	0.15	0.60	0.025	0.025	0.50	2.60	1.13	-	-	-	-	
23	min	0.04	0.10	-	-	-	1.90	0.05	1.45	0.02	0.20	0.0005	N: 0.03 max
	max	0.10	0.60	0.030	0.010	0.50	2.60	0.30	1.75	0.08	0.30	0.0060	
24	min	0.05	0.30	-	-	0.15	2.20	0.70	-	-	0.20	0.0015	N: 0.012 max Ti: 0.06- 0.10
	max	0.10	0.70	0.020	0.010	0.45	2.60	1.10	-	-	0.30	0.0070	

Table 3. The compositions of low alloy steels based on ASTM Standard.

The effect of adding or changing the level of different elements on the microstructure and properties of the alloys is obvious. Due to the same basic composition and the same structure T/P23 and T/P24 mostly have similar physical properties (including the oxidation resistance) as T/P22. This is true for the physical properties. However, large differences exist for the mechanical properties including creep. The alloying additions have led to a strong increase of strength. The values of minimum yield strength for T/P23 and T/P24 are higher by almost a factor of 2 compared to T/P22. The most important property of a heat resistant steel is its creep rupture strength. Similar to the tensile properties the steels T/P23

and T/P24 reveal considerably higher values. Test results at 550°C are shown in figure 3. The rupture points are close to the mean lines of the steel grades. Figure 4 shows the 10⁵h creep rupture strength of T/P24 is only slightly below T/P91 in the lower temperature range. Although the values for T/P23 are somewhat lower at 500-550°C, they still lie considerably above T/P22. The T/P23 curve approaches T/P24 with increasing temperature and crosses it at 575°C. Due to the limited oxidation resistance of the two steels, it is not recommended to use them at temperatures higher than 575°C for long-term service.

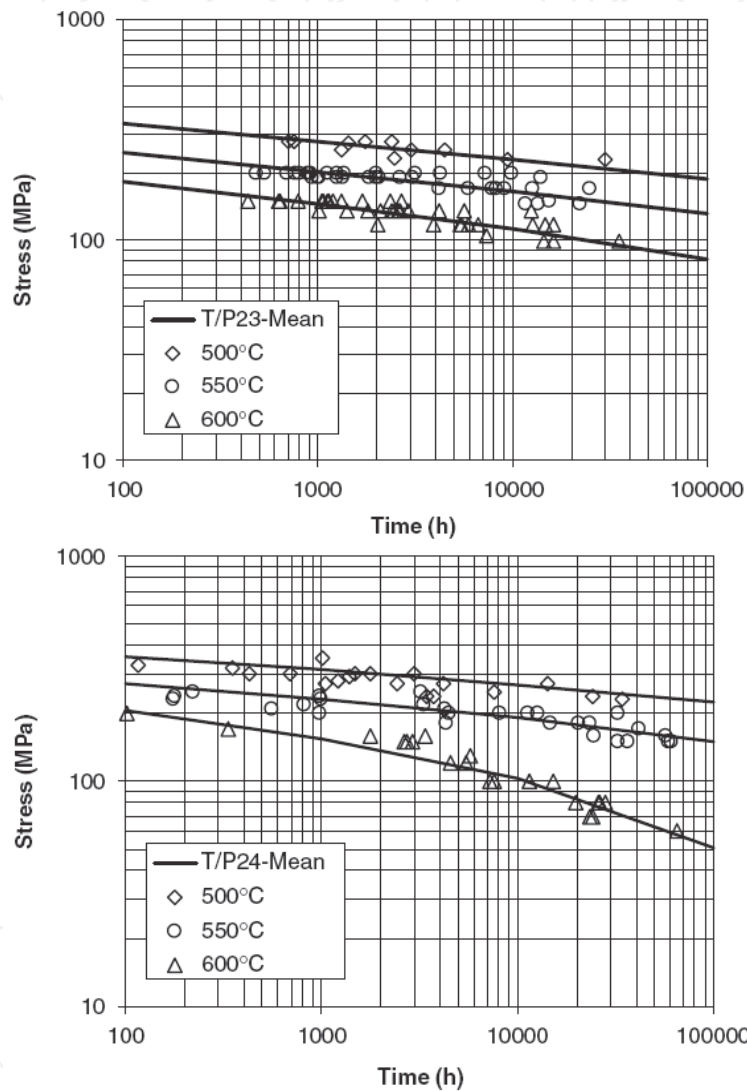


Fig. 1. Creep test on Grades 23 and 24 for the temperature range 500-600 °C [from ref.31]

Alloy	Mechanical properties			Alternative nomenclature
	Yield Stress, MPa	UTS, MPa	Elongation, %	
Grade 11	205	415	30	P11/T11/13CrMo 4 4
Grade 22	205	415	30	P22/T22/10CrMo 9 10
Grade 23	400	510	20	P23/T23/HCM2S
Grade 24	580	670	20	T24/7CrMoVTiB 10-10

Table 4. Mechanical properties for low alloy steels at room temperature

The most recent advancement in low alloy steel is the development of 3Cr-3W(Mo)V steels, which has a higher creep strength than 2.25Cr-1Mo steel (T22) and 2.25Cr-1.6W-VNb steel (T23) [28,29]. Fig.2 shows the extrapolated 10^5 h creep rupture strength for T22, T23, T24 and 3Cr-1.5W-0.75Mo-0.25V without Ta (Grade A) and with 0.1Ta (Grade B) as a function of temperature, comparing with martensitic T91 steel. The creep rupture strength of the Grade B steel is higher than T23 and T24 steels for the entire test temperature range and also higher than T91 steel up to 615°C.

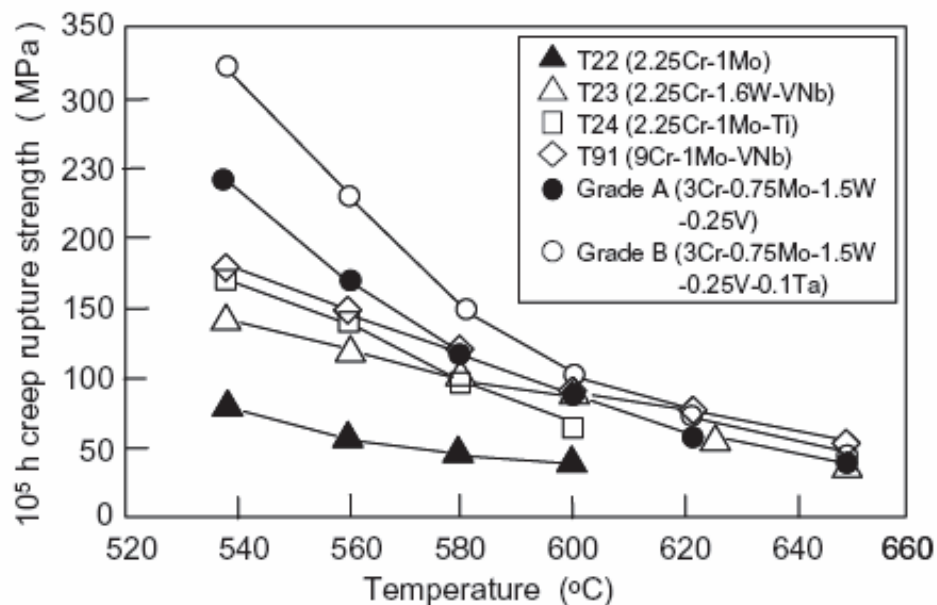


Fig. 2. Creep rupture strength of 10^5 h as a function of temperature of Grade A and B of 3Cr-1.5W-0.75Mo-0.25V steel, comparing with T22, T23, T24 and T91 [from ref.6].

In general, Cr-Mo low-alloy ferritic steels are tough and ductile at lower operating temperatures and maintain good strength at higher temperatures. Unfortunately, when subjected to prolonged exposure to intermediate service temperatures, these steels can become embrittled with an associated decrease in fracture toughness and a shift in ductile-to-brittle transition temperature (DBTT) to higher temperatures [30,31]. The embrittlement is mainly caused by changes in the microchemistry of grain boundaries, which is referred to as temper embrittlement. Temper embrittlement is non-hardening embrittlement and arises from grain boundary segregation of impurity elements such as P, Sb and Sn as a result of long-term exposure in the temperature range of 350–600°C. Several reports reveal that phosphorus is the major one of these embrittling impurity elements in steel.

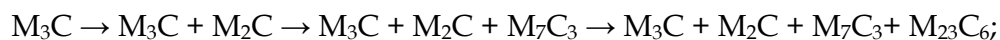
Another type of low alloy extensively used for various engineering components in thermal power plants of China, India, Russia and former Soviet Union countries and Eastern European countries CrMo steels, such as 12Cr1MoV, 12X1MΦ(Russian Grade), 14CrMo4-5 (ISO 9328-2, 1991), 13CrMo4-5 (EN 10028-2, 1992), or 12C1.1 (ASTM A182-96) et al. They are the heat resistant steels with lowest of alloy additions in chemical composition. Generally, the pipelines used to transport superheated steam in the temperature range 500 – 560 °C and under a pressure, $P = 10 - 15$ MPa.

