# PRECIPITATION HARDENING OF TEMPERED MARTENSITE LATH STRUCTURE IN A 10%Cr-3%Co-3%W-0.2%RE STEEL UPON CREEP AT 650 °C

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## Abstract

9-12% Cr martensitic steels are used as materials for fossil power plants with steam temperature more than 600 °C. Superior creep strength of these steels is attributed to a dispersion of nanoscale boundary $M_{23}C_6$ carbides and Laves phase particles. The aim of present work is to reveal the mechanisms of grain boundary pinning by precipitates and their effect on the thermal stability of lath martensitic structure of a Re-containing (in wt %) 10Cr, 3Co, 3W steel. The structural evolution in a Re-containing (in wt %) 10Cr, 3Co, 3W steel with a low N content (0.002 wt %) and high B content (0.01 wt%) after creep at temperature of 650 °C under the stresses of 200 - 140 MPa was investigated. The time to rupture after creep test at 650 °C/140 MPa was about 11,000 h. Tis steel was solution treated at 1050 °C and tempered at 770 °C, formerly. The structure in the grip portion of the crept specimen changed scarcely after creep exposure for ~11,000 h. In contrast, the structural changes in the gauge portion were characterized by transformation of the tempered martensite lath structure into relatively coarse subgrain structure. The formation of a well-defined subgrain structure in the gauge section was accompanied by the coarsening of $M_{23}C_6$ carbides and precipitations of Laves phase during creep.

**Keywords:** Martensitic steels, tempered martensitic lath structure, particles, recovery

## 1. INTRODUCTION

9 --12 wt %Cr martensitic steels are prospective materials for fossil power plants with service temperature 600-620 °C [1-2]. The high creep strength of 9 - 12 %Cr martensitic steels is provided by tempered martensite lath structure, which is stabilized by precipitates [1]. Boundary $M_{23}C_6$ carbides, having a face-centered cubic crystal structure with a lattice parameters 1.066 nm, effectively pin migration of lath/subgrain boundaries under creep condition. NbX carbonitrides, having a face-centered cubic crystal structure with a lattice parameters 0.447 nm, precipitate inside martensitic laths and serve as obstacles for dislocation rearrangement. The Laves phase particles, having a hexagon close-packed crystal structure with a lattice parameters $a$ = 0.473 nm and $c$ = 0.770 nm, precipitate, mainly, at the boundaries of prior austenite grains and martensitic laths during creep or ageing at 550-650 °C [1,3,4]. The growth of $M_{23}C_6$ carbides, NbX carbonitrides and Laves phase facilitates the detachment of the grain/subgrain/lath boundaries from precipitates during long-term ageing or creep at elevated temperatures that decreases the long-term creep strength of high-Cr martensitic steels [1-4]. The slowing down of precipitate coarsening is provided by addition of alloying elements such as Co, W, Mo, Re and B. These elements decrease the rate of diffusion-controlled processes and the interfacial energy between precipitations and matrix [5,6]. The aim of present work is to reveal the mechanisms of grain boundary pinning by precipitates and their effect on the thermal stability of lath martensitic structure of a Re-containing (in wt %) 10Cr, 3Co, 3W steel.

## 2. EXPERIMENTAL PROCEDURE

A steel, which is denoted here as 10Cr-3Co-3W-0.2Re, with the chemical composition (in wt %) Fe (bal.)-0.11C-9.85Cr-3.20Co-2.86W-0.13Mo-0.22Cu-0.03Si-0.14Mn-0.03Ni-0.23V-0.07Nb-0.002N-0.008B-0.17Re, was prepared by vacuum induction melting as 100 kg ingots. Square bars with a 11 mm x 11 mm cross-section were cast and hot forged by the Joint Research Center, «Technology and Materials», Belgorod National Research University, Belgorod, Russia. This steel was solution treated at 1050 °C for 1 h, cooled in air, and subsequently tempered at 770 °C for 3 h. Flat specimens with a gauge length of 25 mm and a cross section of 7 mm × 3 mm were crept until rupture at 650 °C under the applied stresses of 160, 180 and 200 MPa, and cylindrical specimen with gauge length of 60 mm and a 6 mm diameter was crept until rupture at 650 °C under an applied stress of 140 MPa. The structural characterization was carried out using a transmission electron microscope JEOL-2100 (TEM) with an INCA energy dispersive X-ray spectrometer (EDS) on ruptured creep specimens. Identification of the precipitates was performed based of combination of EDS composition measurements of the metallic elements using the manufacturer's library of internal reference standards and indexing of the electron diffraction patterns using TEM. The TEM specimens were prepared by electropolishing at room temperature using a solution of 10 pct perchloric acid in glacial acetic acid with Struers «Tenupol-5» machine. The precipitates were identified from both the chemical analysis and the selected-area diffraction method on at least 200 particles on each portion by using extraction carbon replicas. The carbon replicas were prepared by using Q 150REQuorum vacuum deposition machine. The volume fractions of the precipitated phases were calculated using the Thermo-Calc software with the TCFE7 database. The following phases were selected independently for calculation: BCC, FCC, $M_{23}C_6$ carbide, Laves phase ($Fe_2$(W,Mo) (C14).

