

EFFECT OF TEMPERING TEMPERATURE ON STRUCTURE AND MECHANICAL PROPERTIES OF RE-CONTAINING 10%CR MARTENSITIC STEEL

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Abstract

The effect of heat treatment on the microstructure and mechanical properties of a (in wt. %) 10 Cr-3Co-3W-0.2Re martensitic steel was investigated. The microstructure and mechanical properties of the steel subjected to the normalizing at 1050 °C and tempering at different temperatures ranging from 750 to 800 °C were studied. After normalizing at 1050 °C, the average size of prior austenite grains was $59 \pm 5 \mu\text{m}$ and no evidence of δ -ferrite was observed. The tempering temperature strongly affected the tempered martensite/ferrite lath structure: the lath width increased from 280 ± 30 to 710 ± 70 nm and dislocation density decreased from 3×10^{14} to $1.5 \times 10^{14} \text{ m}^{-2}$ when tempering temperature increased from 750 to 800 °C. The boundary M_{23}C_6 and M_6C carbides and randomly distributed within matrix Nb-rich MX carbonitrides were detected. Increasing the tempering temperature led to the significant growth of all secondary phase particles. No depletion of Re from the solid solution during tempering under any temperatures was revealed. Impact toughness was independent of tempering temperature, whereas tensile properties and hardness decreased with increasing tempering temperature. This steel tempered at 770 °C was subjected to the short-term creep tests at 650 °C under the applied stresses ranging from 200 to 140 MPa with a step of 20 MPa. High creep resistance of this steel under short-term creep testing was revealed which is attributed to the stability of tempered martensite/ferrite lath structure.

Keywords: Martensitic steel, heat treatment, microstructure, mechanical properties, precipitation

1. INTRODUCTION

Nine to 12 wt. % of Cr martensitic steels are used for critical components of boilers, steam main tubes and turbines of fossil power plants with increased thermal efficiency [1-8]. Several strengthening mechanisms ensure the improved creep resistance of these steels [1]. Precipitation strengthening is provided by M_{23}C_6 -type carbides and MX carbonitrides (where M is V or/and Nb and X is C or/and N) precipitated at grain boundaries and within the ferritic matrix, respectively, during tempering as well as Laves phase $\text{Fe}_2(\text{W},\text{Mo})$ precipitated at grain boundaries during creep/aging. MX carbonitrides, which are highly effective in pinning the lattice dislocations, play a vital role in a superior long-term creep resistance of the high-chromium martensitic steels, whereas boundary M_{23}C_6 carbides and Laves phase exerting a high Zener drag force stabilize the tempered martensite lath structure [1,9-13]. Solid solution strengthening is provided by a presence of Co, W, Mo atoms in the ferritic matrix at elevated temperatures. However, in contrast with cobalt, the tungsten and molybdenum have limited solubility within ferrite, and their excessive content leads to the precipitation of such W/Mo-rich particles as Laves phase $\text{Fe}_2(\text{W},\text{Mo})$ or M_6C carbides [1,9-13]. Depletion of solid solution by these elements highly deteriorates creep resistance [10]. In Ref. [6] it was noted that keeping the high content of solute tungsten in the solid solution during creep increased the long-term creep rupture strength, and this was attained by not increasing initial tungsten content by doping rhenium. Rhenium does not only act as a solid solution element, but also has an effect to maintain the sufficient amount of solute tungsten in the matrix during creep or thermal aging at 600 and 650 °C [2,5-7,9]. The aim of the present work is to investigate the effect of tempering temperature on the structure and mechanical properties of a Re-containing 10 %Cr martensitic steel and to estimate the effect of Re on the structure and mechanical properties.