The initial microstructure of power plant low alloy steels is ferrite bainite or ferrite-pearlite [32,33]. Generally, The Cr-Mo and Cr-W elevated-temperature steels are used in the normalized-and-tempered condition. Normalizing consists of austenitizing by

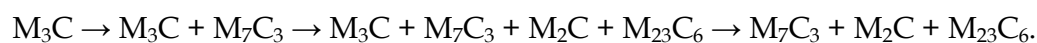
annealing above A_1 , the equilibrium temperature where ferrite (body-centered-cubic structure) transforms to austenite (face-centered-cubic structure), and then it is air cooled. In low alloy steels with $<5\%Cr$, bainite (ferrite containing a high dislocation density and carbides), polygonal ferrite, or a combination of these two constituents form, depending on the section size of produces. Their creep strength enhanced by the formation of precipitates, which are stable alloy carbides and intermetallic compounds obtained following normalizing heat treatment later on subjected to very severe tempering (about $700^\circ C$ for several hours).

Steels destined for power plant applications might contain any of the following precipitates: carbides or carbonitrides M_3C , $M(C, N)$, $M_2(C, N)$, M_7C_3 , $M_{23}C_6$, M_6C , Laves phase (M stands for metallic solute atom) and intermetallic precipitates. It was determined in that the precipitation sequences at elevated temperature for steels are as follows [34,35]:

- a. steel 2.25Cr1Mo



- b. steel 3Cr1.5Mo



- c. steel Cr1MoV



The precipitation sequence in different low alloy steels is obviously different in the evolution of carbide precipitation even the thermodynamic driving forces are apparently similar. It is believed that the precipitation sequence difference is related to the changeable driving force for various precipitates in different steels.

During long time service in creep regime to such conditions the microstructure of steel changes, bainite/pearlite decomposes as well as carbides precipitation at the grain boundaries and carbides coarsening processes proceed. Structure changes cause formation of cavities and development of internal damages [36]. It is well known that there is a close coherence between changes in microstructure and deterioration of mechanical properties. So many attentions have been paid to investigation of the carbides precipitation kinetics of power plant heat resistant steels during ageing or long-term service at elevated temperatures. The aim on purpose is try to determine any microstructural parameters that may be used to estimate service history and may be practicable for assessment of remnant life of equipments.

There is a demand for higher strength steels for waterwalls to improve the creep behavior at the higher temperatures in supercritical plant. With the continuing effort to achieve higher efficiencies and lower costs in power generating components, the materials of Grade 23 and 24 and any alloy with higher strength but with no requirement for post-weld heat treatment would be an attractive material. It would be significant improvement.

3.2 Martensitic/ferric steels

Martensitic heat-resistant steels include medium-chrome steel containing 5-9% Cr and high-chrome steel containing 12% chrome, which have been introduced into power plant

materials more than half century. The 9-12% Cr martensitic steels are currently used in both boilers and in steam turbines for many components. In boilers, these steels are used for tubing in superheaters and reheaters, operating with metal temperatures up to above 620°C currently. The thick-section parts such as headers and steam pipes are also fabricated from these materials. It has been recognized that the 9-12% Cr steels are the key materials to increase the thermal efficiency of steam power plants. In the last three decades, a number of new 9-12%Cr steels with improved creep strength have been developed for long-term service at temperatures close to 650°C in high-temperature components of ultra supercritical power plants [37]. This is a great progress to develop high creep strength and corrosion resistance steels at ever increasing temperature. The steadily improved creep rupture strength of new martensitic 9-12% Cr steels has been used to construct new advanced fossil-fired steam power plants with higher efficiency. The applications of these new alloys achieve not only high efficiencies, but also reducing the emission of CO₂ and other environmentally hazardous gases at least 20% [18,38].

Increase in steam parameters from subcritical 180 bar/530–540°C to ultra-supercritical values of 300 bar and 600°C has been realised, and this has led to efficiency increases from 30–35% to 42–47%, equivalent to approximately 30% reduction in specific CO₂ emission.

For the long-term application of the new steels, it is necessary to assess the microstructural changes that are likely to occur during service exposure and to evaluate the effect of such changes on the hightemperature creep behavior. Only with this information can the design values for components be correctly assigned.

In general these alloys have lower coefficients of thermal expansion and higher thermal conductivities than austenitic steels and should therefore be more resistant to thermal cycling. The development of 9-12% chromium steels is originated a century ago with the manufacture of a 12% Cr and 2-5% Mo steel for steam turbine blades by Krupp and Mannesmann in Germany [39]. The high-chromium, high-carbon martensitic steels were hard and were subsequently developed commercially for applications such as cutlery knives, razors, scalpel blades, and heat-resisting tools and bearings in competition with austenitic stainless steels.

Beginning with the 12CrMoV steel introduced in power plants in the middle of 1960s, steel development over the past decades has led to new steam pipe steels like the modified 9Cr steel P91, introduced in plants in 1988s, to the tungsten-modified 9Cr steels P92 introduced in plants in 2001 and E911 introduced in 2002. Similar steels have been developed and applied for large forgings and castings of steam turbines. The 9-12% Cr steels with lower carbon (0.1% max) contents and additions of Mo, W, V, Nb, N and other elements, possessing higher creep-rupture strengths combined with good oxidation and corrosion resistance at elevated temperatures, have subsequently been developed. These steels have been used or considered for use in electrical power plants, petrochemical and chemical plants, gas turbine engineering, aircraft and aerospace industries, and as nuclear fission and fusion reactor components as well.

In order to develop these new alloys with advanced characteristics, many efforts have been made to investigate the metallurgy mechanism. Many strengthening mechanisms have been proposed to explain the improved creep strength. Much more attentions have been paid to research the effects of various additions, for instance, in the course of development of 12 CrMoV steels nickel was added to improve impact properties and to suppress the presence of δ -ferrite in the microstructure. It also was attributed to solid solution hardening and a

reduced solubility of carbon. However, the excessive amounts of nickel, greater than 0.6 wt. %, caused an accelerated reduction in the creep rupture strength, which maybe partly attributed to reduced stability of M_2X phase and precipitation of M_6X particles [40]. Mod.9Cr-1Mo steels have attained their high creep strength by the addition of V, Nb and N which form fine precipitates MX, and the creep strength of high Cr ferritic steels have been improved further by replacing part of Mo with W[41,42,43].

Specific alloys in this class generally include 12Cr and 9Cr martensitic steels. One famous 12Cr steel is X20CrMoV12.1. Since the X20CrMoV12.1 was developed in 1950s, it has been successfully used in power plants over several decades up to temperature of about 566°C. The creep strength of X20 is based on solid solution strength hardening and precipitation of $M_{23}C_6$ and MX carbides. Specific alloys in 9Cr class include Grade 9, Grade 91, E911, Grade 92, HT 9, HCM12 etc and the compositions are given in following Table 5.

Steel Type	Designation	Country of Origin	Analysis(wt. %)										
			C	Si	Mn	Cr	Ni	Mo	V	Nb	W	N	B
9Cr-1Mo	9Cr-1Mo*	UK	0.10	0.70	0.50	9.5	0.20	1.0					
	T9	Japan	≤0.15	0.25-1.00	0.30-0.60	8.0-10.0		0.90-1.10					
	EM10*	France	0.10	0.30	0.50	9.0	0.20	1.0					
9Cr-2Mo	HCM9M*	Japan	0.07	0.30	0.45	9.0		2.0					
	NSCR9*	Japan	0.08	0.25	0.50	9.0	0.10	1.6	0.15	0.05		0.030	0.003
	EM12	Belgium/France	0.08-0.12	0.30-0.50	0.90-1.20	9.0-10.0		1.9-2.1	0.25-0.35	0.35-0.45			
	JFMS*	Japan	0.05	0.67	0.58	9.6	0.94	2.3	0.12	0.06			
9Cr-MoVNb	Tempaloy F-9	Japan	0.04-0.08	0.25-1.00	0.40-0.80	8.0-9.5		0.90-1.1	0.15-0.45	0.20-0.60			≤0.005
	T91	USA	0.08-0.12	0.20-0.50	0.30-0.60	8.0-9.5	≤0.40	0.85-1.05	0.18-0.25	0.06-0.10		0.030-0.070	
9Cr-MoVNb W	COST 'B'*	Europe	0.17	0.10	0.10	9.5	0.10	1.5	0.25	0.05		0.005	0.010
	E911*	Europe	0.10	0.20	0.40	9.0	0.20	1.0	0.20	0.08	1.0	0.070	
	TF1*	Japan	0.12	0.20	0.50	9.0	0.80	0.60	0.26	0.06	1.6	0.050	0.003
	TB9(NF616)(T92)	Japan	0.07-0.13	≤0.05	0.30-0.60	8.5-9.5	≤0.40	0.30-0.60	0.15-0.25	0.04-0.09	1.5-2.0	0.050-0.070	0.001-0.006

Table 5. Compositions for martensitic steels

Alloy development programs have concentrated on improving the creep properties of 9-12Cr steels for decades. Based on the Grade 9, the aim to improve creep resistance has been resulted in alloys such as Grade 91,92, E911, Grade 122 and TAF Fig.3 shows the extrapolated 105 h creep rupture strength for some 9-12Cr martensites as a function of temperature. The creep rupture properties of P92 and TAF have been improved obviously.