## 3. RESULTS AND DISCUSSION

The mean size of prior austenite grains is approximately 50 μm, the mean transverse martensitic lath size is ~300 nm and the dislocation density is about $2\times10^{14}$ $m^{-2}$ (**Figure 1**). The mean size of $M_{23}C_6$ carbides is about 70 nm after tempering at T=770 °C (**Figures 1b,c**). Nb-rich MX carbonitrides with round shape have an average size of ~30 nm (**Figures 1b,d**).

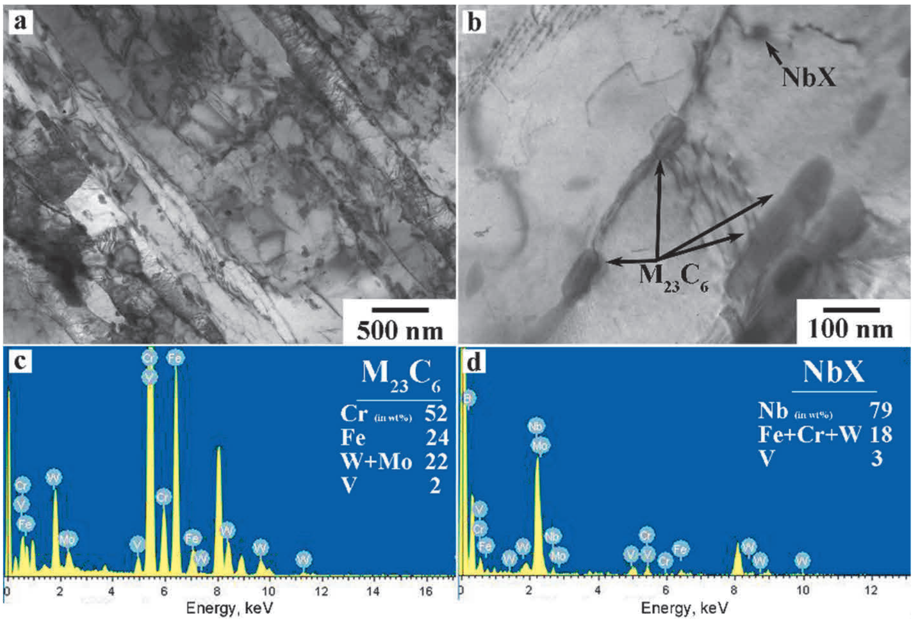

**Figure 1** Tempered martensite lath structure after normalization at 1050 °C and tempering at 770 °C. The amount of main elements in the particles is indicated in wt % measured from extraction carbon replicas by EDS with TEM.

Effect of long-term ageing on microstructure and a dispersion of secondary phases were studied in the grip section of samples, in which the thermally aged condition without stress occurred, compared to the gauge section. **Figure 2** demonstrates the structural changes during long-term ageing and creep at 650 °C in the steel studied. The results of the structural investigations after creep and long-term ageing at 650 °C are summarized in **Table 1**. Creep strongly provokes the subgrain formation.

