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Study of the microstructure of the Grade 91 steel after more than 100,000h of creep exposure at 600°C

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Abstract:
This paper presents results on the evolution of microstructure (both matrix and precipitates) of an ASME Grade 91 steel that has been creep tested for 113,431h at 600°C under a load of 80MPa. The microstructure was investigated using transmission electron microscopy (TEM) and revealed chromium rich $\text{M}_2\text{C}_6$ carbides, MX-type precipitates, Laves phases and modified Z-phases. Only a small amount of modified Z-phase was found. In order to quantify coarsening of precipitates and growth of new phases during creep, the size distributions of the identified precipitates were determined by analysis of TEM images. In addition to this, the size distribution of Laves phases was determined by image analysis of scanning electron micrographs.

Substructure modifications and creep damage were investigated on cross section of the creep specimen using Electron Backscatter Diffraction and Scanning Electron Microscopy.

Keywords: P91 steel, creep, microstructure, Laves phases, modified Z-phase, SEM, TEM

1. Introduction

There are few published data available on the microstructure of 9-12% chromium heat resistant steels after nearly 100,000h of exposure to creep. Further development of new heat resistant steels such as ASME Grade 91 steel, presently successfully used for components in fossil power plants operating at temperatures around 550-600°C [1] rely on a better understanding of their long-term microstructural evolution. Previous works [2, 3, 4] presented data on the microstructure of the ASME P91 steel after long term creep exposure, but for exposure times lower than 100,000h.

It has been shown that extrapolation of short-term creep data (e.g. for lifetime lower than 10,000 hours) can lead to an overestimation of the creep strength after long term creep [5, 6]. This overestimation is probably due to the metallurgical evolution of the steel during creep. This paper presents data on the microstructure of the Grade 91 after more than 100,000h of creep exposure, which will be useful for a better understanding of the loss of long-term creep strength.

2. Literature data on precipitate evolution in 9-12% Cr steels during creep

The microstructure of the as received ASME Grade 91 steel consists of a tempered martensite matrix with high dislocation density and precipitates. There are two kinds of precipitates: $\text{M}_2\text{C}_6$ (M=Cr, Fe, Mo) carbides located at prior austenite grain boundaries (PAGBs) and at other (packet, block, martensite lath) boundaries and finely dispersed MX-type (M=V, Nb and X= C, N) carbonitrides within laths. Carbides of type MC, $\text{M}_2\text{C}$ [7] can be also identified in Grade 91 steels, but most of the precipitates present at boundaries (PAGBs, laths, blocks, packets) are $\text{M}_2\text{C}_6$ carbides.

There is a microstructural evolution of the ASME Grande 91 steel during creep exposure: precipitation of new phases (Laves phases, modified Z-phases), coarsening of precipitates (primarily $\text{M}_2\text{C}_6$ carbides) and recovery of tempered martensitic lath structure.

Intermetallic Laves phases precipitate during creep or aging. Their precipitation is observed after relatively short-term creep exposure, for times shorter than 4,000h [8]. Laves phase precipitation decreases the amount of Mo dissolved in the matrix, reducing solid solution strengthening. Quantitative studies on the evolution of the size of Laves phases during creep or aging have revealed a significant growth rate during the first 10,000h of exposure [9].
Modified Z-phase is a complex (Cr,Fe)(Nb,V)N nitride. Its composition for metal elements is 50 at.% (Cr + Fe) and 50 at.% (Nb+V) [10]. In the ASME Grade 91 steel, modified Z-phase formation is observed after very long term creep, for example after 34,141 h, at 600°C, under a load of 100 MPa [11]. The precipitation of modified Z-phases is also reported in the heat-affected zone (HAZ) of welded joints [12, 13]. The modified Z-phase precipitation occurs at the expense of MX precipitates, possibly leading to partial or complete disappearance of those precipitates and suppression of MX-induced strengthening. For this reason, the modified Z-phase precipitation could be detrimental to service life of 9-12% Cr ferritic-martensitic steels. In fact, it was suggested to be the major cause of premature loss of creep strength of some 11-12% Cr heat resistant steels after relatively short term (<15,000h) creep [14]. It is more intense in the 11-12% Cr steels content than in 9% Cr steels [10]; for the ASME Grade 91 steel, the effect of precipitation of modified Z-phase on creep strength is not fully understood.