An outstanding position is held by TAF steel with relatively high Cr-contents of 10.5 wt% and B-contents of 0.027– 0.040 wt%. However, the other attempts to develop high strength alloys of this type to promote creep strength maybe achieved, but these developments fail due to a lack of long-term stability at much higher temperature. It is believed that steam oxidation resistance might limit the maximum operating temperature of these materials, so alloy development is now focused on developing materials with higher chromium contents with a creep strength equivalent to Grade 92.

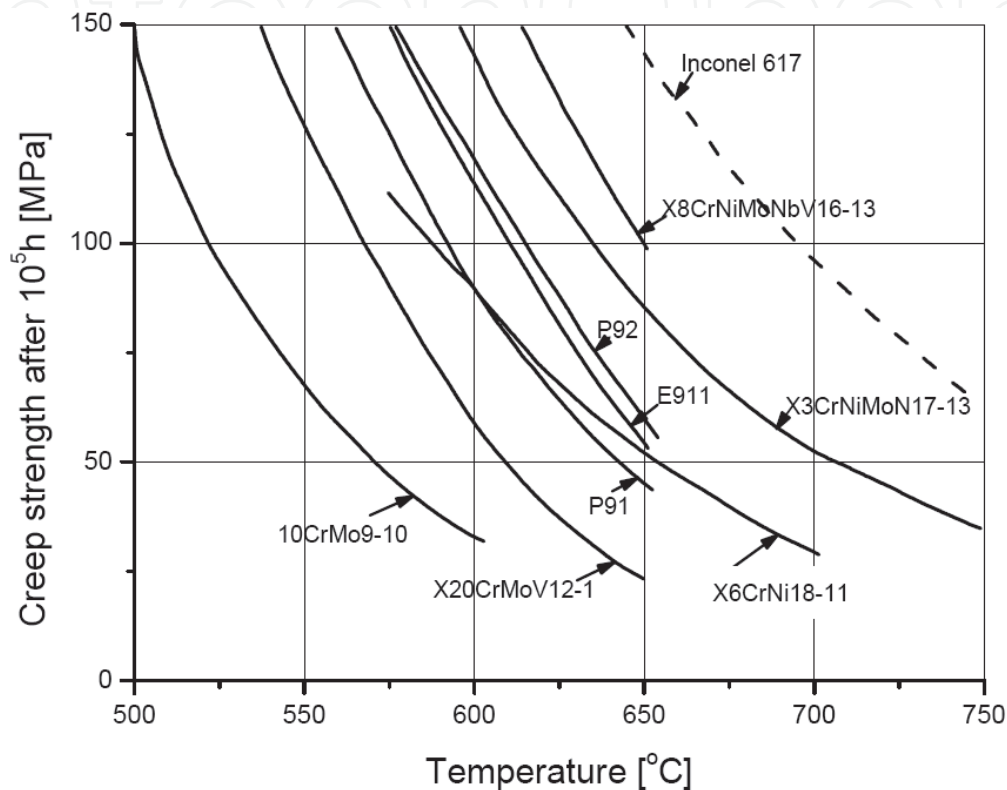


Fig. 3. Creep Strength of Exposed (10^5 h) Materials as a Function of Temperature [ref.⁴⁴].

Many investigations have shown that alloying additions appear to be the effective way to improve the creep strength of the 9–12%Cr steels. Fujita^[45] found a substantial improvement of creep strength by adding B, and he confirmed the positive effect of 0.040 wt.% B in creep of TAF steel up to 130,000 h at 650 °C, where the target of 10⁵ h creep life at 650 °C and 100MPa was almost achieved [46]. Apart from B, Cr is a key element influencing both the oxidation resistance and the creep strength. Experience shows that 12 wt% Cr are needed to raise the oxidation resistance to an expected level [47].

Work carried out in Japanese and European programmes has resulted in the improved 9%- and 12%-Cr alloys that can be used for thick-section components intended for use in the operating range 565–620°C. Materials such as Grade 92 and Grade 122 are used in sub and supercritical units where their higher strengths allow the use of thinner sections, thereby reducing the threat of fatigue due to thermal cycling. The reduction in weight brought about by thinner walls also has the effect of reducing stresses at the boiler and turbine connections, as well as on the structural steel work, all of which contributes to increased life of components and reduced costs. The European companies

and research institutes carried out a joint program (COST 501) to develop and qualify modified 10%Cr steels. Results showed that the fatigue properties of the 10%Cr material were improved compared to conventional 11-12 %Cr steels. An added advantage of the 10%Cr material compared with conventional low alloy steels is that the lower thermal-expansion coefficient allows a greater temperature rise to be tolerated at start-up. Another aim of the new COST 522 programme is to develop 9-12%Cr steels for applications up to 650°C.

An extensive study [48] of the microstructural development of these alloys during thermal exposures has shown a starting microstructure of elongated dislocation cells and sub-grains aligned with $M_{23}C_6$ particles, together with smaller VN and M_2X particles inside the sub-grains. During long-duration creep tests some softening of the material occurred in the specimen threads due to thermal exposure. Some of this softening was associated with Oswald-ripening of existing particles but precipitation of new particles, in particular Laves phase, was observed. In parallel, the dislocation density decreased such that few dislocations were observed inside the sub-grains. All these microstructural changes occur more slowly in steels that contain boron [49].

Alloy	Composition, wt%									
	C	Mn	Si	Cr	Mo	V	N	W	B	Other
Grade 9	0.12	0.45	0.6	9	1					
E911	0.12	0.51	0.2	9	0.94	0.2	0.06	0.9		0.25Ni
Tempaloy F12M				12	0.7			0.7		
Grade 91	0.1	0.45	0.4	9	1	0.2	0.049			0.8Ni
Grade 92	0.07	0.45	0.06	9	0.5	0.2	0.06	1.8	0.004	
HCM12	0.1	0.55	0.3	12	1	0.25	0.03	1.0		
Grade 122	0.11	0.6	0.1	12	0.4	0.2	0.06	2.0	0.003	1.0Cu
TAF	0.18			10.5	1.5	0.2	0.1		0.04	0.05Ni
TB12	0.08	0.5	0.05	12	0.5	0.2	0.05	1.8	0.3	0.1Ni
NF12	0.08	0.5	0.2	11	0.2	0.2	0.05	2.6	0.004	2.5Cu
SAVE12	0.1	0.2	0.25	10		0.2	0.05	3.0		3.0Co, 0.1 Nd
X20CrMoV121	0.20	1.0	0.5	12	1.0	0.3				0.6Ni
X12CrMoVNbN101	0.12			10	1.5	0.2	0.05			
X18CrMoVNbB91	0.18			9	1.5	0.25	0.02		0.01	

Table 6. Compositions of martensitic steels

The microstructure for these 9-12Cr materials is tempered martensite with creep resistance imparted by controlled precipitation of carbides and nitrides. In general, 9-12Cr steels are

also used in the normalized-and-tempered condition. Fig.5 shows a typical TEM micrograph of tempered 9Cr martensite. Martensite forms when products are normalizing by austenitizing above A1 and then air cooled. During this process, the formation of δ -ferrite should be avoided as this may cause embrittlement, resulting in fabrication problems. Subsequent tempering above 700°C for hours, the strengthening precipitates form. The types of precipitates formed in martensitic heat-resistant steels also depend on the composition, temperature history during fabrication, and time and temperature of service exposure. The main precipitate in the 9–12%Cr steels is the $M_{23}C_6$ carbide consisting of Cr, Fe, Mo, (W), and C. This carbide produces the basic creep strength of 9-12%Cr steels by precipitating on subgrain boundaries during tempering. The $M_{23}C_6$ carbides increase creep strength by retarding subgrain growth, which is a major source of creep strain in 12%Cr steels. The thermal stability of $M_{23}C_6$ is relatively high. The MX precipitates in 12%Cr steels consist mainly of V, Nb, and N, which precipitate within subgrains where they pin down free dislocations and increase creep strength. Thermal stability of the MX precipitates is very high, leading to high creep strength. It is interesting to note that equilibrium calculations indicate that the strengthening effect of vanadium in martensites is by precipitation of vanadium nitrides. This means that even though nitrogen is not a specified alloying element in these steels, the trapped nitrogen contributes to the high strength.

Their compositions and mechanical properties are given in Table 6 and table 7.

