LONG TERM MICROSTRUCTURAL EVOLUTION OF 9-12%CR STEEL GRADES FOR STEAM POWER GENERATION PLANTS

A. Di Gianfrancesco, S. Tiberi Vipraio, D. Venditti

Centro Sviluppo Materiali SpA, Via di Castel Romano 100, Rome, 00128, Italy
E-mail: a.digianfrancesco@c-s-m.it - Tel. & Fax: +39-06-5055275; +39-06-5055461

Abstract

The 9%Cr steel grades were developed in the last 25 year in order to favourite the target of the improvement of the steam temperature and pressure necessary to increase the efficiency of the modern coal fired power plant for electricity production. Now a relevant experience in testing and service conditions has been generated and it is possible to produce consistent assessments of the mechanical and creep behaviours for long term application.

On the other hand the further trials to increase the Chromium content to improve the corrosion-oxidation behaviours of the 9%Cr grades, despite the very promising short term properties, generate unpredicted premature failure after long term exposure. This failure was identified in the instability of the compositions with the appearance of Z-phase, with consequent drop down of the creep behaviours below their parent 9%Cr grades.

This paper summarize the maturated knowledge in the field of the microstructural evolution of the 9-12%Cr steels, as well as, the current status of development of these steel grades.

1. INTRODUCTION

In the last 25 years many R&D actions in USA, Europe and Japan, have been carried out to increase the efficiency and to reduce the CO₂ emissions of coal fired power plants. The improvement in the behaviours of the high temperature resistant steels jointly with the introduction new modelling tools for the design of the burners and combustion processes, as well as, construction of boiler and turbine components generate a progressive increase of temperatures and pressures used in the advanced coal fired Ultra Super Critical plants that recently reached 600-620°C temperature and 250-300 bar of pressure of steam temperature.

Several new 9-12%Cr martensitic steels developed, such as ASTM Grades 91, 92 and 911, are currently used in the new high efficiency Ultra Super Critical power plants [1, 2, 3].

Creep resistant 9-12%Cr steels were originally developed for gas turbine applications in the 50’s. Steels like 12CrMoVNb and X19CrMoVNbN-11-1, developed in UK, France and Germany, showed a high hardenability due to the high content of alloying element, so that after heat treatment, a martensitic microstructure was formed even in large sections at relatively low cooling rates. In the mid of 70’s the 9Cr1Mo alloy, used for tubing in the UK, was modified by ORNL with the addition of V, Nb and N and was included in the ASTM standard as Grade 91. The optimization of alloy content resulted in improved fracture toughness, weldability and very stable long term creep properties. At 600°C the first forecast was established as 105 MPa to obtain the fracture in 100,000 hours: around 50% greater than that of the previous generation of 12CrMoVNb steels [4].

In the same years, a similar work began in Japan on materials suitable for rotor forgings. The Japanese steels were similar in concept to the modified 9Cr1Mo steel, but with a slightly higher Cr (about 10%), C (about 0.14%) and Mo contents and addition of W amount. The increase of C content, together with optimized tempering treatments, enabled higher creep resistance and improved levels of fracture toughness to be achieved [5].
The worldwide efforts in the field of high alloyed Cr-Mo steels resulted in the most recent ASTM Grades 91, 92, 911 and more recently 122, with even higher content of Cr (up to 12.5%), to improve the resistance to oxidation and corrosion, W (up to 2.5%), Co (up to 3%) and Cu (1.70% max) amounts. Some boron was added too (0.007% max) to improve creep properties. These steels are commonly known as “advanced Cr ferritic-martensitic steels” [6].

Short creep tests (elaborated with time-temperature-parameter methods, i.e. Larson Miller equation) usually give an over-estimation of the long-term creep properties of 9-12%Cr steels. The different results of the creep assessments of Grade 92 (also known as NF616) are a typical example: the creep resistance of this grade was initially evaluated in 600°C/160MPa/100,000h by means of the extrapolation of short creep tests; recently the assessed creep strength was reduced to 113MPa (ECCC assessment, 2005) [7, 8, 9]. The slight lowering of creep strength in 9%Cr steels at very long times is a consequence of the availability of more long term creep data points which corrects the original over-estimation of their creep strength.