3. Experimental procedure

The investigated creep specimen was cut from a pipe, 121 mm in outside diameter and 20 mm in wall thickness. The chemical composition of the pipe was (wt%): 0.1C–0.36Si–0.41Mn–0.015P–0.003S–0.059N–0.022Al–8.43Cr–0.92Mo–0.04Cu–0.068Nb–0.11Ni–0.20V. The pipe had been given the following heat treatment: 1050°C for 60 min, air cooling followed by 730°C for 60 min and 750°C for 60 min, air cooling. The investigated creep specimen with a rupture time of 113,431 h at 600°C (80 MPa) exhibited an elongation of 7.3% and a reduction of area of 37%. During creep the specimen showed a minimum creep rate of $1.8 \times 10^{-7} \text{ h}^{-1}$.

TEM investigations were performed with a Tecnai F20 transmission electron microscope. TEM investigations were carried out on single carbon extractive replicas and thin foils. The carbon replicas of precipitates were prepared as follows. First, the creep sample was polished and Villela etched. Then, a carbon coating was evaporated onto the polished and etched surface; after that the sample was immersed in a 1% HCl solution in methanol to detach the carbon layer from the specimen. The carbon replicas were recovered on round copper grids. Thin foils from the gauge part of the creep specimen were prepared combining electropolishing and ion beam milling. An acid solution (45% acetic acid, 10% perchloric acid, 45% Butoxyethanol) cooled down to -1°C was used for electropolishing. The electropolished foils were further thinned by ion beam milling for a few minutes at low angle using a Gatan Precision Ion Polishing System (PIPS).

The chemical composition of each precipitate was determined by Energy dispersive X-Ray spectrometry (EDS) in conjunction with TEM. The identification was done using the following criteria: $M_23C_6$ carbides are enriched in Cr, Laves phases are enriched in Mo, modified Z-phase are made out of ~50 at.% (Cr + Fe) and ~50 at.% (V+Nb) and MX are enriched in V and Nb. More then 600 precipitates were investigated on several extractive replicas.

It is not sure that all precipitates are extracted on the carbon replica. As a consequence, special attention was paid to select an investigation area that is representative of the microstructure of the steel after etching.

Literature reports an average diameter of MX precipitates of 20 to 40 nm [15]. MX-type precipitates were identified on investigated extractive replicas; nevertheless, attention was focused to identify only larger precipitates after long-term creep, which could have a significant influence on the loss of creep strength. Thus, EDX analyses were mainly conducted on precipitates with an average diameter higher than 90 nm. MX-type precipitates were observed on thin foils.

Creep damage was investigated using a Scanning Electron Microscope (SEM) (Leo 1450 VP, with a tungsten filament) on longitudinal cross sections. One broken half of the creep specimen were cut into two halves (i.e. quarters of “complete” specimens) by spark erosion. The half containing the specimen axis was used for metallographic examinations. A final mechanical-chemical polishing with colloidal silica was then carried out to reveal cavities without opening them, as chemical etching could have done. The creep damage was quantified as a fraction of porosity determined by image analysis of SEM images with a magnification of ×400.

Electron backscatter diffraction (EBSD) maps were acquired from the same cross-section with a Zeiss DSM 982 Gemini field emission gun (FEG) SEM equipped with a Shottky filament, a Hjelen-type camera and TSL OIM facilities. The specimen for EBSD maps was also polished with colloidal
silica. All EBSD measurements were conducted with a step size of 0.15 µm at 20kV, working distance 19 mm, aperture 120 µm, probe current between 0.1 and 1nA.