2. EXPERIMENTAL PROCEDURE

The experimental steel denoted here as 10Cr-3Co-3W-0.2Re with chemical composition (in wt. %) 0.11C - 0.03Si - 0.14Mn - 9.85Cr - 3.2Co - 0.13Mo - 2.86W - 0.23V - 0.07Nb - 0.03Ni - 0.008B - 0.002N - 0.22Cu - 0.17Re was produced by vacuum-induction melting 100 kg ingot. Square bar with a cross-section of 150 mm × 150 mm and a height of 50 mm was homogenized at 1150 °C for 16 h and forged at 1150 °C. Then, the steel was normalized at 1050 °C for 1 h and tempered at temperatures of 750, 770 and 800 °C for 3 h and air cooled. Tensile tests were carried out on specimens that had a cross section of 1.5 mm × 3 mm and a 21 mm gage length using an Instron 5882 machine at 20 and 650 °C with a strain rate of $2 \times 10^{-3} \text{ s}^{-1}$. Hardness was measured under a load of 750 N using a Wolpert 3000BLD device at ambient temperature. Charpy impact tests were carried out on standard 10 mm × 10 mm × 55 mm specimens with a 2 mm V-notch in accordance with the ASTM E23-05 standard using an Instron IMP460 machine at ambient temperature. Flat specimens tempered at 770 °C with a gage length of 25 mm and a cross section of 7 mm × 3 mm were crept until rupture at 650 °C under an applied stress ranging from 140 to 200 MPa with a step of 20 MPa. The structure was analyzed using an optical microscope an Olympus GX7 and a transmission electron microscope JEOL-2100 (TEM) with an INCA energy dispersive X-ray spectrometer (EDS). For the optical metallography, the specimens were ground, polished and etched in a solution of 2 pct HNO₃ and 1 pct HF in 97 pct H₂O. The foils for TEM analysis were subjected to electrolytic polishing in a solution of 10 pct perchloric acid in a glacial acetic acid with Struers "Tenupol-5" machine. XRD spectra of the precipitated phases were recorded using a Rigaku Ultima IV diffractometer equipped with a Cu-K_α radiation source and a semiconductor detector. Equilibrium volume fractions of phases were calculated with the Thermo-Calc software using the TCFE7 database.

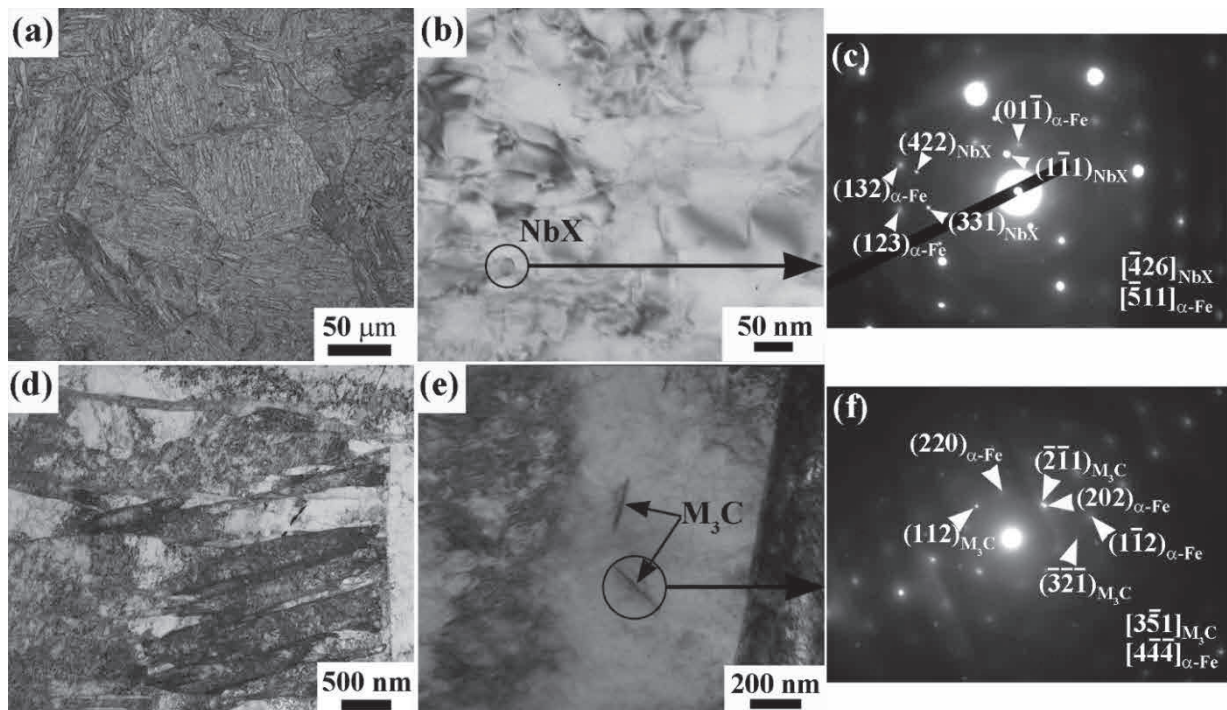


Figure 1 Structure of the 10Cr-3Co-3W-0.2Re steel after normalization at 1050 °C for 1 h, air cooling, obtaining by a) optic microscopy, b-f) TEM

3. RESULTS AND DISCUSSION

3.1. Normalized structure

Figure 1 shows the microstructure of the steel studied after normalization at 1050 °C for 1 h followed by air cooling.

