

Chapter 2

Conventional Heat-Resistant Steels

Abstract A change of the slope at about 660 °C on the dilatometry curve of 9Cr martensitic heat-resistant steel during heating process is explained by the large amount of carbonitride precipitation in the steel. The normalising temperature has little effect on mechanical properties of 10Cr steel at room temperature, while the tempering temperature has a greater effect. The toughness increases with increasing tempering temperature. Laves phase is one of the most significant precipitates in ferritic/martensitic heat-resistant steels. Co in the steel could accelerate the growth of Laves phase. Coalescence of the large Laves phase precipitates would lead to the brittle intergranular fracture. The nitride-strengthened martensitic heat-resistant steel is precipitation strengthened only by nitrides. In the latter part of the chapter, the effect of nitride precipitation behaviour on the impact toughness is discussed. When the tempering temperature is increased, a large amount of nitrides form in the matrix. The impact energy is greatly increased. The ductile-brittle transition temperature also decreases when the tempering temperature is increased from 650 to 750 °C. The nitride precipitation while increasing tempering temperature is responsible for the improved impact toughness.

2.1 Key Alloying Elements and Alloy-Design Philosophy of 9–12Cr Steels

The chemical compositions of the typical 9–12 %Cr ferritic/martensitic heat-resistant steels have been widely reported in literature (Klueh and Nelson 2007; Huang et al. 2004a). The functions of some important alloying elements such as Cr, Mo, W, Co, Nb, Ta, V, Si and B are briefly explained here. Cr is a vital element to offer the high oxidation resistance and provide Cr_{23}C_6 precipitates for the steels. It has been revealed that the optimum Cr content is 9 %, by which the longest creep life could be achieved (Masuyama 2001). However, in order to obtain better oxidation resistance, the Cr content was increased to 10–12 %, although this might decrease

the rupture life slightly. Mo and W could improve the high-temperature strength by increasing the binding force among atoms but the Fe_2W Laves phase could be formed during long time service at high temperature. Co can improve the Curie point, reduce the diffusivities of atoms and decrease the growth rate of M_{23}C_6 carbides (Gustafson and Ågren 2001). Boron was also revealed to improve creep strength by inhibiting the growth of M_{23}C_6 carbides (Abe 2007; Abe et al. 2007a). Nb, Ta and V are added to form MX type of carbonitrides to make an important contribution to the creep strength. However, Nb and Ta are easy to form carbonitrides at relatively high temperature in the austenite region while V is in the ferrite at low temperature. Ta, rather than Nb, is a low activation element. Si can improve the oxidation resistance (Ennis and Quadakkers 2002; Ishitsuka et al. 2004). Si has also been revealed to accelerate the precipitation of Laves phase (Aghajani et al. 2009a, b).

2.2 Slope Change on Dilatometry Curve

In order to save fossil fuel resources and reduce CO_2 gas emissions, (ultra) supercritical thermal power generation technology is currently being actively developed. 9–12 %Cr ferritic/martensitic steel is a new generation of ultra-high strength creep-resistant steels widely used in (ultra) supercritical thermal power generating units (Wang et al. 2003; Zhao 2000; Yang et al. 2004). When measuring static phase transition points of vacuum induction melted 9Cr martensitic steel (Table 2.1), slope change in the dilatometry curve before the ferrite to austenite phase transition occurs. Kapoor et al. (2003) studied this phenomenon in maraging steel in detail and found that with the increase of the heating rate, the change in the slope becomes smaller. The slope change in the 9Cr martensitic steels is significantly different from Kapoor et al. (2003)'s results. When the heating rate for the martensitic steel is only $0.05\text{ }^\circ\text{C/s}$, the slope change in the dilatometry curve is similar to the slope change in maraging steel at heating rate of $55\text{ }^\circ\text{C/s}$, but is quite different from maraging steel with the heating rate of $0.055\text{ }^\circ\text{C/s}$. This section is concerned with slope changes of the dilatometry curve of the 9Cr martensitic steel, during slow heating before the phase transition temperature.

Table 2.1 Chemical compositions of some conventional heat-resistant steels (wt%)

Steel	C	Cr	Mn	W	V	N	Si	Mo	Nb	Ni	Other
9Cr	0.089	8.58	0.50	1.65	0.18	0.040	0.31	0.40	0.060	0.39	1.64Co
10Cr	0.088	10.42	0.50	2.55	0.18	0.058	0.31	0.40	0.056	0.33	2.19Co
P92	0.11	8.77	0.46	1.73	0.17	0.048	0.37	0.42	0.057	0.41	0.15Cu
NS	0.005	8.63	1.06	1.53	0.19	0.033	—	—	0.062	—	1.47Co

2.2.1 Maximum Precipitation Temperature

The microstructures of the 9Cr steel at the original rolled state and after heat treatment at three temperatures are shown in Fig. 2.1. The prior austenite grain boundaries in the microstructure of original rolled steel are not clear (Fig. 2.1a). Grain boundary contours of the steel heated to 600 °C are not very clear under an optical microscope either (Fig. 2.1b). When it is heated to 660 and 750 °C, the prior austenite grain boundaries are clearer in the microstructure of the steel, with small differences in the microstructure of the two (Fig. 2.1c, d, respectively). There is a darker shade after etching, compared to the previous two conditions.

When the steel is heated at 600 °C, a small amount of precipitates form on the prior austenite grain boundaries. They sketch out the grain boundaries of austenite grains, which reveal a pancake-like shape. A certain amount of precipitates has formed in the matrix. When the steel is heated to 660 and 750 °C, compared to the steel heated to 600 °C, the number of precipitates in the microstructure within the grain and on grain boundaries increases significantly. The distribution is denser, and depicts the prior austenite grain boundaries showing the pancake