4. Creep damage

A high number density of cavities was observed throughout the specimen section even far from the fracture surface, using either backscatter electron (BSE) or secondary electron (SE) imaging (Figure 1). Many cavities can even be observed using a light microscope. Figure 2 reports data on the average equivalent diameter of cavities and number of cavities observed at a magnification of ×400. At this magnification cavities with a minimum equivalent diameter of 0.7 µm can be revealed. Creep damage was quantified on areas of 342µm×214µm. In figure 1b is represented a typical SEM image used for creep damage quantification, arrows show creep cavities. Cavities seem to nucleate at boundaries next to large particles such as Laves phases (Figure 1a). At a distance lower than about 0.5mm from the fracture surface, coalescence of cavities was observed.

![Figure 1](image1.png)

**Figure 1** Creep damage in the P91 steel after creep at 600°C for 113,431h 7mm from fracture surface, SEM images, BSE-mode (a) and SE-mode (b)

![Figure 2](image2.png)

**Figure 2** Average equivalent diameter (a) and number of cavities (b) calculated on areas of 342µmx214µm along the creep specimen axis

5. Hardness

The gauge portion of the investigated creep specimen exhibits hardness with about fifty units lower than in the as-received P91 steel. This decrease in hardness can be due to both the presence of cavities and microstructural evolution of the steel during creep. Close to the fracture surface, one observes a slight decrease in hardness compared to that of the rest of the gauge portion of the specimen. This can be related to creep damage development. The head of the creep specimen shows a less important decrease in hardness, about twenty units lower than the as received P91 steel. This small decrease is probably due to microstructural evolution.
Figure 3 Evolution of hardness along the tensile direction of investigated creep specimen (circles) compared to that of a similar piece of as-received steel from the same pipe (squares)

The difference in hardness between gauge and specimen head could be due to either the effect of stress on microstructural evolution or damage development, or both. Thus, three states of the microstructure of the P91 steel were investigated:

- the as received state,
- the head of the creep specimen (stress-free thermal ageing),
- the gauge portion far from fracture surface (microstructural evolution under stress/strain).

6. Microstructural evolution during creep

6.1 Scanning Electron Microscopy results

In the as-received state, precipitates are too small to be analysed using SEM. The precipitates that can be seen in Figure 4a are $M_23C_6$ carbides mainly located at boundaries. There are also small MX-type precipitates finely distributed within the martensite laths and Mo atoms in solid solution in the matrix.

Figure 4 Microstructure of the a) as received P91, b) after creep at 600°C for 113,431h (gauge); c) typical EDS (FEG-SEM) spectra for $M_23C_6$ carbides, Laves phases and matrix, respectively
After long-term creep, $M_{23}C_6$ carbides have obviously grown (Figure 4). FEG-SEM investigations revealed precipitation of Laves phases. Small-size precipitates (~40nm) finely distributed was also observed by FEG-SEM in the crept specimen. They were too small to be identified by FEG-SEM; they could be MX-type precipitates. To study this kind of precipitates, TEM investigations are needed.

The precipitates indicated in Figure 4b were identified by EDS analysis coupled with FEG-SEM. The large size of some precipitates after long-term creep allowed their chemical identification by EDS analysis (Figure 4c).

Figure 5a shows the size distribution of Laves phases after creep. Because Laves phases are enriched in Mo, they can be easily evidenced using BSE images, which are sensitive to the mean atomic number of the probe area. Figure 5b shows a typical BSE image used for quantification of Laves phases, white spots being Laves phase particles. The precipitation of Laves phases occurs during high-temperature exposure; in the as-received state there are no Laves phases, as can be seen in the micrograph of Figure 6b.

![Figure 5](image)

**Figure 5**

(a) Size distribution of Laves phases in the P91 steel in the head (squares) and in the gauge portion (circles) of the creep specimen

(b) Microstructure of the P91 steel after creep, showing Laves phases (white)

There is no significant difference between the size of Laves phases in the gauge portion compared to the head portion. The slight difference between curves of Figure 5a could be due to the scatter of measurements.