Alloy	Mechanical properties			Alternative nomenclature
	Yield Stress MPa	UTS, MPa	Elongation %	
GRADE 9	205	415	30	P9/T9/STBA26
E911				
Tempaloy F12M	470	685	18	
GRADE 91	415	585	20	X10CrMoVNb 91, GRADE 91
GRADE 92	440	620	20	P92, T92
HCM12				SUS410J2TB
Alloy 122	400	620	20	HCM12A
TAF				
TB12				
NF12				
SAVE12				
X20CrMoV121	495	680	16	
X12CrMoVNbN101				
X18CrMoVNbB91				

Table 7. General mechanical properties for typical martensites

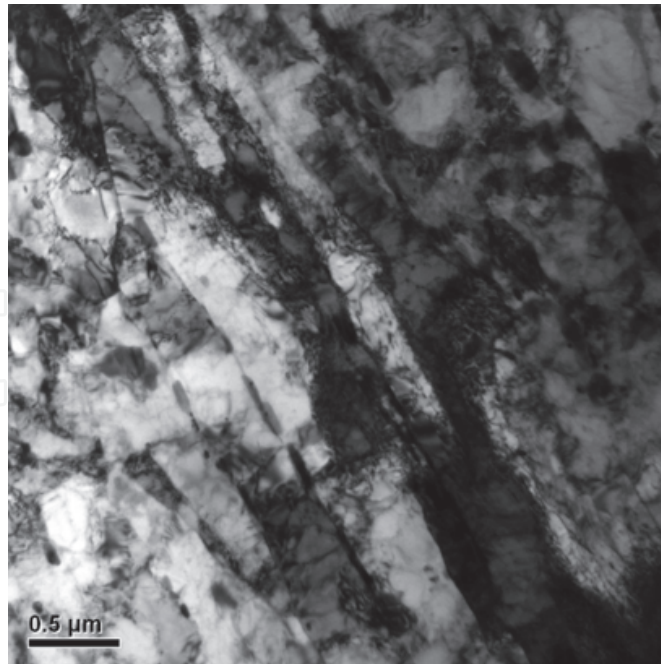


Fig. 4. TEM micrograph of tempered 9Cr martensite

3.3 Austenitic steels and other materials

Austenitic stainless steels are FeCrNi alloys with chromium content more than 13wt% with an austenitic structure at room temperature. Austenitic steels are more expensive than ferritic steels for their high alloy element additions. Traditionally, applications for austenitic steels are restricted to the higher temperature boiler tubes as well as to specific situations where severe corrosion conditions occur. Austenitic materials are often used as weld overlay on ferritic materials to repair corroded areas or to provide protection in areas where corrosion could be a problem.

Austenitic steels are developed based on 18%Cr-8%Ni, originated from AISI 302. In order to obtain the required properties, other alloying elements are added. Except the interstitial elements such as carbon and nitrogen, some substitutional elements such as Mn, Mo, W, Cu, Al, Ti, Nb, V, etc are added. These alloying elements are classified as ferrite stabilizers or austenite stabilizers by their effects to promote a ferritic structure or an austenitic structure. Their contributions can be evaluated using the notation of chromium and nickel equivalents as presented below [50]:

$$Ni_{eq} = Ni + Co + 0.5Mn + 0.3Cu + 30C + 23N(\text{mass}\%)$$

$$Cr_{eq} = Cr + 2.0Si + 1.5Mo + 1.75Nb + 1.5Ti + 5.5Al + 0.75W(\text{mass}\%)$$

Various types steels of this class have been produced by increasing the strength with the addition of alloying elements. Table 8 and table 9 give the composition and properties of common austenitic steels. Nb, Ti and V can greatly improve the creep strength of austenitic stainless steels by precipitating fine carbides or carbonitrides. Furthermore, addition of these elements can stabilize the alloy against intergranular corrosion. Metallurgical physics of austenite development is to increase the volume fraction of strengthening precipitates by replacing chromium carbides with other more stable carbides, which, at the same time, frees chromium back to the matrix to give improved corrosion resistance. However,

Alloy	Composition, wt%											Other
	C	Mn max	P max	S max	Si max	Cr	Mo	N	Nb	Ni	B	
AISI 302	0.15	2	0.045	0.03	1	18				9		
AISI 304	0.08	2	0.045	0.03	1	18				8		
AISI 321	0.08	2	0.045	0.03	1	17				11		0.15Ti
AISI 347	0.08	2	0.045	0.03	1	17				11		0.8 Nb+Ta
AISI 316	0.08	2	0.045	0.03	1	17	2.5			12		
AISI 309	0.2	2	0.045	0.03	1	23				14		
AISI 310	0.25	2	0.045	0.03	1.5	24				19		
ASME TP347HFG	0.08	1.6			0.6	18			0.8	10		
Tempaloy A-1	0.12	1.6			0.6	18			0.1	10		0.08 Ti
Tempaloy A-3	0.05	1.5			0.4	22		0.15	0.7	15	0.002	
Super304H	0.1	0.8			0.2	18		0.1	0.4	9		3.0 Cu
HR3C	0.06	1.2			0.4	25		0.2	0.45	20		
Hr6W	0.10	2.0	0.03	0.03	1.0	23			0.4 max	40		6.0 W, 0.2 maxTi
NF709	0.15	1			0.5	20	1.5		0.2	25		0.1 Ti
Esshete 1250	0.09	6	0.03	0.003	0.6	15	1	0.04		10	0.004	0.02Al, 0.9Nb, 0.25V, 0.14Cu

Table 8. Chemical composition for different austenitic steels

investigations have reported that the presence of secondary phase particles can strengthen austenitic steels, but these secondary phase particles has also been seen to affect the fatigue behavior.

Table 8 shows the compositions of some heat resistant austenitic stainless steels, mainly AISI 300 series alloys. Austenitic steels such as AISI 316 and 304 are used extensively as structural materials in heavy sections for pressure vessels and pipes in power plant. In fact, austenitic steels are used in many areas, which are subjected to varying temperatures and temperature gradients. Austenitic steels generally have low thermal conductivities and high coefficients of thermal expansion, it is noticed that the high thermal stresses can develop resulting in fatigue cracking.

Alloy 800HT is an austenitic nickel-iron-chromium alloy. This alloy is characterized by high creep strength and very good resistance to oxidation. Super austenitic stainless steels 253MA or UNS S30815 and 353MA or UNS S35315 are austenitic chromium-nickel steels alloyed with nitrogen and rare earth metals. They have high creep strength and very good resistance to isothermal and, above all, cyclic oxidation. Fig.5 presents the creep strength of some austenitic steels at temperature above 600°C.

In the recent decades, the developing high strength ferritic steels have been used instead of the austenitic steels for their cost-effective, good weldability and fracture toughness, but there is still a place for these austenitic steels which are primarily used in the place where oxidation resistance and fireside creep become more important. Especially with the global increase in energy consumption requires more energy production. Meanwhile the concern on the environmental impact from energy production is continuously focusing. Today, coal-fired thermal power generation is still the most important methods in the foreseeing long-

term future, as coal is available at a competitive price and satisfy to safety way. However, the biggest challenge facing coal-fired power plants is to improve their energy efficiency. This can be accomplished by increasing the maximum steam temperature and the steam pressure. Conventionally, the heat efficiency of coal-fired power plants has stayed at around 41% in the super critical (SC) condition with a temperature of 550°C and pressure of 24.1 MPa. In order to attain a power generating efficiency of about 43%, ultra super critical (USC) conditions with a steam temperature at about 600°C should be reached. By increasing the temperature from 550 to 600°C (at most present power plants) to 650–700°C (at next generation power plants), the power plant efficiency can be increased from 36% to more than 50% and the CO₂ emission can be reduced about 30% [51]. Currently, in a power plant operating at SC condition and lower, the ferritic/martensitic heat resistant steels are the dominant materials for steam generation and partial for boiler. In USC operating conditions, the ferritic/martensitic materials (including the higher chrome steels) do not have sufficient creep rupture strength and resistance to high temperature corrosion. Austenitic stainless steels are therefore used as the dominant materials. Although nickel base alloys can meet the requirement, they are too expensive to application.

Alloy	Mechanical properties			Alternative nomenclature
	Yield stress MPa	UTS MPa	Elongation %	
AISI 302	240	585	60	
AISI 304	215	505	70	
AISI 321	240	585	55	
AISI 347	240	620	50	
AISI 316	250	565	55	
AISI 309	275	655	45	
AISI 310	275	655	45	
ASME TP347HFG	205	550	35	
NF709	270	640	30	SUS310J2TB
Esshete 1250	272	359	45	

Table 9. Room temperature mechanical properties for austenitic steels.

The materials used for the next generation power plants are expected to have even higher yield strength at elevated temperature, creep strength (typically 100,000 h rupture strength of around 100 MPa) and high temperature corrosion resistance [52]. However, no current heat resistant alloy can meet these requirements. Therefore, the EU-project 'Advanced (700°C) PF Power Plant – AD700' to develop new advanced heat resistant materials for next generation power plants has been organised. One of the aims was to develop materials for superheaters and reheaters in USC boilers for use at temperatures up to 700°C. One material successfully developed is the austenitic stainless steel grade UNS S31035 (Sanicro 25) [53]. This material provides very high creep strength and good corrosion resistance at high temperatures. Another material, Alloy 800HT is a candidate material for generation IV nuclear power plants.