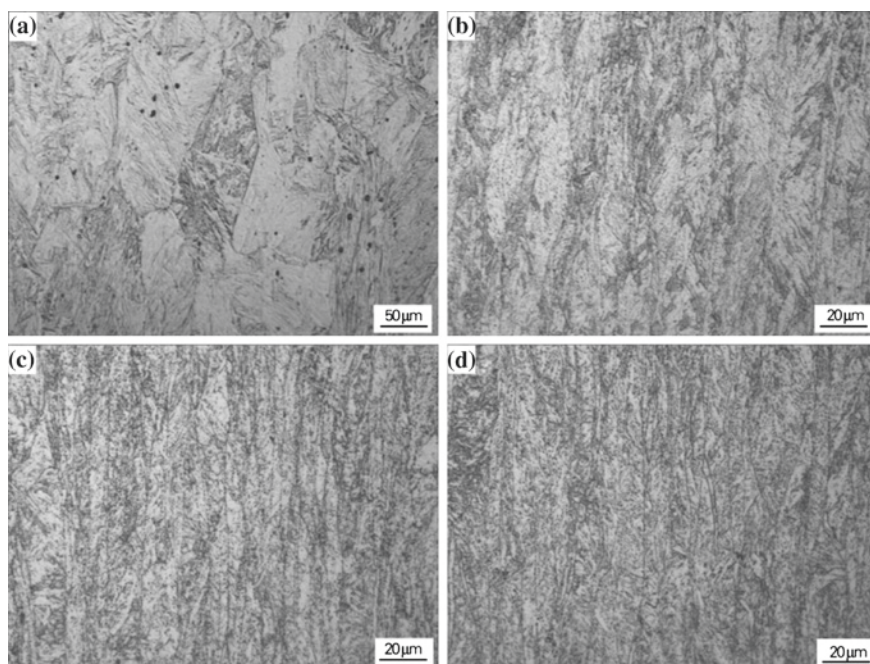


Fig. 2.1 Microstructure of 9Cr steel after heat treatment at different temperatures. **a** As-rolled; **b** 600 °C; **c** 660 °C; **d** 750 °C. (Reproduced with permission from Hu et al. 2009a)

formation of austenite after rolling. Also, precipitates have smaller size and dispersed distribution in the microstructure of steel, and are not linked together into lines on the boundaries, after heating to 600 °C. In the steel heated to 660 and 750 °C, precipitates are larger in size. A large number of precipitates are distributed along the grain boundaries, outlining the contours of the grain boundaries. The size of precipitates on the grain boundary is significantly larger than the size of the precipitate inside the grain. The microstructural morphology is the typical structure of 9Cr martensitic steel. The distribution of a large number of slightly larger size $M_{23}C_6$ (M mainly Cr and Fe elements) type grain boundary carbide precipitates strengthens grain boundaries. MX (M is Nb and V elements, and X is C and N elements) type carbonitride precipitation is dispersed within the grains and strengthen the matrix phase (Taneike et al. 2004; Abe et al. 2007b).

Carbonitride precipitates in large quantity at 660 °C are the cause of slope change in the dilatometry curve of the 9Cr steel. Slope change temperature of the curve is the maximum precipitation temperature of the 9Cr steel. There are two main ways of carbonitride precipitation. One is the precipitate nucleation on grain boundary, and the other is precipitate nucleation on dislocation. Precipitation nucleation on grain boundary generally precedes the precipitation nucleation on dislocation. Martensite is a non-equilibrium state of the microstructure, in which there are many defects. In the process of the rolled steel being heated at 600 °C, only the grain boundary, lath boundaries and certain areas having high stored energy due to local deformation can produce precipitation. Therefore, at this time the precipitates are mainly at grain boundaries, lath boundaries and the total amount of precipitation is small (Fig. 2.2a, b). When the temperature is raised to the fastest precipitation temperature, precipitation is not only in the grain boundary and lath boundaries, but also a large number of precipitates form in the

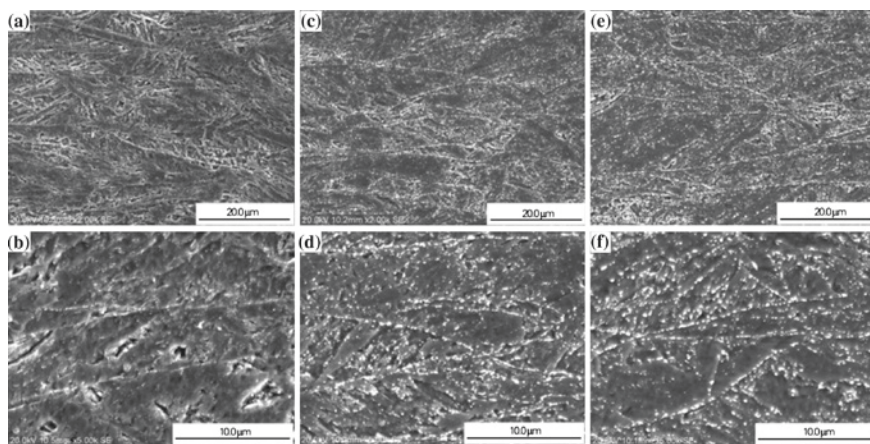


Fig. 2.2 SEM images of 9Cr steel after heat treatment at different temperatures. **a, b** 600 °C; **c, d** 660 °C; **e, f** 750 °C. (Reproduced with permission from Hu et al. 2009a)

lath interior. At this time, there is a large increase in the total precipitation amount. Due to the precipitation of carbonitrides in 9Cr steel, large amounts of carbon and nitrogen in solid solution are consumed, reducing the lattice distortion of the martensite. Therefore, the maximum precipitation nucleation temperature of the steel is also when the slope change in the dilatometry curve occurs. The precipitation of carbonitride precipitates in microalloyed steel has the following rules. A variety of carbonitride precipitates in microalloyed steel have maximum nucleation rate at temperature of about 600 °C, and the fastest precipitation temperature is about 700 °C. Thus, in the heating process, when the temperature is higher than 600 °C but lower than 660 °C, carbonitrides already have nucleation, but cannot grow a lot. Only in part of the high-energy region are precipitates capable of forming, as previously mentioned on the grain boundaries and lath boundaries. When the temperature reaches 660 °C, a large number of carbonitrides, already nucleated, rapidly grow in the matrix. This process of change causes the slope change in the dilatometry curve. At 660 °C (Fig. 2.2c, d) and above, precipitation of carbonitride is substantially complete. Compared with steel heated to 750 °C (Fig. 2.2e, f), the number and distribution of the precipitates have no major change.

2.2.2 Number and Size of Precipitates and the Degree of the Change in Dilation Slope

Kapoor et al. (2003) studied the influence of heating rate on maraging steel dilation behaviour, including precipitate start and end points, and martensite transformation start and end points. They found that the precipitation in maraging steel was controlled by a thermal diffusion mechanism. With increasing heating rate, precipitation behaviour in maraging steel was suppressed.