The average size of prior austenite grains (PAGs) was $59 \pm 5 \mu\text{m}$, wherein no evidence for the formation of δ -ferrite in the steel studied was found by optical metallography (**Figure 1a**).

The average transverse dimension of martensitic laths was $183 \pm 20 \text{ nm}$, and a high dislocation density of $4 \times 10^{14} \text{ m}^{-2}$ was observed within the martensitic laths (**Figure 1d**). Two types of dispersoids were revealed after normalization. First, fine round-shape Nb-rich MX particles (**Figures 1b,c**) with an average size of $33 \pm 5 \text{ nm}$ remain undissolved under normalization. Second, Fe-rich M_3C platelets with an average length of $230 \pm 30 \text{ nm}$ were found (**Figures 1e,f**). Both these types of dispersoids are distributed uniformly within the martensitic laths (**Figures 1b,e**). It is apparent that these cementite particles precipitate on the NbX interfaces or homogeneously during auto-tempering [14] (**Figure 1e**).

3.2. Tempered structure

The structures of the 10Cr-3Co-3W-0.2Re steel after tempering at temperatures of 750, 770 and 800 °C for 3 h are shown on **Figure 2**. The formation of tempered martensite lath structure occurred at any tempering conditions. With increasing tempering temperature from 750 to 800 °C, tempered martensite lath structure was gradually transformed into the subgrain structure (**Figure 2**), wherein the average transverse dimension of the martensitic laths increased from 280 ± 30 to $710 \pm 70 \text{ nm}$ and the dislocation density within the laths insignificantly decreased from 2.8×10^{14} to $1.6 \times 10^{14} \text{ m}^{-2}$. The average size of subgrains in the structure of the steel tempered at 800 °C reached $580 \pm 60 \text{ nm}$.