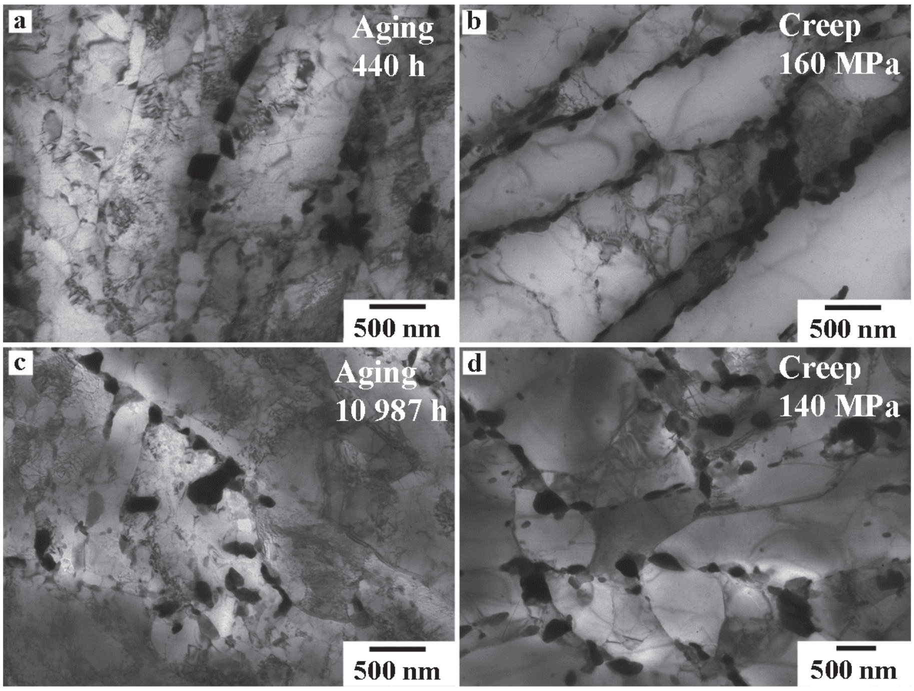

**Figure 2** Microstructures in the grip sections (a,c) and gauge sections (b,d) of the specimens crept at 650 °C under the applied stress of 160 MPa, 440 h (a,b) and 140 MPa, 10,987 h (c,d)

**Table 1** Structural parameters of the 10Cr-3Co-3W-0.2Re steel in the gauge sections and in the grip sections of crept samples at 650 °C

| **Parameters** | **200 MPa, 8 h** | | **180 MPa, 83 h** | | **160 MPa, 440 h** | | **140 MPa, 10,987 h** | |
|---|---|---|---|---|---|---|---|---|
| | **Grip** | **Gauge** | **Grip** | **Gauge** | **Grip** | **Gauge** | **Grip** | **Gauge** |
| Lath size, nm | 33 8± 50 | 500 ± 40 | 225 ± 50 | 680 ± 50 | 348 ± 60 | 573 ± 50 | 350 ± 50 | 1220 ± 50 |
| Subgrain size, nm | 389 ± 50 | 554 ± 50 | 317 ±70 | 550 ± 60 | 363 ± 65 | 600 ± 60 | 390 ± 50 | 1100 ± 50 |
| Dislocation density, $\times 10^{14}$ $m^{-2}$ | 1.4 ± 0.1 | 0.7 ± 0.1 | 1.5 ± 0.1 | 0.7 ± 0.1 | 1.4 ± 0.1 | 1.0 ± 0.1 | 1.2 ± 0.1 | 0.1 ±0 .05 |
| $M_{23}C_6$ carbide size, nm | 65 ± 10 | 75 ± 10 | 65 ± 10 | 64 ± 10 | 73 ± 10 | 81 ± 10 | 75 ± 10 | 120 ± 10 |
| NbX carbonitride size, nm | 30 ± 5 | 30 ± 5 | 36 ± 5 | 42 ± 5 | 45 ± 5 | 50 ± 5 | 50 ± 5 | 50 ± 5 |
| Laves phase size, nm | - | - | 122 ± 15 | 110 ± 15 | 136 ± 20 | 123 ± 20 | 190 ± 20 | 201 ± 20 |