Maraging steels mainly rely on ageing precipitation hardening. Precipitation amount and number are much larger than in 9Cr martensitic steel. Under rapid heating, there are still a considerable amount of precipitates, comparable to precipitation in 9Cr martensitic steel, resulting in a similar deflection curve. The sizes of precipitates in the two types of steels are different. During slow heating process of the two types of steels, a considerable amount of precipitates forms. The precipitation in maraging steel has bigger effect on matrix volume, relative to the carbonitrides in 9Cr steel. During slow cooling, curve deflection for maraging steel is more pronounced.

In summary, a large number of carbonitride precipitates in 9Cr martensitic steel are the reason for slope change in dilatometry curve. The temperature corresponding to the change of slope is the maximum carbonitride precipitation temperature in the heat-resistant steel. The amount of precipitation has impact on the matrix phase volume, and directly affects the shape of the dilatometry curve during the precipitation phase.

2.3 Heat Treatment

In order to conserve fossil fuel resources and reduce CO₂ greenhouse gas emissions, high strength creep-resistant steels are being actively developed to meet the requirements of improved efficiency of generating units in power plant (Toda et al. 2005). The key to improving thermal power generation efficiency is to raise the temperature and pressure of the working medium of the unit, to make it work under supercritical or ultra-supercritical conditions. Therefore, to develop supercritical and ultra-supercritical thermal power technology, the key is to develop steel having good high-temperature properties (Wang et al. 2003). Currently, the most used 9–12 %Cr ferritic heat-resistant steel in the supercritical or ultra-supercritical generating units is Mo strengthened T/P91 steel. Its enduring strength is about 90 MPa at 600 °C, 10⁵ h condition. In recent years, in order to meet the development requirements of high parameters of ultra-supercritical thermal power units, based on the alloy-design ideas of increasing W, lowering Mo and adding Co, ferritic heat-resistant steels with longer life and higher temperature creep rupture strength have been developed (Zhao 2000; Yang et al. 2004; Huang et al. 2004b). By increasing W and reducing Mo, W hardened T/P92 steel (Table 2.1) and P122 steel have been developed. The creep rupture strength can be increased to about 140 MPa, at 600 °C, for 10⁵ h. After further addition of Co in steel on the basis of T/P92 and P122, a higher level of heat-resistant steel, NF12 (10Cr steel in Table 2.1) and SAVE12 steel, has been developed, with creep rupture strength of about 180 MPa at 600 °C, for 10⁵ h (Zhou and Fan 2005; Zhou et al. 2006; Zhang 2004). While heat treatment process for T/P91, T/P92 and P122 steels has been very mature, optimal heat treatment process for NF12 and SAVE12 steels has not been reported. This section discusses heat treatment process of this type of heat-resistant steel, using research on vacuum induction melted laboratory-scale NF12 steel.

2.3.1 Mechanical Properties

The mechanical properties of the 10Cr steel (Table 2.1) are different after using different heat treatment processes. When the tempering temperature is 780 °C, the impact toughness of steel is higher. With the tempering temperature increasing, the yield strength and tensile strength of the material decrease, and ductility increases. This is entirely consistent with the general rules of the properties change of the steel material.

2.3.2 Microstructure

When the tempering temperature is 780 °C, the steel microstructure after normalising at different temperatures is shown in Fig. 2.3. The microstructure is tempered

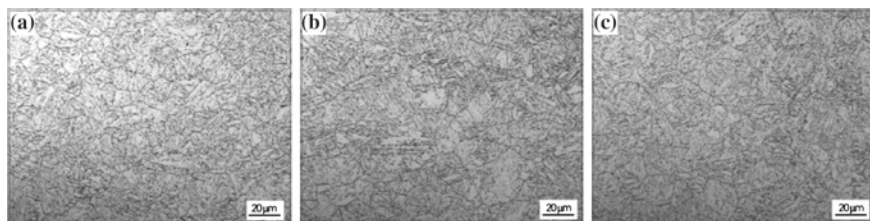


Fig. 2.3 Microstructure of 10Cr steel normalised at different temperatures. **a** 1050 °C; **b** 1080 °C; **c** 1100 °C. (Reproduced with permission from Yan et al. 2009)

martensite. The prior austenite grain size in the steel is the minimum, about 15 μm , when normalised at 1050 °C. Grain size after normalising at 1080 and 1100 °C is similar, about 25 μm .

2.3.3 Prior Austenite Grain

When the steel is normalised at 1050 °C, compared with normalising at 1080 and 1100 °C, smaller grain size is obtained. According to usual point of view, after tempering at same temperature, steel normalised at 1050 °C should have a higher strength. However, this is not the case. The steel normalised at 1050 °C has the lowest yield and tensile strength. This shows that, in martensite, for grain size within a certain range, the prior austenite grain size is no longer the major factor affecting strength of heat-resistant steel. The finer lath martensite structure affects the performance of the matrix and should be a major factor. These problems require more in-depth study. As we all know, the grain boundaries are negative factors affecting high-temperature creep rupture performance of heat-resistant steel. Many heat-resistant steels aim to minimise the amount of grain boundaries, within the allowed range. So, for this kind of ferritic heat-resistant steels, an appropriate increase in the steel normalising temperature can reduce the amount of grain boundaries while not decreasing strength.

2.3.4 Heat Treatment and Mechanical Properties

The strength of the steel is sensitive to changes in tempering temperature. With increase in the tempering temperature, the strength of the steel decreases significantly, but the toughness is largely improved and more stable. This shows that the way to strengthen the steel is mainly precipitate strengthening. After tempering at 730 °C and over, the lattice distortion in martensite structure is greatly reduced, and the dislocation density is greatly reduced. So, when the tempering temperature

risks, the changes in these strengthening factors in the matrix are small, while there will be major changes in the number, size and distribution of the precipitates in the matrix. The higher the tempering temperature, the stronger the diffusion capacity of carbon and nitrogen atoms. The nucleation of carbonitrides in the matrix is fast. A greater number of finer size precipitates can be obtained, with more uniform distribution. Such precipitation is extremely beneficial, for increasing strength and toughness of the material. However, large amount of precipitates consumes a lot of carbon and nitrogen atoms, greatly reducing the solid solution strengthening effect in martensitic matrix, but also thereby imparting better matrix ductility. Therefore, the change of strength and toughness of the steel with tempering temperature essentially reflects the changes of the amount of carbonitride phase in the matrix, and the size and distribution of precipitation, with the tempering temperature.