During high temperature service, 9-12%Cr steels undergo a continuous degradation of their initial microstructure. In order to improve creep resistance, specific alloying additions are designed to promote the precipitation of small particles, such as nitrides and carbides, to retard the microstructural changes. Generally, small variations of alloying elements can lead to large differences in creep strength of metals [10, 11, 12].

It has been recently found [13,14] that the precipitation of the modified Z-phase, the complex nitride Cr(V,Nb)N, occurs in 9-12%Cr steels during exposure at temperatures in the range between 600°C and 700°C and it has been accredited with a very detrimental effect on the creep strength in 12%Cr steels. It is currently assumed that the Z-phase formation is responsible for the decrease in creep properties, since it consumes the small and finely distributed MN nitrides, which are considered to have important strengthening effects against hot deformation. In addition, Z-phase forms as large particle and does not contribute to precipitation strengthening.

Recently, the Z-phase formation has investigated in commercial 9-12%Cr steels by the TUD/DONG Energy/CSM group [15-18] and a thermodynamic model using experimental data and a literature survey has been proposed. They concluded that the driving force for Z-phase formation increases with increasing the chromium content, which explains why advanced 12%Cr steels suffer from abundant formation of Z-phase, whereas 9%Cr steels do not.

Sawada et al. [19, 20] have demonstrated that, after creep exposure, Z-phase particles are located preferentially on prior austenite grain boundaries, packet boundaries and delta ferrite grains. He also showed that the content of metallic elements of the Z-phase does not depend on the precipitation sites. Very little is known about the time-temperature regions in which Z-phase formation may occur and there are still unresolved questions about the formation mechanism.

2. MATERIALS AND PROPERTIES

The investigated materials come from industrial tubes and pipes of Grades 91, 911, 92, 122, and X20. The chemical compositions of the tubes, their mechanical properties (tensile and hardness) and heat treatment conditions were in agreement with ASTM A213 (for tubes) and ASTM A335 (for pipes) and DIN requirements (Table 1) [21, 22].

All tubular product are supplied in normalized (1040-1080°C) and tempered (740-780°C) conditions, in order to confer the mechanical properties at high temperature. The normalizing gives the desired martensitic microstructure and provides a good carbide and nitride solubilisation into the matrix as well as a homogeneous microstructure. The subsequent tempering softens the material and promotes the formation of $M_23C_6$ and fine MX precipitates, resulting in a high creep resistance. The desired final microstructure is constituted of a tempered martensitic matrix with V and Nb carbonitrides and Cr carbides: $M_23C_6$ carbides.
nucleate predominantly at prior austenite grain boundaries and along martensite lath boundaries after tempering; diffuse MX carbonitrides are finely distributed inside the matrix.

For grades 91, 911 and 92 the precipitation states after normalizing and tempering is due to MX carbonitrides, mainly located within subgrains, and $M_{23}C_6$ carbides on grain and subgrain boundaries. These were measured and exhibit comparable dimensions: respectively 50 and 130nm. Figure 1 show an example of the microstructure for grade 911 with different microscopy analysis techniques.

Creep properties of 91, 911 and 92 steels have been widely investigated in Europe, USA and Japan by very long tests in the range of 550-650°C and over 100,000 testing hours. The last results from ECCC (European Creep Collaborative Committee) data assessment for rupture in 100,000 at 600°C for these grades are respectively: 90, 98 and 113 MPa [23].

3. MICROSTRUCTURAL EVOLUTION

The microstructure of 9%Cr grades was investigated after long aging and creep tests to give a metallurgical explanation of the reduction of creep resistance with increasing service time and temperature. Several samples have been investigated after creep testing in a wide range of times and temperatures: all samples were taken from the head of creep specimens. The crept samples were observed by LM and SEM too; afterwards the microstructures were investigated by STEM/TEM and XRD techniques.