The structure in the grip sections of the crept specimens changed scarcely after creep exposure for ~11,000 h. The mean transverse size of martensitic laths and mean size of subgrains insignificantly increased from 338 and 389 nm to 350 and 390 nm, respectively, with increasing time of ageing from 8 h to 10,987 h (**Table 1**). In contrast, the structural changes in the gauge section were characterized by transformation of the tempered martensite lath structure into relatively coarse subgrain structure. The mean size of subgrains reached to 1.1 μm after 10,987 h of long-term creep under the applied stress of 140 MPa (**Table 1**). The formation of a well-defined subgrain structure in the gauge section was accompanied by the coarsening of $M_{23}C_6$ carbides (**Table 1**) and precipitation with following growth of Laves phase during creep (**Figure 3, Table 1**). Creep accelerates the coarsening of $M_{23}C_6$ carbides and does not affect the coarsening of NbX carbonitrides and Laves phase. The volume fractions of $M_{23}C_6$ carbides, Laves phase and NbX carbonitrides at 650 °C are 2.01 %, 1.85 % and 0.67 %, respectively, according to Thermo-Calc prediction.

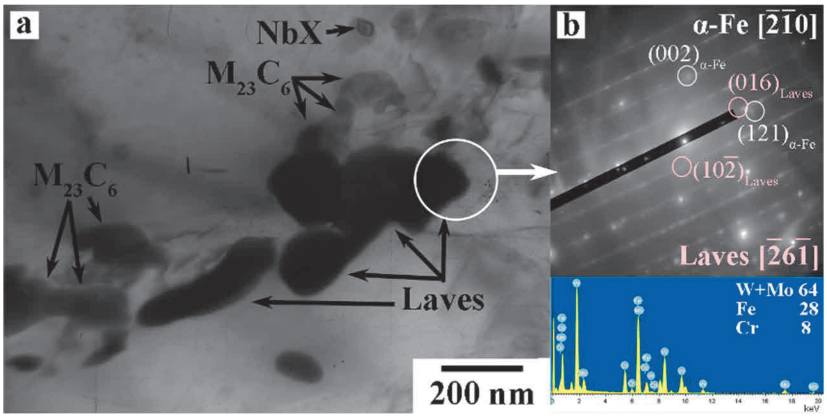

**Figure 3** Precipitation of Laves phase in the gauge section of the specimen crept at 650 °C under an applied stress of 160 MPa, 440 h. Electron diffraction pattern (b) is obtained from the Laves phase particle shown by circle in (a). The amount of main elements in the particles is indicated in wt % from extraction carbon replicas.

Subgrain coarsening is attributed to the balance between the pinning and driving pressures for grain/subgrain growth. Two driving forces may induce subgrain coarsening. One of them is driving force originated from stored free lattice dislocations, and second one is driving force attributed to subboundary energy [7, 8]. No difference in dislocation density in neighbor subgrains leads to negligible driving force due to stored dislocations. Driving force originated from low-angle boundary (LAB) energy can be evaluated as [7, 8]:

$$P_{LAB} = \frac{2\gamma}{r} = \frac{2\gamma}{\alpha D} \tag{1}$$

where $\gamma$ is the boundary surface energy per unit area (J m$^{-2}$), $r$ is radius of curvature of subgrains (μm), which is proportional to grain/subgrain size $D$, $\alpha$ is constant. The retarding force (Zener pressure) exerted by the particles, which are randomly distributed in ferritic matrix, can be evaluated as [7-10]:

$$P_z = 3\gamma \frac{F_v}{d} \tag{2}$$

where $\gamma$ is surface energy per unit area of the subgrain boundary (J m$^{-2}$), $d$ is the particle size (nm), $F_v$ is volume fraction of particles (-). So, particles exerting the retarding force must prevent the growth of subgrain structure. An equilibrium subgrain size which may be achieved during polygonization can be estimated on the assumption of the driving and retarding forces are in a balance as follows:

$$D_{P2=Pz} = \frac{2d}{3\alpha F_v} \tag{3}$$

where α=4 [11]. Volume fraction and the mean size of particles determine the value of equilibrium subgrain size. High level of retarding force exerted by fine $M_{23}C_6$ carbides and the Laves phase particles occurs if their sizes are less than 100 and 200 nm, respectively, after both long-term ageing and creep (**Table 2**).

On the other hand, the subgrain size depends on the applied stress under creep condition and can be estimated as (4) [1]:

$$D_{\infty} = 10\frac{Gb}{\sigma} \tag{4}$$

where *G* is a shear modulus (MPa), *b* is Burgers' vector (m), *σ* is an applied stress (MPa). The calculated values of subgrain size in the steel studied in comparison with the experimental values are presented in **Table 2**.