2.3.5 Summary

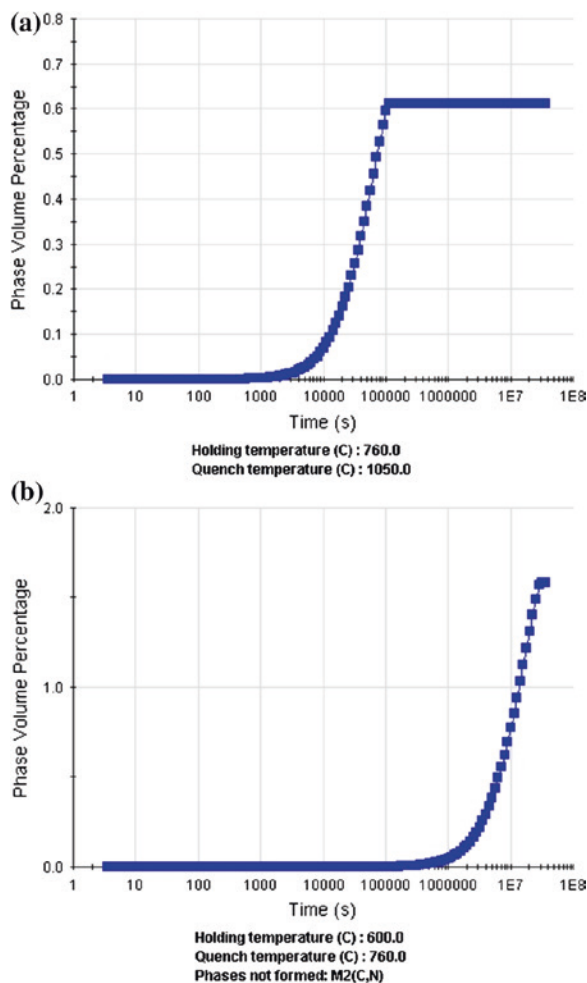
The new 10Cr heat-resistant steel contains more alloying contents relative to T/P92 (Table 2.1) and other high-quality heat-resistant steels. The steel tempering temperature should be chosen in order to ensure desirable material toughness. The main factor in the strength of steel is not the prior austenite grain size of tempered martensite. Precipitation hardening is the main mechanism of steel strengthening, impacting on the tempered martensite strength and toughness. Changes in the strength and toughness with tempering temperature essentially reflect changes of the amount, size and distribution of carbonitride precipitation in the matrix phase.

2.4 Laves Phase

2.4.1 Thermodynamic and Kinetic Calculations

The volume fraction of Laves phase in the 10Cr steel (Table 2.1) at 1050, 760 and 600 °C are 0, 0.6 and 1.6 %, respectively, in the equilibrium state, according to thermodynamic calculations. These temperatures are used for normalising, tempering and creep testing (Chap. 7), respectively. So, no Laves phase should be formed at 1050 °C, but it should exist as an equilibrium phase at 760 and 600 °C. The equilibrium amount of Laves phase at 600 °C is larger than at 760 °C. It will take time for the amount of Laves phase to reach the equilibrium. It is illustrated in Fig. 2.4a that the Laves phase starts to form at 760 °C after a short incubation period of about 30 min, but its volume percentage can just reach 0.05 % even after 90 min, the usual length of time for tempering. Therefore, in the as-tempered steel, the dominant precipitates in the microstructure are MX and $M_{23}C_6$, and most of Laves phase in the steel should form during creep exposure at 600 °C. Figure 2.4b

Fig. 2.4 Diagrams showing change of Laves phase volume percentage with time at **a** 760 °C and **b** 600 °C. (Reproduced with permission from Hu et al. 2009b)



shows that for the as-tempered steel creep tested at 600 °C, Laves phase starts to precipitate after a long incubation period of almost 140 h, but then its volume percentage increases rapidly and reaches a plateau of about 1.6 % after about 8330 h.

It is also illustrated in Fig. 2.4 that the formation of Laves phase can be clearly separated into two stages. One is the nucleation stage, which is characterised by the incubation period; the other is the growth stage, during which the volume percentage increases rapidly with time. When the growth of Laves phase is over, the coarsening stage begins. However, the volume percentage of Laves phase will keep constant in the coarsening period.

It is hinted by this calculation that Laves phase is still at the growth stage, within the rupture life of 3230 h. Therefore, in the following depiction, Laves phase will be discussed at the growth stage.

2.4.2 Initial Microstructure

In the 10Cr steel (Table 2.1), in the initial microstructure of the tempered martensite, the prior austenite grain boundaries and lath boundaries are outlined by particles of $M_{23}C_6$ and MX precipitated during tempering. The δ -ferrite phase, which often forms in the high Cr martensitic steels and is adverse to the creep rupture strength, is scarcely there. The prior austenite grain size is about 15 μm .

2.4.3 Effect of Co on Laves Phase

The driving force for precipitate growth stems from the interfacial energy and the growth rate is controlled by the volume diffusion. It is believed that Co can retard the diffusion of metal atoms in steels, because the diffusion coefficient is dependent on the Curie-temperature that is raised by Co addition. Various precipitation processes are retarded by Co. Therefore, addition of Co in this steel is supposed to inhibit the growth of Laves phase. Hald (2008) found that the size of Laves phase reached nearly 0.1 μm after about 10,000 h creep exposure and almost stayed constant at 600 °C in P92 steel (Table 2.1). Lee et al. (2006) also found that the size of Laves phase increased to nearly 0.13 μm after about 25,000 h creep exposure at 600 °C in P92 steel. However, the average size of Laves phase has arrived at about 0.2 μm after only 1600 h in the 10Cr steel. The fact that Laves phase shows higher growth rate in this 10Cr steel with Co addition than in P92 steel without Co is contradictory to the claim that Co has an effect of retarding precipitation. Co is also an important element added to maraging steels and there are also arguments on the influence of Co on the precipitate behaviour. Experiments on maraging steels confirm that Co could lower the solubility of Mo in matrix and promote the precipitation of Laves phase (Fe_2Mo). In the work on Fe-10 %Cr-6 %W alloys by Cui et al. (2001), Co was found to be responsible for enhancing growth of the Laves phase. Comparing the growth rate of Laves phase between P92 steel and the 10Cr steel, it can be inferred that Co in the latter could accelerate rather than inhibit the growth of Laves phase, which may be explained by considering that Co can prevent the formation of δ -ferrite phase so that more W and Mo can be maintained in the matrix after normalising, which could provide both more W and Mo needed for the growth of Laves phase and the driving force.