Microstructural evolution of 9-12%Cr steels during creep exposure consists of nucleation, growth and coarsening of second phases: $M_{23}C_6$ and MX precipitates are present already after tempering, while Laves and Z-phase nucleate during creep service.

3.1 Carbide coarsening

The growth and coarsening of $M_{23}C_6$ and MX carbonitrides appears stable enough against coarsening. In particular MX precipitates are only slightly affected by ageing, and their equivalent diameter remains below 100 nm even after 100,000 hours at high temperature; at 600°C the equivalent diameter of $M_{23}C_6$ carbides remains below the critical diameter of 250 nm (Figure 2).

3.2 Laves phase nucleation and growth

The addition of Mo and W contents respect to the parent Grade 9 lead to the formation of intermetallic Laves phase during thermal service, $(\text{Fe,Cr})_2(Mo,W)$, which nucleates mostly on subgrain boundaries and on prior austenite grain boundaries (PAGB). The Laves phase nucleates and grows relatively fast during the first 1,000-10,000 hours in the temperature range 600°C-650°C: below 600°C this phase remains relatively small even at very long time, but it can reach very large dimensions at 650°C especially in Grades 91 and 911 (equivalent diameter up to 2µm).

By the creep strengthening point of view the precipitation of Laves phase has two aspects. On one hand, high amounts of Mo and W contents are incorporated in this phase, causing a depletion of these elements from the solid solution and thus a reduction of their contribution to the overall creep resistance. On the other hand, the increased volume fraction of secondary phases leads to a higher precipitation strengthening during the first precipitation phase: at the beginning, the precipitation of fine Laves phase increases the creep resistance. However when the mean diameter of these particles reaches micrometric dimensions, their effect on creep behaviour is lost. An example of Laves phase precipitates in Grade 92 after 57.715 hours at 650°C are shown in Figure 3, together with $M_{23}C_6$ carbides, by TEM thin foil.

3.3 Z-phase particles appearance

Modified Z-phase is a nitride, which nucleates in the range of 600-650°C during creep service. This phase is common to all 9-12% Cr steels with high Nb and V content; MX carbonitrides during thermal exposure slowly
transform in favour of a more stable composition, \( \text{Cr(V,Nb)}N \), which is called modified Z-phase. The particles of this phase form thin plates within the matrix.

It is experimentally proved [15,24] that high amount of Z-phase nucleates and grows in large number and size mostly in 12%CrMoV steels which show the so-called “sigmoidal” shape of isothermal creep curves, leading to a dramatic drop of creep resistance. MX carbonitrides are one of the most effective strengthening precipitates in the 12%Cr advanced ferritic steels. However, Z-phase is formed at the expense of MX particles during high temperature exposure. It grows rapidly and cannot contribute to strengthening. The premature creep breakdown in 12%Cr steels has been explained by the disappearance of MX carbonitrides and the fast coarsening of Z-phase.

4 STUDY OF FORMATION OF Z-PHASE

The Z-phase which forms in 9-12%Cr industrial steels is primarily a Cr-V-based nitride, but contains also small quantities of Nb and Fe, and it is usually addressed as modified Z-phase. The crystal structure of the modified Z-phase has been reported to be tetragonal, with lattice parameters \( a = 0.286 \text{nm} \) and \( c = 0.739 \text{nm} \) [15], as shown in Figure 4.

Recently, Danielsen et al. [17] have evidenced by electron diffraction that modified Z-phase has a not unique crystal structure since it can exhibit diffraction patterns typical of a FCC lattice, similar to those found in MN precipitates, though with a slightly smaller lattice parameter, \( a = 0.405 \text{nm} \). The cubic structure has been found to coexist with the tetragonal structure. The proposed hybrid crystal structure is shown in Figure 5b. Further investigations have shown that the cubic structure is predominant in 9-12%Cr steels exposed for relatively short times, while the tetragonal structure is more frequent in more aged samples [10].