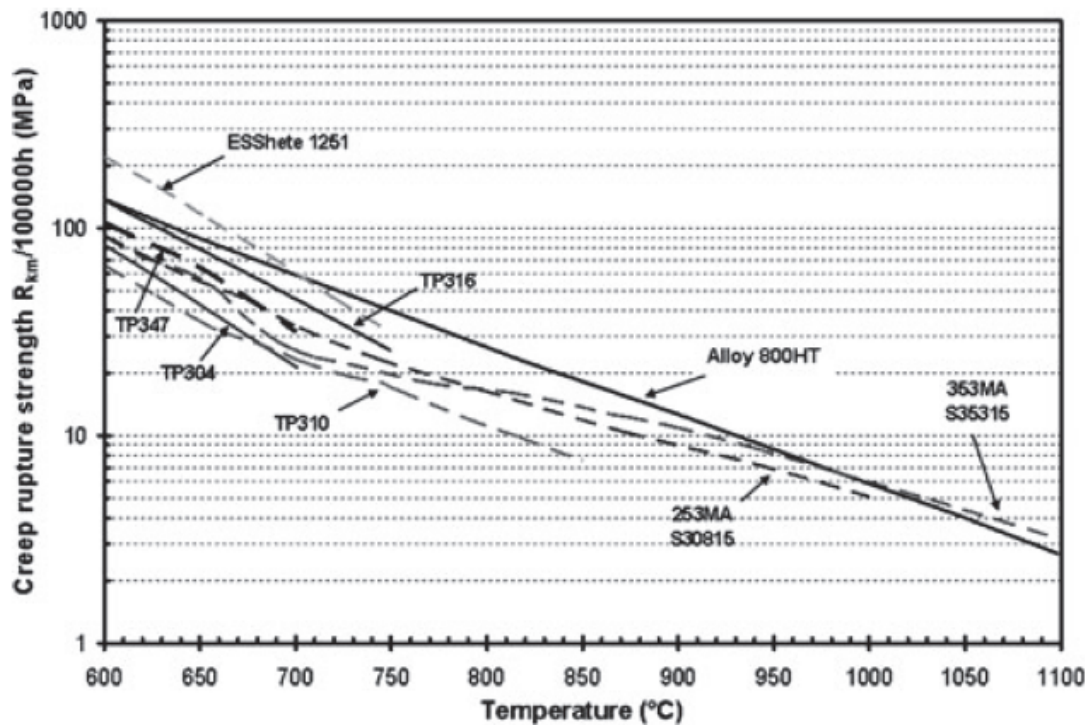


Fig. 5. Creep strength of some austenitic steels at 100,000 hours [54].

A major concern that remains with the use of austenitic steels is how to join the materials to components manufactured from other material classes. Publications [55,56] discussed the welding technique and process as well as the behaviour of transition joints between austenitic and martensitic/ferritic steels. They found that the location of the failure varied with test parameter. In the high stress at relative low temperature regime failure usually occurred in the parent ferritic material or weld metal, and failure was close to the weld interface (heat affected zone) when low stresses were applied over a range of temperatures. The relatively high costs of these materials coupled with the disadvantages of high thermal expansion coefficient and poor thermal conductivity, will probably continue to limit their applications in advanced power plant. There are two possibilities for further development. Firstly, there could be some value in developing a low-cost austenitic steel, possibly based on Mn rather than Ni. Secondly, the modified austenitic materials developed at ORNL 33-34 could be introduced commercially. The high strength capability of these alloys could give advantages in terms of thinner sections and improved heat-transfer characteristics.

As to other heat resistant materials maybe used in power plant in the future, Oxide Dispersed Strengthened (ODS) Alloys are promised, which are characterised by good creep strength at high temperatures (i.e. >1000°C). Thus the alloys are seen as being useful for higher temperature applications where the strength of the superalloys was inadequate. These alloys are commonly produced by mechanical alloying. Because the processing route was complex and difficult to control in large-scale processing and as a result these alloys were characterised by poor reproducibility of microstructure and inconsistency of mechanical properties. ODS alloys can be classed in iron base and Ni base for the difference of main composition. Researches indicates their good high temperature behavior oxidation resistant is correlated with the dispersive oxide, such as Y_2O_3

It is believed that ODS materials will be most beneficial in areas such as combustor cans and heat exchanger tubing where high temperatures are commonly found but the loading is low in comparison to other areas. Efforts to improve strength and to develop better fabrication techniques will continue, and other major effort will be on the establishment of reliable joining techniques. In addition, it will address advanced joining methods, including laser welding, brazing and coating systems. More attention to improve oxidation resistance will also continue, especially paid to Fe-base materials.

4. Microstructure evolution in inservice materials

The creep properties of heat-resistant steels are controlled by chemical composition and microstructure of these steels. If the chemical composition is given, the microstructure of these steels depends on the heat treatment, temperature and time of creep exposure [57]. The most important strengthening mechanisms in these steels, operating during high temperature creep exposure, are precipitation strengthening and solid solution strengthening. Precipitation strengthening in ferritic steels is predominantly affected by the dispersive MX particles. It has been shown that both the proof stress at room temperature and creep rupture strength increase while density of second phases increase. At the same time, the creep rate decreases.

It is clear that the mechanical properties of heat-resistant steels would deteriorate when it exposed at elevated temperature for long-term. Correspondingly, their microstructure also degrades obviously.

As to the characteristic of microstructure evolution, the main phenomena of degradation are given below:

1. Precipitates coarsening and phase transformation;
2. The original microstructure decomposition;
3. Microvoids forming at grain boundaries.

These microstructural evolutions directly connect the deterioration of creep strength and other properties, so they are often considered as a demonstration of overheating exposure, and have been commonly accepted as a qualitative thermal degradation index.

From the investigations in past decades, different class material has different characteristic in microstructure evolution.

4.1 Microstructure evolution in ferritic steels

The low alloy steels or pearlite/bainite steels show the tendency to pearlite/bainite spheroidisation after long-term exposure at high temperature. The typical lamellar structure in CrMoV pearlite change to particle structure. Service exposure has a considerable effect on strength and ductility. Classification of microstructural deterioration in steels has also been established and adopted as regulations, such as carbides spheroidization in 12Cr1MoV steel, Fig.6 gives the states of carbide spheroidization in 12Cr1MoV steel according to the spheroidization evaluation standard [58]. Five levels of degradation are assigned based on the development of carbide spheroidization. The classification specifies Level 1 as having no spheroidization, Level 2 as having slight spheroidization, Level 3 as having medium spheroidization, Level 4 as having complete spheroidization and Level 5 as having serious spheroidization. From Level 1 to Level 5, the lamellar structure in pearlite changes to a particle structure. The pearlite structure disappears at Level 4 and Level 5, which results in deterioration of mechanical properties.

Fig. 7 gives an example of the microstructure in a boiler header in service for 25years. It clearly shows that the degree of spheroidisation in final superheater outlet is much visible than that in the primary superheater outlet. The operating temperature in the former is

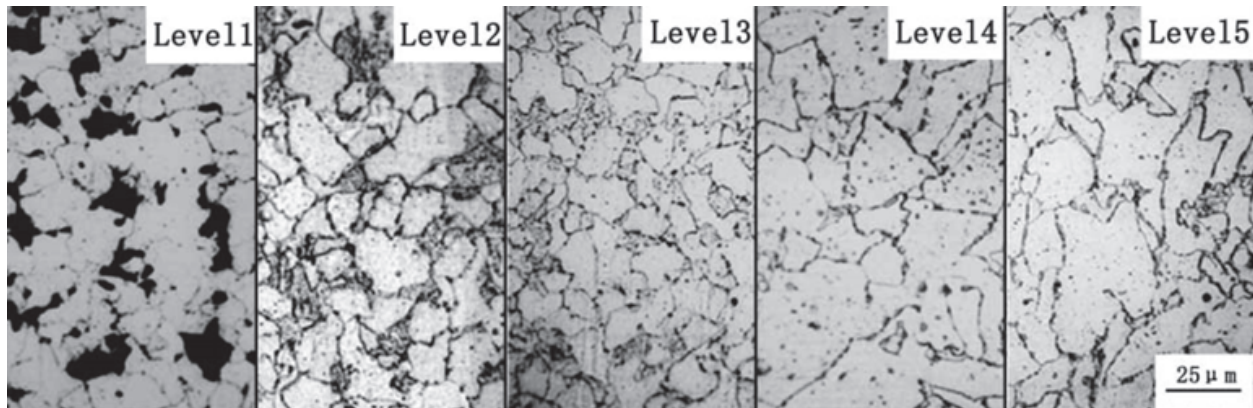


Fig. 6. The evolution standard of carbide spheroidization in 12Cr1MoV steel [from ref.58].