2.4.4 Summary

The Laves phase grows to a large size in a relatively short exposure time. The increasing amount of Laves phase could decrease the solid solution strengthening effect due to the consumption of dissolved W and Mo atoms. Addition of Co is believed to increase the growth rate of Laves phase.

2.5 Nitride-Strengthened Heat-Resistant Steel

The efficiency of power plants could be improved by enhancing the steam parameter. At present, heat-resistant steels for the high-steam parameter of 650 °C are being developed. This has put heat-resistant steels such as T/P91, T/P92 and E211 out of consideration because of the loss of the microstructure stability during service at the high temperature (Weisenburger et al. 2008). More advanced steels should be developed to meet this requirement.

It is well accepted in heat-resistant steels that highly stable microstructure will produce excellent creep strength. The precipitates are basically $M_{23}C_6$ and MX, the carbonitride of Nb, V or Ti. The MX-type carbonitrides show much better stability than the $M_{23}C_6$ type carbide. In order to achieve microstructure with high stability, stable precipitates such as MX-type carbonitrides are expected in heat-resistant steels.

In addition to this initial tempered martensitic microstructure, long-term microstructure stability requires attention. Such coarse precipitates as Laves phase (Fe_2W or Fe_2Mo) and Z phase ($(Cr,Nb)N$) should be delayed, although they could only form after a long service time (Sawada et al. 2006). The formation of Laves phase and Z phase is a thermally automatic process which cannot be avoided (Shen et al. 2009). However, this process can be delayed by reducing the content of tungsten, molybdenum and nitrogen.

Nitride-strengthened martensitic heat-resistant steel is developed, based on the above ideas. Following the alloy design and the mechanical properties of the nitride-strengthened martensitic steels, the excellent impact toughness of the steel after tempering will be presented.

Different from Chap. 4, this section and Sect. 2.6 are concerned with conventional nitride-strengthened martensitic heat-resistant steel, i.e. without the low activation properties.

2.5.1 Microstructure and Nitride Precipitation

The steel (NS in Table 2.1) normalised at 980 °C for 30 min has full martensitic microstructure. After normalising, the steel is tempered at 650, 700 and 750 °C for 90 min. Almost no precipitates are formed when the steel is tempered at 650 °C, as illustrated in Fig. 2.5a. The tempering temperature of 650 °C is not high enough for the nitrides to precipitate. However, when the tempering temperature is increased to 700 °C, the precipitates are noticed in the matrix (Fig. 2.5b). Finally, when the tempering temperature is increased to 750 °C, Fig. 2.5c, the quantity of the precipitates increases promptly and the nano-sized precipitates are in a sharper and clearer shape than those tempered at 700°C. 750°C is widely accepted as the peak precipitation temperature of nitrides.

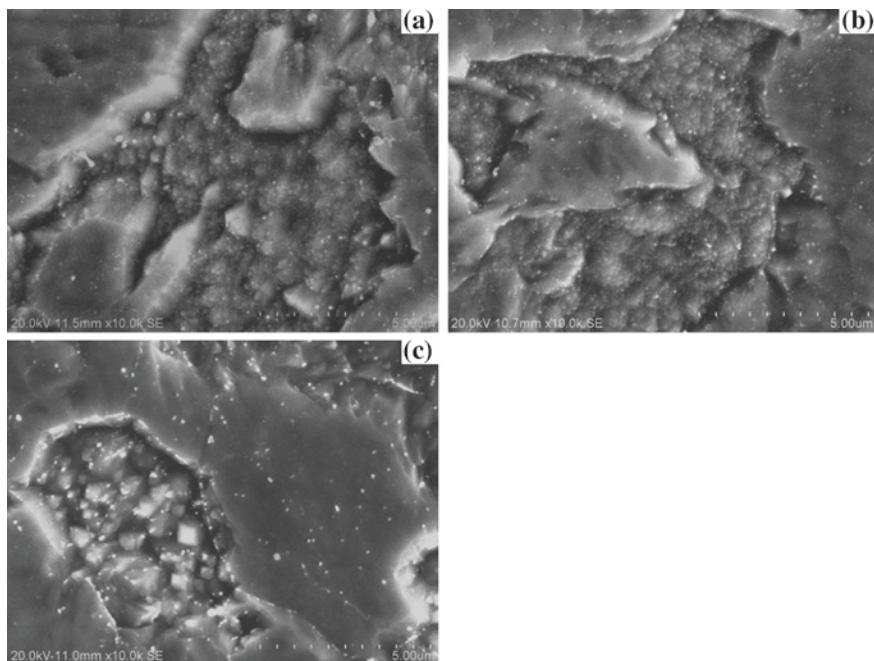


Fig. 2.5 The tempered microstructure of the nitride-strengthened steel at **a** 650 °C, **b** 700 °C, **c** 750 °C. (Reproduced with permission from Zhang et al. 2012)

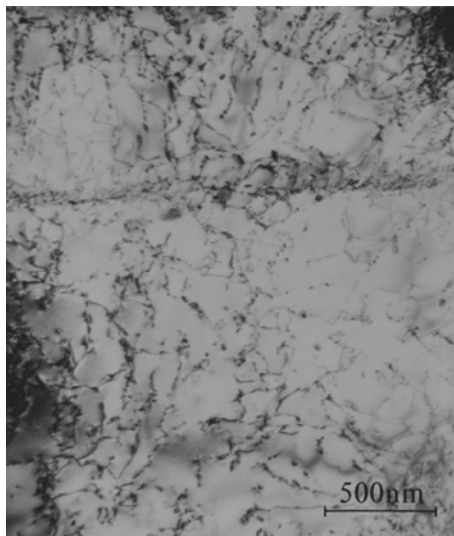
Since the carbon content in the steel is decreased to such a low level of 0.005 % in wt% (Table 2.1), it is very difficult to form carbides in the steel. This is proved by the microstructure shown in Fig. 2.5 that no such big size carbides as Cr_{23}C_6 are observed. However, the nitrogen is at a high level in the steel. Therefore, it is reasonable to believe that the precipitates formed in the steel are nitrides of niobium and vanadium, which are very fine and in the cubic shape shown in Fig. 2.6.