Cipolla in his project for PhD thesis [27] investigated the early stage of Z-phase formation using a model steel specifically designed to form only the modified Z-phase, \( \text{Cr(V,Nb)}N \), after a relatively short time during high temperature ageing. In this steel the carbon content has been kept at an extremely low level (45 ppm) to avoid the formation of carbides, such as \( \text{Cr}_2\text{C}_6 \) as well as \( \text{NbC} \). Tungsten and molybdenum have not been added to prevent the formation of Laves phase, \( \text{Fe}_2(\text{Mo,W}) \), precipitating during ageing. Nb and V content were selected similar to that in industrial 9-12%Cr steels (Grades 91, 92, 122).

The microstructure of the normalized and tempered material consists entirely of tempered martensite; samples of this alloy have been aged up to 10,000h at 600°C, 650°C and 700°C.

The microstructure of as-treated and aged samples has been investigated by a TEM and XRD.

Niobium and vanadium nitrides with 30-40% atomic average content of Cr + Fe have been observed in all aged samples, except in 650°C/10,000h sample. With these analyses it has been found also the intermediate range of chemical composition of the Cr-rich MN clearly located between that of MN and that of long-time aged \( \text{Cr(V,Nb)}N \). A further investigation of the Cr-rich MN particles has revealed that they contain at the same time regions with different chemical composition, typical of both MN and Z-phase, so that they have been defined hybrids. For the sake of simplicity, the typical composition ranges are schematically summarised altogether in the ternary diagram of Figure 5.

A recent work of Yoshizawa et al [28] has confirmed the existence of such Cr-rich MN particles in the commercial Japanese steel grade P122. After 10,000h at 650°C all particles are either \( \text{Cr}_2\text{N} \) or \( \text{Cr(V,Nb)}N \) and only two NbN particles were identified.

In general, composition profiles of hybrid particles show a smooth transition from Cr-rich areas at the rim, with chemical composition close to that of the Z-phase, towards Cr-poor areas at the core, with composition close to that of V-rich MN. Figures 6 show two examples of hybrid particles found in the sample aged for 1,000h at 650°C: an highly symmetric hybrid particle, with the entire rim has a full Z-like composition, while
the core has a considerably lower chromium content; a particle where one side of the particle has the composition of MN, while the other has the composition of the Z-phase.

More complex structures have been also observed in larger particles, which often show a Nb-rich core, and a V-rich area surrounding it either completely or in two symmetrically opposite regions. The V-rich outer layers may undergo Cr uptake in the outermost edges.

In large particles, it is unlikely that Cr diffuses into the centre of the particles.

Investigation of the hybrid particles suggests that the formation of Z-phase may occur by means of a physical transformation of (V,Nb)N into Z-phase through Cr diffusion from the ferritic matrix into the nitride. Figure 7 shows the formation of parallel Z-phase particles which occurs when several Cr-rich areas form separately on larger MN particles with Nb-rich centres. The Z-phase tends to form on the opposite sides of the particle, resulting in parallel Z-phase particles.

Although Z-phase forms everywhere in the microstructure, TEM investigations indicate a faster formation along the grain boundaries, where the MN particles dissolve faster compared to the interior of the grain and the Z-phases are also generally larger. This can be explained by the higher value of diffusion coefficients at the grain boundaries.

Figure 8 shows the comparison between extraction replica images from as-treated material as well as 650°C/1,000h aged sample: continuous lines indicate the location of grain boundaries, while dotted lines indicate the precipitates depletion area around grain-boundaries of aged sample.

5. APPLICATION TO INDUSTRIAL STEELS

An extension of the results obtained from 12%Cr model alloy to industrial 9-12%Cr steels is the searching for hybrids particles in long-term crept samples. TEM investigation confirms the existence of hybrid particles in industrial steels, such as ASTM Grades 91, 92, X20, 122.

Hybrid particles are very few in 9%Cr steels, where the driving force for Z-phase formation has lower value than in 12%Cr steels. Z-phase was recognized also in 9%Cr steels [25, 26, 27], but in a far smaller amount: no dramatic drop in volume fraction of MX was observed in association to the nucleation of this phase, therefore it is believed that the modified Z-phase does not affect negatively creep properties of Grades 91, 911 and 92.