**Table 2** Total retarding force from precipitates and calculated and experimental subgrain sizes

| Conditions | Long-term ageing | | | Creep | | | |
|---|---|---|---|---|---|---|---|
| | $\Sigma P_z$, MPa | $D_{exper}$, μm | $D_{P2=Pz}$, μm by Eq. (3) | $\Sigma P_z$, MPa | $D_{exper}$, μm | $D_{P2=Pz}$, μm by Eq. (3) | $D_{\infty}$, μm by Eq. (4) |
| Tempering at 770 °C | 0.19 | 0.30 ± 0.05 | 0.52 | 0.19 | 0.30 ± 0.05 | 0.52 | - |
| 650 °C/200 MPa, 8 h | 0.15 | 0.38 ± 0.05 | 0.51 | 0.13 | 0.55 ± 0.05 | 0.58 | 0.75 |
| 650 °C/180 MPa, 83 h | 0.22 | 0.32 ± 0.07 | 0.35 | 0.23 | 0.55 ± 0.06 | 0.35 | 0.83 |
| 650 °C/160 MPa, 440 h | 0.20 | 0.36 ± 0.06 | 0.39 | 0.19 | 0.60 ± 0.06 | 0.42 | 0.93 |
| 650 °C/140 MPa, 10,987 h | 0.18 | 0.39 ± 0.05 | 0.43 | 0.13 | 1.10 ± 0.05 | 0.64 | 1.07 |

It is seen that the experimental subgrain sizes after long-term ageing in the 10Cr-3Co-3W-0.2Re steel are similar to their equilibrium value, estimated by Eq. 3 excepting tempered state and aged state for 8 h. During long-term ageing the subgrain growth is controlled by coarsening of $M_{23}C_6$ carbides, the Laves phase particles and NbX carbonitrides. Mechanism of grain boundary pinning by precipitates during long-term ageing for 10,987 hours is Zener pressure, exerted by the particles, which are randomly distributed in ferritic matrix. The tempered martensitic lath structure is thermal stable for 10,987 hours of exposure; the precipitates effectively prevent the transformation of lath structure into subgrain structure.

The experimental subgrain sizes after creep in the 10Cr-3Co-3W-0.2Re steel are significantly more than their equilibrium values, estimated by Eq. 3 excepting tempered state and crept state under 200 MPa. At the same time, the experimental subgrain sizes after creep in the 10Cr-3Co-3W-0.2Re steel does not reach its equilibrium values, estimated by Eq. 4 excepting crept state under 140 MPa. Strain-induced coarsening of subgrains takes place during creep and depends on the applied stress. On the other hand, subgrain growth is retarded by $M_{23}C_6$ carbides, the Laves phase particles and NbX carbonitrides during 440 hours of creep. However, decreasing Zener pressure to 0.13 MPa facilitates a detachment of lath and subgrain boundaries from the chains of precipitates. After 10,987 hours of creep under the applied stress of 140 MPa, the subgrain size is the same as equilibrium value, estimated by Eq. 4. This indicates the precipitates do not control the subgrain growth, the transformation of lath structure into full subgrain structure occurs at decreasing Zener pressures from precipitates. Even high Zener pressures from precipitates, which provide the thermal stability of tempered martensite lath structure during long-term ageing, are not able to hold the migration of lath/subgrain boundaries under the action of the applied stress during creep. Both the applied stress and the decreasing Zener pressure from precipitates lead to formation of the well-defined subgrain structure with a subgrain size more than 1 μm.

## 4. CONCLUSION

The structural evolution in a grip and gauge portions of crept samples of a Re-containing (in wt %) 10Cr, 3 Co, 3W steel with a low N content (0.002) and high B content (0.01 wt.%) after creep at temperature of 650 °C under the stresses of 200 - 140 MPa was investigated. During long-term ageing the subgrain growth is controlled by Zener pressures exerted by $M_{23}C_6$ carbides, the Laves phase particles and NbX carbonitrides. The tempered martensitic lath structure is thermal stable for 10,987 hours of exposure; the precipitates effectively prevent the transformation of lath structure into subgrain one. Opposite, strain-induced subgrain coarsening takes place during creep. Both the applied stress and the decreasing Zener pressure from precipitates lead to formation of the well-defined coarse subgrain structure.

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