6.2 Electron Backscatter Diffraction results

SEM-BSE investigations revealed a significant change in the substructure of the steel after long-term creep, as can be seen from Figure 6 compared to Figures 8, 10 and 12.

EBSD maps of the steel in as-received state revealed a typical martensitic matrix with blocks and packets. After creep, EBSD measurements revealed a matrix with more or less equiaxed subgrains (Figures 8a, 10a, 12a). These subgrains are revealed by both BSE imaging and EBSD mapping. The shape of these subgrains is very elongated in the as received state (Figure 6c) and less elongated in the specimen head (Figure 12c). In the specimen gauge, at 25 mm from the fracture surface, equiaxed subgrains are readily found (arrows in Figure 10c). Next to the fracture surface, most subgrains are round-shaped (Figure 8c).
Figure 6 Microstructure of the as-received P91 steel. a) Inverse Pole Figure (IPF) with orientation of sample normal in the crystal frame as key colour; b) BSE image; c) EBSD Image Quality map

Figure 7 a) EBSD map of same area and same colour key as Figure 6a, showing only grains with a size lower than 2 µm; b) Comparison between misorientation angles for small grains and for the whole area

Figure 8 Microstructure of the P91 steel after creep (2mm from fracture surface) a) EBSD IPF (same colour key as in Figure 6a); b) BSE image; c) EBSD Image Quality map
Figure 9  a) EBSD map of same area and same colour key as Figure 8a, showing only grains with a size lower than 2 µm; b) Comparison between misorientation angles for small grains and for the whole area.

Figure 10 Microstructure of the P91 steel after creep (25mm from fracture surface). a) EBSD IPF (same colour key as in Figure 6a); b) BSE image; c) EBSD Image Quality map (some equiaxed subgrains are arrowed).

Figure 11 a) EBSD map of same area and same colour key as Figure 10a, showing only grains with a size lower than 2 µm; b) Comparison between misorientation angles for small grains and for the whole area.
Subgrain evolution occurred both upon thermal aging (head) and creep deformation (gauge) but probably mostly during fast deformation immediately preceding fracture. To assess the metallurgical evolution of the creep specimen it is necessary to separately study what occurred during creep deformation (homogeneously deformed area, Figure 10) and what is due to fast “quasiplastic” deformation at the end of lifetime (next to fracture area, Figure 8). First of all, as creep cavities are uniformly distributed along the gauge length, it can be concluded that extensive recovery leading to round-shaped subgrains is not necessary to induce premature creep failure.

In addition, small equiaxed grains (a few microns in size) delimited by high-angle boundaries (>15°) were revealed in the EBSD maps (Figures 8a, 10a, 12a) although they could not be clearly identified by BSE imaging. Such grains were not so obviously detected in the as received state (Figure 6) and must have appeared during creep.

To further investigate recovery or even recrystallisation in the crept specimen, small grains with a size lower than 2 µm are extracted in Figures 7a, 9a and 11a. Many of such small grains were in fact found in all EBSD maps. They may be (i) martensite packets cut by the sample preparation in such a way that they appear small or (ii) “true” newly appeared small grains. There is no obvious difference between figures 7a, 9a, 11a. However, the misorientation angle histogram of figures 7b, 9b, 11b showed that while in figures 7b and 11b boundaries between small grains have misorientation angles typical of these between martensite variants [16, 17], this is not so clearly the case 2 mm from the fracture surface (figure 9b). This suggests that some continuous recrystallisation might have occurred close to the fracture surface. This is consistent with dynamic recrystallisation occurring in another P91 steel fractured in tension (10⁻³ s⁻¹) at 625°C [18]. Getting more information about this phenomenon requires more detailed EBSD data processing that is beyond the scope of this paper.