So, the precipitates formed in the matrix during tempering are MX-type nitrides. The tempering temperature is critical to the nitride precipitation. Martensitic strengthened by only thermally stable nitrides is a desirable microstructure. Therefore, it is logical to speculate that the nitride-strengthened martensitic heat-resistant steel should have good long-term creep strength due to the microstructure stability (Sawada et al. 2004).

2.5.2 Mechanical Properties, Ductile-Brittle Transition Temperature and Fractography

The precipitation behaviour of nitrides is certain to affect the mechanical properties. The strength changes with the tempering temperature. The strength rapidly

Fig. 2.6 TEM image of the steel tempered at 750 °C for 90 min, showing the MX-type nitrides. (Reproduced with permission from Zhang et al. 2012)

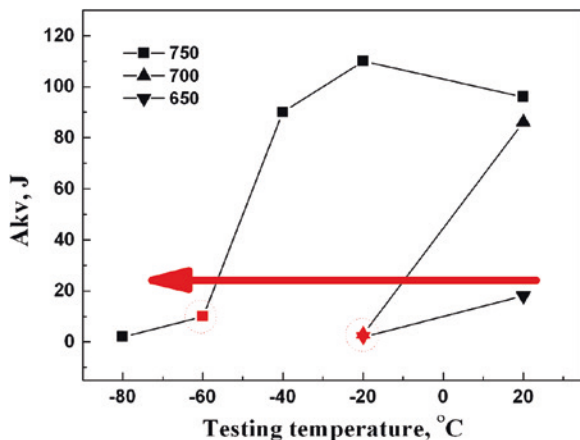


decreases with increasing tempering temperature, especially when tempered at 750 °C. The room temperature yield strength nearly decreases by 100 MPa when the tempering temperature is raised from 650 to 700 °C and by 150 MPa from 700 to 750 °C. The room temperature yield strength decreases more quickly when the steel is tempered at 750 °C. The commercial P92 steel (Table 2.1) was reported in literature to have the yield strength of 345 MPa and the tensile strength of 390 MPa when tempered at 750 °C (Mungole et al. 2008). Compared with P92, the NS steel tempered at 750 °C still has relatively higher yield strength of 515 MPa and tensile strength of 625 MPa. It is proved that the NS steel can have comparable room temperature strength with P92 steel.

The high-temperature yield strength of 600 °C also decreases when the steel is tempered at 750 °C. The yield strength at 600 °C is reduced by 69 MPa when the tempering temperature is increased from 650 to 700 °C and by 86 MPa from 700 to 750 °C. The NS steel tempered at 750 °C has high-temperature yield strength of 307 MPa and tensile strength of 342 MPa, which are also comparable to those of the commercial P92.

Figure 2.7 demonstrates the toughness and the ductile-brittle transition temperature (DBTT) dependence on the tempering temperature. The half-size Charpy V-notch (CVN) impact specimens tempered at 650 °C can only absorb 18 J energy at room temperature and 2 J at −20 °C, which indicates that the steel tempered at 650 °C has a high DBTT of above room temperature. When the steel is tempered at 700 °C, the CVN specimen can take in energy up to 86 J at room temperature but still decreases to 3.5 J at −20 °C, which indicate that the steel tempered at 700 °C has a DBTT of about 0 °C. However, when the tempering temperature is increased to 750 °C, the steel has not only good toughness of 96 J at room temperature, but also similar high toughness at −20 °C, 89 J at −40 °C but

Fig. 2.7 Half-size Charpy value of the steel at different temperatures. (Reproduced with permission from Zhang et al. 2012)



11 J at $-60\text{ }^{\circ}\text{C}$, which indicate that the steel tempered at $750\text{ }^{\circ}\text{C}$ has a low DBTT of around $-50\text{ }^{\circ}\text{C}$. The DBTT of the steel is greatly decreased by increasing the tempering temperature.

The steel broken with low-impact energy exhibits cleavage fracture characteristic, while the steel broken with high-impact energy presents dimple fracture characteristic. The steel tempered at $650\text{ }^{\circ}\text{C}$ has brittle cleavage fracture at both room temperature and $-20\text{ }^{\circ}\text{C}$. The steel tempered at $700\text{ }^{\circ}\text{C}$ has ductile dimple fracture at room temperature, but brittle cleavage fracture at $-20\text{ }^{\circ}\text{C}$ (Zhang et al. 2012). The steel tempered at $750\text{ }^{\circ}\text{C}$ does not exhibit brittle cleavage fracture until the temperature is decreased to $-60\text{ }^{\circ}\text{C}$. When the temperature is above $-40\text{ }^{\circ}\text{C}$, the surface of the impact fracture shows ductile dimple fracture. In the dimples on the fracture surface, there are many big size particles.

2.6 Strengthening Mechanisms of Nitride-Strengthened Heat-Resistant Steel

2.6.1 Effect of Nitride Precipitation on Yield Strength

The strength of the steel shows normal response to the increasing tempering temperature, i.e. the strength decreases with the increase of tempering temperature. However, it is noticeable that the room temperature yield strength decreases much quicker when the tempering temperature is increased from 700 to $750\text{ }^{\circ}\text{C}$ than from 650 to $700\text{ }^{\circ}\text{C}$, as described in Sect. 2.5.2. The (more) complete precipitation of nitrides should be responsible for the quicker decrease. It is known that the formation of precipitates consumes dislocations. The nitride precipitation will decrease much the number of dislocations in the matrix, resulting in weakening of dislocation strengthening. On the other hand, the formation of nitrides consumes

the dissolved nitrogen which could provide strong solid solution strengthening. Therefore, although the nitride precipitation could produce precipitation strengthening, it is not enough to compensate for the loss of dislocation strengthening and nitrogen solid solution strengthening.