Figure 9 shows the X-Ray powder Diffraction profile for extracted precipitates coming from a P91 sample exposed for more 100,000 hours at 600°C and the aspect of present phases including hybrid [18, 26]. The analysis of the peaks confirms the presence of MX, M_{23}C_{6} and Laves phase, but also the presence of Z-phase, as confirmed also with TEM investigations.

6. CONCLUSIONS

The experiences maturated in the microstructural analysis of long term aged 9-12% advanced Cr ferritic-martensitic steels Grades can be summarized in the following conclusions:

- MX carbonitrides, containing Nb and V, remain essentially unchanged throughout creep service even at very long time (>100,000 hours) and highest temperature (650°C);
- M_{23}C_{6} carbides coarsen during creep service, although their average diameter remains below 250 µm at 600°C;
- Coarsening of Laves phase particles over a critical size triggers the cavity formation and the consequent brittle intergranular fracture. The high coarsening rate of Laves phase is the major cause of the slight reduction of long term creep resistance in 9% Cr Grades; the higher creep properties of Grade 92 are explained by the slower Laves coarsening rate;
The microstructural evolution of a 12%Cr model steel during long time ageing in the temperature range from 600°C to 700°C, show that MN nitrides with composition (V,Nb)N are not thermodynamically stable and are transformed into the Z-phase nitride Cr(V,Nb)N by Cr diffusion in to the particles;

Z-phase was recognized in 9%Cr steels, but in a far smaller amount: no dramatic drop in volume fraction of MX was observed in association with the nucleation of this phase, therefore it is believed that the modified Z-phase does not affect negatively creep properties of Grades 91, 911 and 92 in the service temperature range for these steels;

Currently no commercial 12% Cr steels stable steels with same creep properties of Grade 92 is available on the market.

ACKNOWLEDGEMENTS

The authors wish to acknowledge Leonardo Cipolla (formerly working at CSM), now Salzgitter Mannesman Stainless Tubes), since during his work at CSM has given a fundamental contribute to this research activity and Stefano Caminada (formerly working at TenarisDalmine). M. Ballone (CSM) and H.K. Danielsen (DTU) have given excellent support during TEM analyses, while J. Hald (DONG/DTU) and M. A. J. Somers (DTU) have provided a strong contribute with their supervision of the research activity. P. E. Di Nunzio (CSM) is thanked for his technical help during the research activities.

REFERENCES


[21] ASTM Standard A213-A335


[23] W. Bendick, L. Cipolla, J. Gabrel, J. Hald, New ECCC Assessment of Creep Rupture Strength for Steel Grade X10CrMoVNb9-1 (Grade 91): ECCC Creep Conference, 21–23 April (2009), Zurich (CH)


Table 1: chemical composition of the 9-12%Cr steels: (*) ASTM Standard [20]