6.3 Transmission Electron Microscopy results

6.3.1 Modified Z-phase

The main purpose of TEM investigations was to determine the size and number density of modified Z-phase particles in order to decide how to take into account the influence of this phase on the creep strength of the ASME Grade 91 steel.

Figure 13a shows typical precipitates in the P91 steel after long term creep exposure. TEM investigations revealed a low number of modified Z-phase particles compared to the size of the investigated area or the number of investigated precipitates. Only 41 precipitates out of 640 identified precipitates were found to be modified Z-phases. The observed modified Z-phases are large and widely spaced particles with a mean diameter of about 400 nm. Precipitation of modified Z-phase can put the MX-type precipitates into solution. However, TEM investigations on thin foils of the crept portion revealed dislocations still pinned by MX-type precipitates as shown in Figure 13b. This suggests that
precipitation of modified Z-phase did not have a significant influence on the number density of MX-type precipitates; nevertheless, no quantification of MX-type precipitates was done in this study.

As mentioned above, the identification of modified Z phase was based mainly on its chemical composition of about ~50 at.% (Cr + Fe) and ~50 at.% (V+Nb) (metal elements only). Table 1 summarizes EDS results on modified Z-phases identified on extractive replicas of the creep specimen (gauge portion). The Cr/Fe ratio was uniform with a round 46 at.% Cr and 4% at. Fe. The V and Nb contents showed large scatter. Danielsen and Hald [19] found similar variations of Cr/Fe ratio and Nb/V ratio in chemical composition of modified Z-phases of various 9-12%Cr martensitic steels.

![Microstructure of the steel after creep; a) extractive replica; b) thin foil](image)

**Figure 13**

Table 1: Average chemical composition of modified Z-phase found in the P91 steel after 113431h of creep at 600°C

<table>
<thead>
<tr>
<th></th>
<th>Cr</th>
<th>Fe</th>
<th>V</th>
<th>Nb</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>%at.</td>
<td>%wt.</td>
<td>%at.</td>
<td>%wt.</td>
</tr>
<tr>
<td>Min</td>
<td>41.1</td>
<td>34.9</td>
<td>2.1</td>
<td>2.1</td>
</tr>
<tr>
<td>Max</td>
<td>50</td>
<td>47.6</td>
<td>7.7</td>
<td>8.0</td>
</tr>
<tr>
<td>Average</td>
<td>46.5</td>
<td>42.9</td>
<td>3.8</td>
<td>3.8</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Cr</th>
<th>Fe</th>
<th>V</th>
<th>Nb</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>%at.</td>
<td>%wt.</td>
<td>%at.</td>
<td>%wt.</td>
</tr>
<tr>
<td>Standard deviation</td>
<td>2.2</td>
<td>2.9</td>
<td>1.1</td>
<td>1.1</td>
</tr>
</tbody>
</table>

| Danielsen and Hald [19] | 45 | 5 | 40 | 10 |

Number of EDS analysis (modified Z-phase particles): 33

6.3.2 M₂₃C₆ carbides

Table 2 summarizes EDS results on M₂₃C₆ carbides in the as-received state and after long-term creep. A change in average chemical composition of the M₂₃C₆ particles after creep can be observed. For metal elements, an increase in Cr content from about 60 at.% to 70% at. and a decrease in Fe content from about 30 at.% to 20 at.% are observed in the crept specimen.

![Microstructure of carbides](image)

Table 2: Synthesis of EDS analysis of M₂₃C₆ carbides on single extractive replicas (%at.)