However, the high-temperature yield strength of 600 °C does not show an obviously accelerated decrease when tempering temperature is increase to 750 °C. It could be interpreted from two views. The first one is that, at the high temperature of 600 °C, the dislocation is easier to move and annihilate. The advantage of high dislocation density is no longer obvious. The second view is that the more movable dislocation would become easier to reproduce because of nitride precipitation in the steel tempered at 750 °C. Therefore, the precipitation strengthening would mainly compensate for the loss of nitrogen solid solution strengthening. Hence, accelerated reduction is not observed in the high-temperature yield strength of 600 °C.

2.6.2 Dependence of DBTT on Tempering Temperature

The DBTT decreases from above room temperature to −50 °C when the tempering temperature is increased from 650 to 750 °C. In order to reach a clear understanding on DBTT of the steel, it is critical to take an investigation on the yield strength. That is the reason that a detailed discussion on the effect of tempering temperature on the yield strength has been made above.

It is widely believed that the cleavage fracture stress changes with temperature. Thus, it is easy to understand, in a phenomenological way, that the DBTT will be reduced with the decrease of yield strength when the tempering temperature is increased from 650 to 750 °C (Sawada et al. 2003). As discussed previously, the nitride precipitation will lead to the decrease of yield strength. So, it actually can be interpreted that the DBTT decrease is really associated with the nitride precipitation. The nitride precipitation has improved the impact toughness and decreased the DBTT by toughening the steel.

In summary of Sects. 2.5 and 2.6, the nitride precipitation in the steel reaches its peak when the tempering temperature is increased to 750 °C. Tempering at 650 °C or 700 °C could not induce the nitride precipitation, at least not to effective levels. The steel could achieve a martensitic microstructure strengthened by only nitrides after tempering at 750 °C. This microstructure is expected to have good thermal stability and high creep strength. The steel tempered at 750 °C could achieve comparable mechanical properties with the commercial P92 at both room temperature and 600 °C. The room temperature impact toughness of the steel is greatly enhanced from several Joules to nearly a hundred Joules (half-size) by increasing tempering temperature from 650 to 750 °C. The DBTT shows a great dependence on the tempering temperature. It could be reduced from above room temperature to −50 °C when the tempering temperature is increased from 650 to 750 °C.

References

- Abe F (2007) Behavior of boron in 9Cr heat resistant steel during heat treatment and creep deformation. *Key Eng Mater* 345–346:569–572. doi:[10.4028/www.scientific.net/KEM.345-346.569](https://doi.org/10.4028/www.scientific.net/KEM.345-346.569)
- Abe F, Semba H, Sakuraya T (2007a) Effect of boron on microstructure and creep deformation behavior of tempered martensitic 9Cr steel. *Mater Sci Forum* 539–543:2982–2987. doi:[10.4028/www.scientific.net/MSF.539-543.2982](https://doi.org/10.4028/www.scientific.net/MSF.539-543.2982)
- Abe F, Taneike M, Sawada K (2007b) Alloy design of creep resistant 9Cr steel using a dispersion of nano-sized carbonitrides. *Int J Press Vessels Pip* 84:3–12. doi:[10.1016/j.ijpvp.2006.09.003](https://doi.org/10.1016/j.ijpvp.2006.09.003)
- Aghajani A, Somsen Ch, Eggeler G (2009a) On the effect of long-term creep on the microstructure of a 12 % chromium tempered martensite ferritic steel. *Acta Mater* 57:5093–5106. doi:[10.1016/j.actamat.2009.07.010](https://doi.org/10.1016/j.actamat.2009.07.010)
- Aghajani A, Richter F, Somsen C, Fries SG, Steinbach I, Eggeler G (2009b) On the formation and growth of Mo-rich Laves phase particles during long-term creep of a 12 % chromium tempered martensite ferritic steel. *Scr Mater* 61:1068–1071. doi:[10.1016/j.scriptamat.2009.08.031](https://doi.org/10.1016/j.scriptamat.2009.08.031)
- Cui J, Kim IS, Kang CY, Miyahara K (2001) Creep stress effect on the precipitation behavior of Laves phase in Fe-10 %Cr-6 %W alloys. *ISIJ Int* 41:368–371. doi:[10.2355/isijinternational.41.368](https://doi.org/10.2355/isijinternational.41.368)
- Ennis PJ, Quadackers JW (2002) The steam oxidation resistance of 9–12 %Cr steels. In: Lecomte-Beckers J, Carton M, Schubert F, Ennis PJ (eds) *Proceedings of the seventh Liege conference on materials for advanced power engineering*. Liege, Belgium, pp 1131–1142
- Gustafson Å, Ågren J (2001) Possible effect of Co on coarsening of $M_{23}C_6$ carbide and Orowan stress in a 9 %Cr steel. *ISIJ Int* 41:356–360. doi:[10.2355/isijinternational.41.356](https://doi.org/10.2355/isijinternational.41.356)
- Hald J (2008) Microstructure and long-term creep properties of 9–12 %Cr steels. *Int J Press Vessels Pip* 85:30–37. doi:[10.1016/j.ijpvp.2007.06.010](https://doi.org/10.1016/j.ijpvp.2007.06.010)
- Hu P, Yan W, Shan Y, Yang K (2009a) Slope change on dilation-temperature curve of 9Cr martensitic heat resistant steel. *Heat Treat Met* 34(4):52–55
- Hu P, Yan W, Sha W, Wang W, Guo Z, Shan Y, Yang K (2009b) Study on Laves phase in an advanced heat-resistant steel. *Front Mater Sci Chin* 3:434–441. doi:[10.1007/s11706-009-0063-7](https://doi.org/10.1007/s11706-009-0063-7)
- Huang Q, Li J, Chen Y (2004a) Study of irradiation effects in China low activation martensitic steel CLAM. *J Nucl Mater* 329–333:268–272. doi:[10.1016/j.jnucmat.2004.04.056](https://doi.org/10.1016/j.jnucmat.2004.04.056)
- Huang Q, Yu J, Wan F, Li J, Wu Y (2004b) The development of low activation martensitic steels for fusion reactor. *Chin J Nucl Sci Eng* 24(1):56–64
- Ishitsuka T, Inoue Y, Ogawa H (2004) Effect of silicon on the steam oxidation resistance of a 9 %Cr heat resistant steel. *Oxid Met* 61:125–142. doi:[10.1023/B:OXID.0000016280.81734.3f](https://doi.org/10.1023/B:OXID.0000016280.81734.3f)
- Kapoor R, Kumar L, Batra IS (2003) A dilatometric study of the continuous heating transformations in 18wt. % Ni maraging steel of grade 350. *Mater Sci Eng A* 352:318–324. doi:[10.1016/S0921-5093\(02\)00934-6](https://doi.org/10.1016/S0921-5093(02)00934-6)
- Klueh RL, Nelson AT (2007) Ferritic/martensitic steels for next generation reactors. *J Nucl Mater* 371:37–52. doi:[10.1016/j.jnucmat.2007.05.005](https://doi.org/10.1016/j.jnucmat.2007.05.005)
- Lee JS, Ghassemi-Armaki H, Maruyama K, Muraki T, Asahi H (2006) Causes of breakdown of creep strength in 9Cr–1.8W–0.5Mo–VNb steel. *Mater Sci Eng A* 428:270–275. doi:[10.1016/j.msea.2006.05.010](https://doi.org/10.1016/j.msea.2006.05.010)
- Masuyama F (2001) History of power plants and progress in heat resistant steels. *ISIJ Int* 41:612–625. doi:[10.2355/isijinternational.41.612](https://doi.org/10.2355/isijinternational.41.612)
- Mungole MN, Sahoo G, Bhargava S, Balasubramaniam R (2008) Recrystallised grain morphology in 9Cr 1Mo ferritic steel. *Mater Sci Eng A* 476:140–145. doi:[10.1016/j.msea.2007.04.105](https://doi.org/10.1016/j.msea.2007.04.105)
- Sawada K, Kimura K, Abe F (2003) Mechanical response of 9 %Cr heat-resistant martensitic steels to abrupt stress loading at high temperature. *Mater Sci Eng A* 358:52–58. doi:[10.1016/S0921-5093\(03\)00326-5](https://doi.org/10.1016/S0921-5093(03)00326-5)