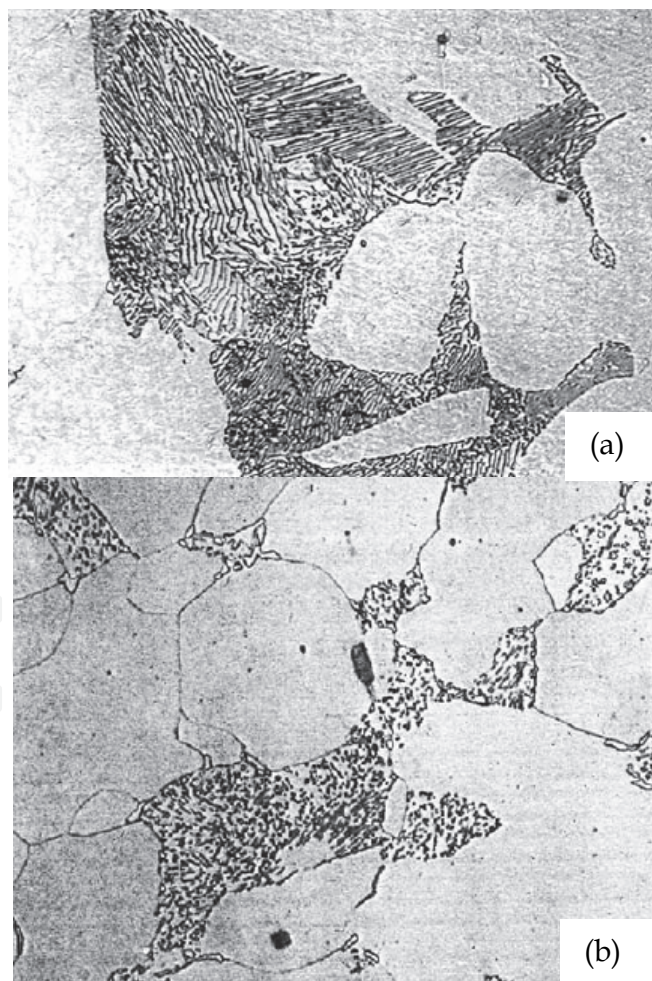


Fig. 7. Microstructure of carbon steel boiler headers in different portions that have been in service for over 25 years (a) primary superheater outlet; (b) final superheater outlet. [from ref.59]

about 30 degree higher than the latter one might be the reason for the difference of microstructure evolution. So the classification of microstructural deterioration in low alloy steels was established by the spheroidization grade. An Italian new reference document for life extension of creep exposed components [60] introduces a classification defined as microstructure evolution based on a reference example relevant to low-alloy steel. The classification with 6 different levels is reported in figure 8. It is easy to judge the header degradation in Fig.7 is about stage B for primary superheater outlet and stages C for final superheater outlet.

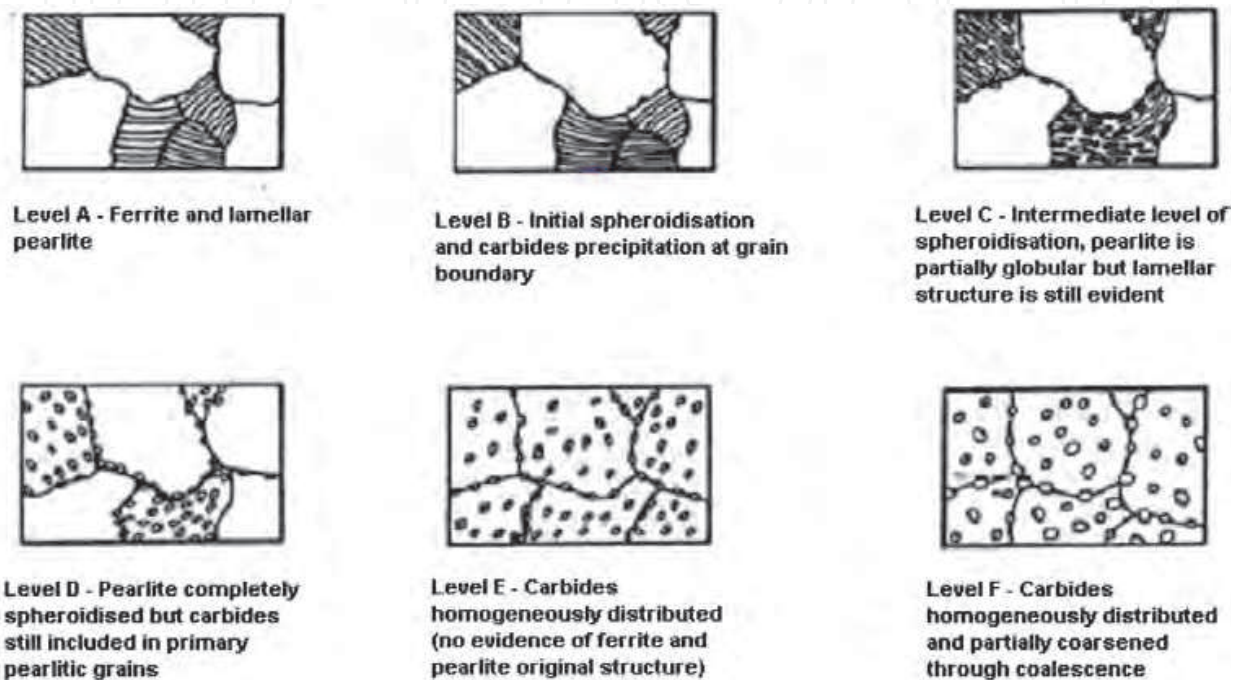


Fig. 8. ISPEL classification for microstructure evolution of ferritic steels

Many studies have been conducted on the evolution of carbides present in steels due to creep exposure [14,61,62,63,64]. Separation and coarsening of carbides are considered as an index of material degradation due to creep exposure.

Microstructure evolution in 9-12Cr martensitic steels shows much complicated characteristics during long-term exposure at elevated temperature. From reports in past decades, much more attention was paid to precipitates coarsening, martensitic substructure transformation and microvoids formation at the stage when material degraded seriously [65,66]. Many articles present estimation of average particle size and remaining life fraction for ferritic steel. In particular the attention has been oriented to $M_{23}C_6$, VC, Laves phase and their compositions. However, different results of particle size and composition have been obtained from different author in terms of absolute size value. Statistical measures have a good agreement in terms of correlation of average particle size on temperature exposure or on time maintaining at a certain temperature. This significant difference in terms of absolute values (size, content, interparticle space etc) is not only strongly influenced by statistical approach in estimating average quality, accuracy in measurement at high magnification and sampling technique adopted, the exposure history of the examined component and its metallurgy factors and forming process are essential causations.

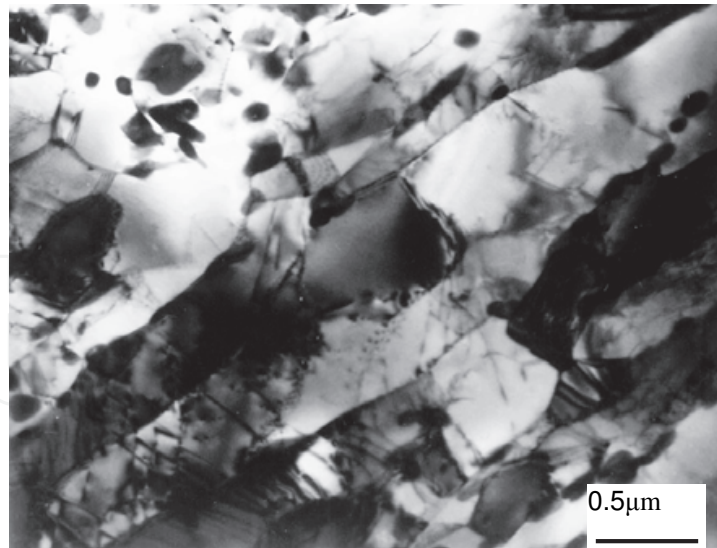


Fig. 9. TEM micrograph of exposed X20CrMoV12.1 for 165,000 hours at 550°C [from ref.67].

Unlike low alloy steels, Martensites infrequently is less sensitive to form intergranular cavities and the impact factors for cavities formation is much complicated, but some evidence of creep damage can be seen in substructure. The shapes of the laths are changed; in particular, the lath boundaries look like bamboo knots, called cell structure, which is a typical microstructure morphology caused by creep. Many low dislocation density regions appeared in the lath structure, and some typical substructures can be seen in Fig.9. The substructure seems to develop as subgrains boundaries are formed by dislocation movement during the creep process. A significant reduction of dislocation density is observed, and few dislocation-free regions can be seen. Extensive carbide precipitates can be seen at prior austenite and martensite lath boundaries, with the finer precipitates in martensitic laths. Large coarsening carbides in irregular spheroid formed along the boundaries. Compared with virgin material, the carbide morphology coarsened distinctly. The observations indicate that the matrix of the tempered martensite has undergone a deterioration during long-term creep. The dislocations climbed or glided and terminated at boundaries. As the number of dislocations at the boundaries increased, networks formed and substructures developed. The carbides morphology in boundaries coarsened distinctly, and most of the strengthening phase have dissolved or coarsened.