<table>
<thead>
<tr>
<th></th>
<th>Cr</th>
<th>Mo</th>
<th>Fe</th>
<th>Mn</th>
<th>V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Minimum</td>
<td>55.2</td>
<td>0</td>
<td>21.4</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Maximum</td>
<td>67.9</td>
<td>10.7</td>
<td>39.7</td>
<td>7.8</td>
<td>5.6</td>
</tr>
<tr>
<td>Average</td>
<td>61.2</td>
<td>5.7</td>
<td>27.7</td>
<td>4.8</td>
<td>0.1</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Cr</th>
<th>Mo</th>
<th>Fe</th>
<th>Mn</th>
<th>V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard deviation</td>
<td>2.8</td>
<td>1.6</td>
<td>2.1</td>
<td>2.0</td>
<td>0.6</td>
</tr>
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Number of investigated carbides: 128

<table>
<thead>
<tr>
<th></th>
<th>Cr</th>
<th>Mo</th>
<th>Fe</th>
<th>Mn</th>
<th>V</th>
</tr>
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<tbody>
<tr>
<td>After 113431h of creep at 600°C</td>
<td>61.4</td>
<td>4.0</td>
<td>11.6</td>
<td>1.0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>77.6</td>
<td>11.9</td>
<td>21.4</td>
<td>10.9</td>
<td>1.3</td>
</tr>
<tr>
<td>70.5</td>
<td>6.8</td>
<td>17.0</td>
<td>5.3</td>
<td>0.1</td>
<td></td>
</tr>
</tbody>
</table>

Number of investigated carbides: 120
K. Kimura et al. [20] found the same change in chemical composition of the \( \text{M}_{23}\text{C}_6 \) in a Grade 91 steel with an exposure time to creep of 34,000h at 600°C. In the as-received state, the chemical composition of the \( \text{M}_{23}\text{C}_6 \) determined in this study is similar to those determined in a similar steel [20].

Figure 14 shows the size distribution of \( \text{M}_{23}\text{C}_6 \) carbides, Laves phases and modified Z-phases identified on extractive replicas by TEM. As Laves phases are large and relatively scarcely distributed, more representative data on the size of Laves phases can be obtained using SEM (see Figure 5a). Thus, to determine the sizes of relative large precipitates such as Laves phases, SEM is better suited [21] because of the possibility of a higher number of precipitates per image which allow a better statistics compared to TEM images. However, TEM is better suited to investigation of modified Z-phases, which are frequently located very close to other particles, so that good spatial resolution is needed to analyse them.

Figure 14 Size of precipitates in the P91 steel after creep (gauge portion) and typical EDX-TEM spectra for \( \text{M}_{23}\text{C}_6 \) carbides, Laves phases and matrix, respectively.

A growth in size of \( \text{M}_{23}\text{C}_6 \) carbides is observed after creep. The average equivalent diameter of \( \text{M}_{23}\text{C}_6 \) carbides increases from about 150-180nm to about 300nm.

7. Conclusions

Quantitative data on the microstructure (both matrix and precipitate) of P91 steel after long-term creep were obtained in this study. After creep for 113,431h at 600°C, significant coarsening of existing \( \text{M}_{23}\text{C}_6 \) carbides, as well as intensive precipitation of coarse Laves phases and a low amount of modified Z-phases were observed.

The investigated creep specimens showed a significant decrease in hardness on the gauge area and a reduced decrease in the head. Creep damage was observed throughout the gauge area, next to coarse Laves phases.

A significant change in the substructure of the matrix was revealed by EBSD measurements. It was accelerated by creep compared to thermal ageing, but no extensive recrystallisation occurred prior to necking. Dislocation pinning by MX precipitates was still observed in the crept area.

This paper suggests that loss of creep strength is probably mainly due to coarsening of \( \text{M}_{23}\text{C}_6 \) carbides, significant precipitation and coarsening of Laves phases, and significant recovery of the matrix, rather than to extensive precipitation of modified Z-phase and significant MX dissolution.
Acknowledgments

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References

8. Hald J., Creep strength and ductility of 9 to 12% chromium steels, Materials at high temperature 21 (1) 41-46, 2004

18. Gaffard, V., Experimental study and modelling of high temperature creep flow and damage behaviour of 9Cr1Mo-NbV steel weldments, p. 34, Ph.D thesis, 2004, Ecole des Mines de Paris, France (in English)