- Sawada K, Taneike M, Kimura K, Abe F (2004) Effect of nitrogen content on microstructural aspects and creep behavior in extremely low carbon 9Cr heat-resistant steel. *ISIJ Int* 44:1243–1249. doi:[10.2355/isijinternational.44.1243](https://doi.org/10.2355/isijinternational.44.1243)
- Sawada K, Kushima H, Kimura K (2006) Z-phase formation during creep and aging in 9–12 %Cr heat resistant steels. *ISIJ Int* 46:769–775. doi:[10.2355/isijinternational.46.769](https://doi.org/10.2355/isijinternational.46.769)
- Shen YZ, Kim SH, Cho HD, Han CH, Ryu WS (2009) Precipitate phases of a ferritic/martensitic 9 %Cr steel for nuclear power reactors. *Nucl Eng Des* 239:648–654. doi:[10.1016/j.nucengdes.2008.12.018](https://doi.org/10.1016/j.nucengdes.2008.12.018)
- Taneike M, Sawada K, Abe F (2004) Effect of carbon concentration on precipitation behavior of $M_{23}C_6$ carbides and MX carbonitrides in martensitic 9Cr steel during heat treatment. *Metall Mater Trans A* 35A:1255–1262. doi:[10.1007/s11661-004-0299-x](https://doi.org/10.1007/s11661-004-0299-x)
- Toda Y, Iijima M, Kushima H, Kimura K, Abe F (2005) Effects of Ni and heat treatment on long-term creep strength of precipitation strengthened 15Cr ferritic heat resistant steels. *ISIJ Int* 45:1747–1753. doi:[10.2355/isijinternational.45.1747](https://doi.org/10.2355/isijinternational.45.1747)
- Wang H, Gu X, Feng H (2003) Development of supercritical thermal power boiler materials. *Shandong Electr Pow* (1):73–75
- Weisenburger A, Heinzl A, Müller G, Muscher H, Rousanov A (2008) T91 cladding tubes with and without modified FeCrAlY coatings exposed in LBE at different flow, stress and temperature conditions. *J Nucl Mater* 376:274–281. doi:[10.1016/j.jnucmat.2008.02.026](https://doi.org/10.1016/j.jnucmat.2008.02.026)
- Yan W, Hu P, Zhao L, Shan Y, Yang K (2009) Heat treatment of a new type heat-resistant steel NF12. *Heat Treat Met* 34(9):59–61
- Yang F, Li W, Ren Y (2004) Alloy steel used for supercritical and ultra supercritical pressure boiler. *Electr Equip* 5(10):41–46
- Zhang X (2004) Material options for supercritical/super-supercritical boilers. *Pow Equip* 18(5):307–312. doi:[10.3969/j.issn.1671-086X.2004.05.015](https://doi.org/10.3969/j.issn.1671-086X.2004.05.015)
- Zhang W, Yan W, Sha W, Wang W, Zhou Q, Shan Y, Yang K (2012) The impact toughness of a nitride-strengthened martensitic heat resistant steel. *Sci China Technol Sci* 55:1858–1862. doi:[10.1007/s11431-012-4903-9](https://doi.org/10.1007/s11431-012-4903-9)
- Zhao Z (2000) The new materials for supercritical and ultra-supercritical power plant units. *Mater Mech Eng* 24(6):1–4. doi:[10.3969/j.issn.1000-3738.2000.06.001](https://doi.org/10.3969/j.issn.1000-3738.2000.06.001)
- Zhou R, Fan C (2005) Review of material research and material selection for ultra-supercritical power plants. *Electr Pow* 38(8):41–47. doi:[10.3969/j.issn.1004-9649.2005.08.012](https://doi.org/10.3969/j.issn.1004-9649.2005.08.012)
- Zhou R, Fan C, Li Y (2006) Current situation and development of production of heat-resistant materials for power generation. *Steel Pipe* 35(1):19–25. doi:[10.3969/j.issn.1001-2311.2006.01.004](https://doi.org/10.3969/j.issn.1001-2311.2006.01.004)

9-12Cr Heat-Resistant Steels

Yan, W.; Wang, W.; Shan, Y.; Yang, K.; Sha, W.

2015, XIV, 218 p. 77 illus., 25 illus. in color., Hardcover

ISBN: 978-3-319-14838-0