Except the coarsening characteristic, martensitic steels have shown common evolution in microstructure is martensite decomposition and substructure change during long-term exposure at high temperature. It is commonly accepted that martensitic structure under a degeneration with creep exposure prolonging. The dislocation density decreases and With the precipitates coarsening and the density of fine particles within the matrix decreases during long-term exposure, the martensitic lath boundaries is indistinct or even disappeared which undergone a degeneration, and coarsening of laths is processing by two ways [68,69,70], the recovery of dislocations within lath boundaries and the recombination of two subgrain boundaries which mainly takes place near the triple point of lath boundaries by moving and causes the disappearance of lath boundaries. Forth more, during moving of lath boundaries to cause progressive local-coalescence, dissolution and re-precipitation of $M_{23}C_6$ carbides distributing along lath boundaries take place repeatedly. Observations did not confirm that the MX precipitates evolve during creep or thermal exposure. The solid solution strengthening effect by alloy elements maybe weaken but was found to be

negligible. The precipitation of Laves phases should not strongly affect resistance of this steel to creep deformation, however, that damage cavities were often found next to Laves phases, so that Laves phases could affect the resistance of that steel to creep fracture.

Generally it is accepted that the increase of Cr content in $M_{23}C_6$ precipitates for all ferritic steels, and the increase of Mo content in precipitate in eutectoidic carbide as M_3C or as M_6C . The composition variation in precipitates and interparticle distance decrease with carbides coarsening are believed as eight indexes of creep exposure and microstructural degradation. However, there is a notable difficulty in correlation of microstructural evolution (such as second phases) to residual life assessment. It is not only necessity to know the actual state of virgin material that for the same type of material can significantly vary from heat to heat or product to product, but the exposure condition and history are also the basis factors to affect the evolution course. Furthermore, there is no quantitative relationship has been established to correlate the parameters of microstructural evolution with life depletion.

The primary difficult for evaluation the life of components with the causation for the degradation of heat-resistant steels

4.2 Microvoids formation in grain boundaries

The concept of microvoid or micro-cavity formation at grain boundaries has been studied and developed in the 1970's and commonly recognized and applied in all European countries with the Neubauer classification and derived methods for decades [71]. The principle is based on the fact that creep evolution of heat resistant steels is related to the appearance of cavities some time before rupture. These cavities gradually form microcracks by interlinkage and at the end come to initiate the rupture. So the emergence of microvoids means that the materials in service damaged seriously.

Assessment class	Structural and damage conditions
0	As received, without thermal service load
1	Creep exposed, without cavities
2a	Advanced creep exposure, isolated cavities
2b	More advanced creep exposure, numerous cavities without preferred orientation
3a	Creep damage, numerous orientated cavities
3b	Advanced creep damage, chains of cavities and/or grain boundary separations
4	Advanced creep damage, microcracks
5	Large creep damage, macrocracks

Table 10. Neubauer schematic assessment of the microstructure

Table 10 is a revision of Neubauer classification is presented in the German VGB "Guidelines for the assessment of microstructure and damage development of creep exposed materials for pipes and boiler components", which is considered as one of the most updated reference document in Europe. Another important aspect of correlation of cavities presence to creep progress can be found in the Neubauer documents, where it is stated that "a noticeable cavity formation takes place at grain boundary at the end of secondary creep". A graphical representation is shown in Fig.10. Although above literature examples of damage grade allocation seem to not completely congruent with the creep curve, it can be considered that grade 4 and 5 should be taken as representative of different stages of tertiary

creep, while grade 3 figured as the transition point among secondary and tertiary and grade 2 considered as representative of secondary creep.

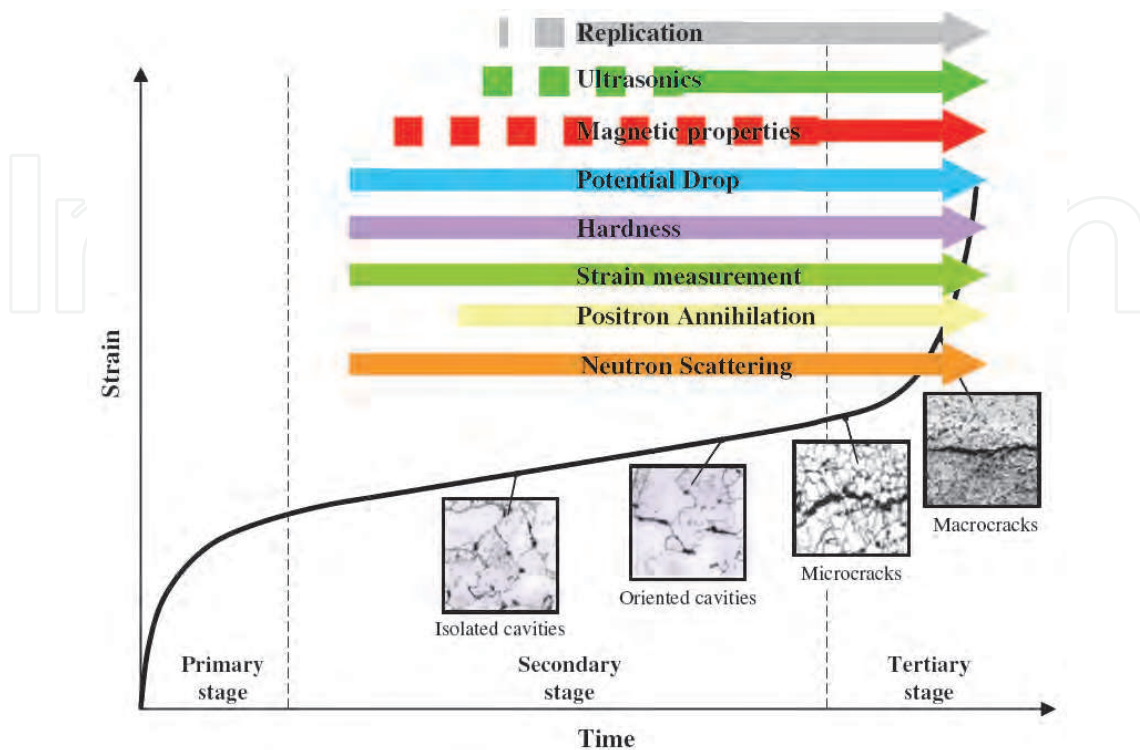


Fig. 10. Typical creep curve with evolution of microstructural damage, and various NDT techniques with indication of applicability ranges [from ref.72].

An interesting summarising is the correlation of microcavities damage and residual life assessment, which is one of the methods followed by some researchers and based on the analysis of experimental results. Graph of the summarising correlation of damage level and expended life fraction is presented in Fig.11. Other reviewers [73,74,75] gave much more critical summary of cavitation. A cavitation derived parameter named A-parameter (number fraction of cavitated grain boundaries) have been used in some studies related to low alloy ferritic steel for pipe and rotor.

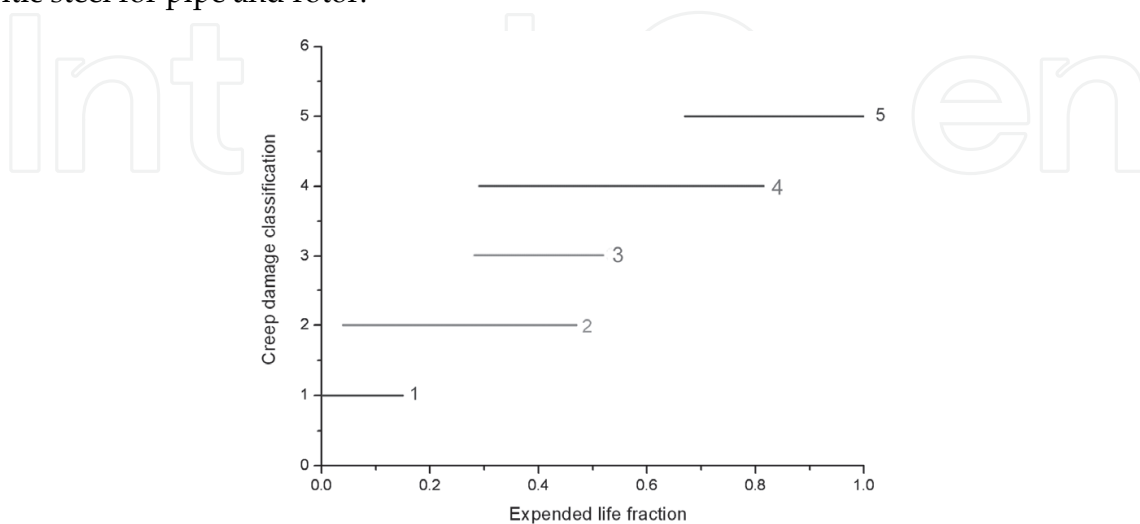


Fig. 11. Creep Damage Classification and Expended Life Fraction

Generally the size and density of the cavities increase as creep progresses, which are also dependant on material type, however it is accepted commonly that the microvoids formation and evolution figure is a prominent index to estimate damage degree.