<table>
<thead>
<tr>
<th>Grades</th>
<th>C</th>
<th>Mn</th>
<th>Si</th>
<th>Ni</th>
<th>Cr</th>
<th>Mo</th>
<th>V</th>
<th>B</th>
<th>Nb</th>
<th>N</th>
<th>Al</th>
<th>W</th>
<th>other</th>
</tr>
</thead>
<tbody>
<tr>
<td>X20</td>
<td>0.2</td>
<td>0.55</td>
<td>0.3</td>
<td>12</td>
<td>1</td>
<td>0.25</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>91</td>
<td>Min</td>
<td>0.07</td>
<td>0.30</td>
<td>0.20</td>
<td>/</td>
<td>8.0</td>
<td>0.85</td>
<td>0.18</td>
<td>/</td>
<td>0.16</td>
<td>0.03</td>
<td>/</td>
<td>(*)</td>
</tr>
<tr>
<td>Max</td>
<td>0.14</td>
<td>0.60</td>
<td>0.50</td>
<td>0.40</td>
<td>9.5</td>
<td>9.5</td>
<td>1.05</td>
<td>0.25</td>
<td>/</td>
<td>0.1</td>
<td>0.70</td>
<td>0.02</td>
<td>(*)</td>
</tr>
<tr>
<td>911</td>
<td>Min</td>
<td>0.09</td>
<td>0.30</td>
<td>0.10</td>
<td>/</td>
<td>8.5</td>
<td>0.90</td>
<td>0.18</td>
<td>0.0063</td>
<td>0.06</td>
<td>0.90</td>
<td></td>
<td>(*)</td>
</tr>
<tr>
<td>Max</td>
<td>0.13</td>
<td>0.60</td>
<td>0.50</td>
<td>0.40</td>
<td>9.5</td>
<td>9.5</td>
<td>1.10</td>
<td>0.25</td>
<td>0.0060</td>
<td>0.10</td>
<td>0.090</td>
<td>0.02</td>
<td>(*)</td>
</tr>
<tr>
<td>92</td>
<td>Min</td>
<td>0.07</td>
<td>0.30</td>
<td>/</td>
<td>/</td>
<td>8.5</td>
<td>0.30</td>
<td>0.15</td>
<td>0.0010</td>
<td>0.04</td>
<td>0.030</td>
<td>/</td>
<td>1.50</td>
</tr>
<tr>
<td>Max</td>
<td>0.13</td>
<td>0.60</td>
<td>0.50</td>
<td>0.40</td>
<td>9.5</td>
<td>9.5</td>
<td>0.60</td>
<td>0.25</td>
<td>0.0060</td>
<td>0.09</td>
<td>0.070</td>
<td>0.02</td>
<td>2.00</td>
</tr>
<tr>
<td>122</td>
<td>Min</td>
<td>0.07</td>
<td></td>
<td></td>
<td>10</td>
<td></td>
<td>0.25</td>
<td>0.15</td>
<td>0.0005</td>
<td>0.04</td>
<td>0.04</td>
<td>/</td>
<td>1.5</td>
</tr>
<tr>
<td>Max</td>
<td>0.14</td>
<td>0.7</td>
<td>0.5</td>
<td>0.5</td>
<td>11.5</td>
<td>0.6</td>
<td>0.30</td>
<td>0.060</td>
<td>0.1</td>
<td>0.1</td>
<td>0.02</td>
<td>2.5</td>
<td></td>
</tr>
</tbody>
</table>

Table 2: Chemical composition of rolled plate of the model alloy (wt%).

<table>
<thead>
<tr>
<th>C</th>
<th>Cr</th>
<th>Ni</th>
<th>Nb</th>
<th>V</th>
<th>N</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0048</td>
<td>11.85</td>
<td>1.29</td>
<td>0.076</td>
<td>0.18</td>
<td>0.06</td>
<td>0.40</td>
<td>0.32</td>
<td>&lt;0.005</td>
<td>&lt;0.003</td>
<td>Bal.</td>
</tr>
</tbody>
</table>

**Fig 1:** examples of microstructure of grade 911 pipe after normalizing and tempering by LM (a), SEM (b), TEM on extraction replica (c: low magnification; d: high magnification)

**Fig 2:** Growth and coarsening of Grade 91 particles

**Fig 3:** Grade 92 microstructure (57.715h; 650°C).
Fig 4: Tetragonal and hydrid structure associated with Z-phase;

Fig 5: Typical composition ranges Cr₂N, MN, Z-phase and hybrids particles

Fig 6: Hybrid particles after 1,000h at 650°C and Cr concentration gradients

Fig 7: Formation of two parallel Z-phases in 12%Cr model alloy.
Fig 8: Comparison between (a) as-treated and (b) 650°C/1,000h aged microstructures in 12%Cr model alloy

Fig 9: XRD Profile of the residues extracted from grade P91 aged for 104,000 hours at 600°C, Z-phase particles (Grey arrow: MX; black arrows: M$_{23}$C$_6$; white arrows: Cr(V,Nb)N) and Hybrid Z-phase particle.