As to the theoretical research about microvoid formation, past studies[75,76] indicate that cavity nucleation is associated with grain boundary and second phase particles in it, and the presence of surface active elements such as P and Sn in grain boundary makes cavity nucleation easier. The density of cavities (number of cavities per unit grain boundary area) increases with creep exposed time and temperature, and the applied stress enhances the cavity density too. Cavities growth is controlled by two mechanisms: diffusion growth and constraint growth, the former is dominating at high stress level, and the latter one is dominating at much lower stresses.

The size of microvoid is in the range of micron and it cannot be detected by conventional NDT techniques, so metallographic investigation is required to observe its morphology and distribution.

5. Techniques for the residual life assessment of components in power plant

Assessing the integrity and stability of high-temperature, service-exposed components is an interesting topic for power plant users. The primary reason for microstructure damage and mechanical property deterioration is the degenerative creep behavior in long-term exposure at elevated temperature. The residual life assessment is an important procedure in routine examination.

5.1 Inspection method on in-service components

Except the various NDT techniques given in fig.10, the technology of investigation of microstructure to correlate the material microstructural evolution and creep exposure has been performed is metallographic observation of the creep specimen after tests, and the microstructural investigation on actual in-service components is usually gained with replica technique. As a non-destructive technique, replica can be assumed to be or at least very low invasive technique, and this is the first requirement for an investigation applied for residual life evaluation.

The replica technique is essentially application of the metallographic specimen preparation (grinding, polishing, and etching) to a limited area to investigate on the examined component, then the reproduction of the prepared surface on a thin foil of polymeric material. The reproduction of prepared surface on plastic material is achieved by softening of polymeric thin foil with adequate solvent and then hardening the plastic foil due to solvent evaporation. Removed replica can be observed by optical microscope. With further preparation by coating a conductive support (carbon or gold), replica can be observed with scanning electron microscope achieving the possibility to observe reproduced microstructure aspect with higher magnification. If microstructure evolution is the goal, removing a layer of surface (about 0.3-0.5mm thickness reduction) is recommended to avoid the external layer of oxidation or decarburized material.

In order to observe and identify the second phases in the examined material, an extractive replica should be prepared. It is prepared following the same procedure of above morphological replica preparation, in addition to these the critical for the extractive replica is etching the surface to remove the metal matrix without any perturbation on carbides and other precipitates. The extractive replica removed from the examined surface contains the precipitates that can be observed later with electron microscope (SEM). Alternative

techniques for carbon extraction replica are available analyzed by TEM. The sample is prepared by transferring the carbides and precipitates from polymeric resins (dissolved) to a thin layer of graphitic carbon.

Today, metallographic replica testing is the most common inspection method for creep damage monitoring in piping systems and steam boilers. As ductile materials, 9-12Cr martensites show that cavity formation is less distinct, and this process starts very late. Furthermore, cavity formation investigations show some differences between the various heat resistant steels, even difference between various batches of the same material. So their creep damage propagation needs to be characterized by additional methods. Classical replica testing are the small inspection area and the analysis limited to the outer surface only, without information on damage within the wall. For this purpose other methods of condition monitoring need to be found.

US-laminography represents an advanced test method for damage detection, which allows to inspect larger areas [77]. Creep deformation or creep strain measurements by capacitive gauges represent another traditional creep expansion measurement using special “warts” or “pips” at the outer surface to measure diameter or circumference, which is a costful effective method. Thus, extensive efforts have to be undertaken to investigate these materials and material degradation. The classical replica test will remain one method of creep damage monitoring in the future. However, it needs to be accompanied by other qualified methods for ductile materials like 9Cr steels. As mentioned above, past studies show that martensitic structure and precipitates coarsen obviously in 9-12Cr ferritic steels during long-term exposure at high temperature. Meanwhile, the mechanical properties present variation, ex-service materials incline to embrittle at room temperature, and the combination of phosphorus segregation and carbide coarsening at grain boundary does account for the embrittlement tendency [78]. However, more representative characteristics or parameters have to be proposed. The residual life maybe predicated from consumed life by sophisticated calculations, using material data from NDT and/or available data from the as received steel condition. Such as Z-Factor-Method is one of the potential procedures [79].

5.2 Life assessment methodology for components

It is generally agreed that at present the only valid technique for quantitative evaluation of damage to service-exposed material is the creep-rupture testing of the service exposed samples. Hence, a more accurate and reliable residual life assessment (RLA) of power plant components is strictly related to the improvement of this technique. Moreover, various reasons, for instance, the high cost of restoration of the sampled zone in the inservice component, the induced long times of plant shut-down and the occasional inability to sample specific components or their localized areas, have influenced the tendency towards non destructive methods.

For the integrity analyses of plants and residual life studies, the analysis technology is summarized in some papers [87,80,81], which usually combines the following integrated life assessment methodologies:

1. Finite element analysis to define component loading situation (stress and temperature fields);
2. Mechanical tests to define the material's response in the real service aging condition;
3. NDT to define existence of cracks, metallographic investigation to estimate microstructure evolution;
4. Computer codes to assess component integrity and to calculate residual lives.

Advanced codes of integrity and life assessment as well as some cases are proposed by electric companies or research institutes, such as ENEL, Electric Power Research Institute (EPRI) and

CISE etc. The code damage analysis is based on appropriate materials data. They also provide advanced test methodology assessment and verifications of damage analysis methods.

The present methodology for estimating residual creep life involves accelerated iso-stress creep-rupture tests at operative temperature or above on service-exposed material, and then the life predictions are estimated by extrapolations of test results.

Therefore, the operative stress field in the component must be calculated firstly in order to determine the stress utilized during the iso-stress creep-rupture tests.

Based on the metallographic examination and finite element analysis, experimental data combine with suitable calculations will enable an integrated access for estimating the remaining life of the imitation components with more accurate and realistic forecast of failure.

5.3 Summary and comments

VGB guidelines for the assessment of microstructure and damage development in power plant components is considered commonly in worldwide, and this guidelines are accepted as the most updated reference document for microstructure and residual life assessment correlation.

For residual life assessment of power plant components, different materials have their own degradative characteristics, so it is important to remark that all other, except cavities, microstructural observed parameters need to be evaluated on the basis of the as received material correspondent status in order to avoid any misleading deduction from generic or recommended microstructure variation not actually correlated to service exposure. Particularly the 9-12Cr martensites are complex metallurgically, they need careful control of heat treatment to avoid δ -ferrite formation and ensure transformation to martensite fully. During tempering stage, the conventional balance between strength and ductility is required. When components manufactured, the processes, such as bending and welding, must follow the strict control procedures. Some investigations reveal that the some defects, like microvoids, may formation during these processes [82]. Many reports about components failure in power plants show that the primary causations are related to inadequate heat-treatment or welding defects. Some theoretical researches [83] reveal that these improper processes induce abnormal microstructure and lead to creep strength deterioration.

It is believed that the life of equipments in power plants is closely related with the microstructure revolution. In other words, microstructural evolution in exposed to service materials is a key tool for a correct evaluation of material status and allowable service extension. However, with the complicated reasons mentioned above, reliable life assessment shouldn't be made only by means of microstructure inspections, it is preferable that together with other inspections and mechanical tests are included. For the widely applied ferritic low alloyed steels, the evaluation of micro-cavitation presence and creep damage evolution seems to be the most consolidated approach. For every other microstructural aspect (except microcavities) to be monitored, it is very important that the evaluation is made by comparison with the original status in virgin material. Some materials microstructure and their evolution are very sensitive to their factual statuses and exposure conditions.

From the view point of the techniques applied for monitoring microstructure on in-service components, replica are surely a consolidated and reliable technique, attention should be paid in any case also to alternative low invasive techniques for sampling as the ones applied for small punch or impression creep specimen preparation.

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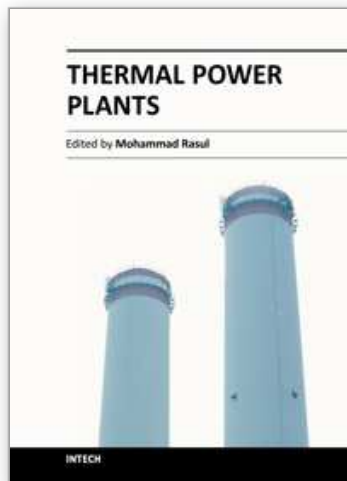
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Thermal power plants are one of the most important process industries for engineering professionals. Over the past few decades, the power sector has been facing a number of critical issues. However, the most fundamental challenge is meeting the growing power demand in sustainable and efficient ways. Practicing power plant engineers not only look after operation and maintenance of the plant, but also look after a range of activities, including research and development, starting from power generation, to environmental assessment of power plants. The book *Thermal Power Plants* covers features, operational issues, advantages, and limitations of power plants, as well as benefits of renewable power generation. It also introduces thermal performance analysis, fuel combustion issues, performance monitoring and modelling, plants health monitoring, including component fault diagnosis and prognosis, functional analysis, economics of plant operation and maintenance, and environmental aspects. This book addresses several issues related to both coal fired and gas turbine power plants. The book is suitable for both undergraduate and research for higher degree students, and of course, for practicing power plant engineers.

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