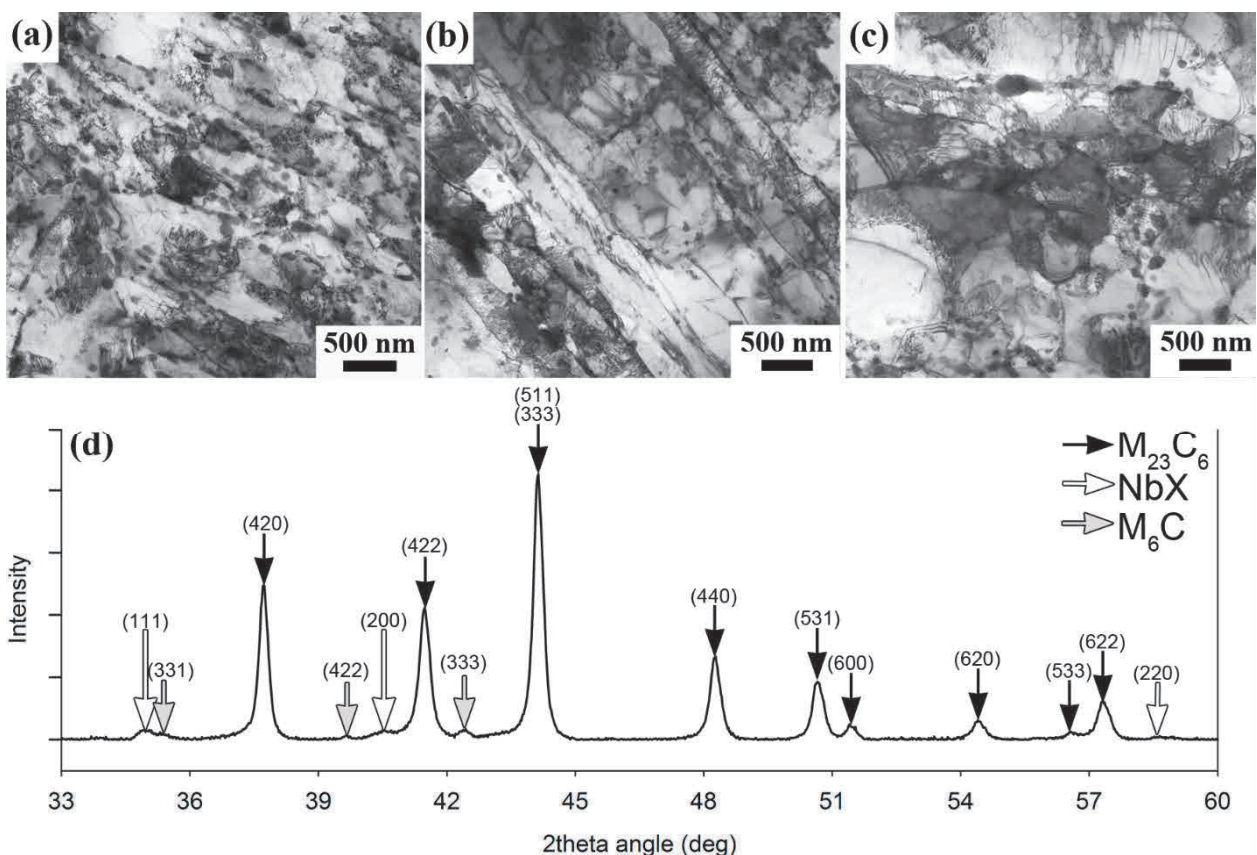


Figure 2 Structure of the 10Cr-3Co-3W-0.2Re steel after tempering at 750 °C (a), 770 °C (b), 800 °C (c) and X-ray spectra of the steel studied after tempering at 770 °C (d)

The chemical composition of the ferritic steel studied after tempering at different temperatures was (in wt. %) 79Fe - 9Cr - 3.6Co - 3.3W - 0.1Mo - 0.2Re - 0.2V. No depletion of W, Co, Mo, Re and V from the solid solution during tempering under any conditions was revealed. The decrease in the Cr content from 9.8 % to

9 % and absence of Nb in the solid solution after tempering at all temperatures indicated the precipitation of Cr-rich and Nb-rich phases. Three types of the precipitates were observed after tempering at all conditions according to **Figure 2d**. First, Cr-rich $M_{23}C_6$ carbides instead of Fe-rich M_3C carbides having a round shape precipitated along the boundaries of PAGs, blocks, packets and martensitic laths. This phase was dominant at all tempering temperatures. Increasing the tempering temperature from 750 to 800 °C led to an increase in the average size of $M_{23}C_6$ carbides from 67 ± 7 to 88 ± 9 nm, while the volume fraction of this phase was nearly the same for all tempering temperatures according to Thermo-Calc prediction. Second, fine Nb-rich MX carbonitrides with round shape precipitated inside the martensitic laths. An average size of Nb-rich particles after tempering at 750 °C is less than that in the normalized condition that is attributed to the additional precipitation of this phase during tempering. Increasing the tempering temperature from 750 to 800 °C resulted in about 2-fold increase in the average size of Nb-rich MX carbonitrides from 21 ± 2 to 46 ± 5 nm. Third, W-rich M_6C carbides precipitated along the boundaries of martensitic laths; the average size of these carbides increased from 20 ± 2 to 51 ± 5 nm with increase in the tempering temperature from 750 to 800 °C. The volume fractions of two last phases were negligible.

To estimate the effect of Re on the structural changes during tempering, the structure of the 10 % Cr Re-free steel with similar contents of interstitial elements was investigated after tempering at 770 °C [15]. The comparison of structures of the 10 % Cr Re-free and Re-containing steels showed that the doping by Re together with increasing the W content and decreasing the Mo content resulted in the increase in the average PAG size from 35 to 59 μm and decrease in the average transverse dimension of martensitic laths from 500 to 290 nm. No effect of Re on the dispersoids was detected.

3.3. Mechanical properties

The effect of tempering temperature on the engineering stress-strain curves, total elongation, uniform elongation and area of reduction is shown in **Figure 3**. The yield stress (YS) and ultimate tensile strength (UTS) at 20 and 650 °C testing, the impact toughness (KCV) and hardness (HB) at room temperature are summarized in **Table 1**.

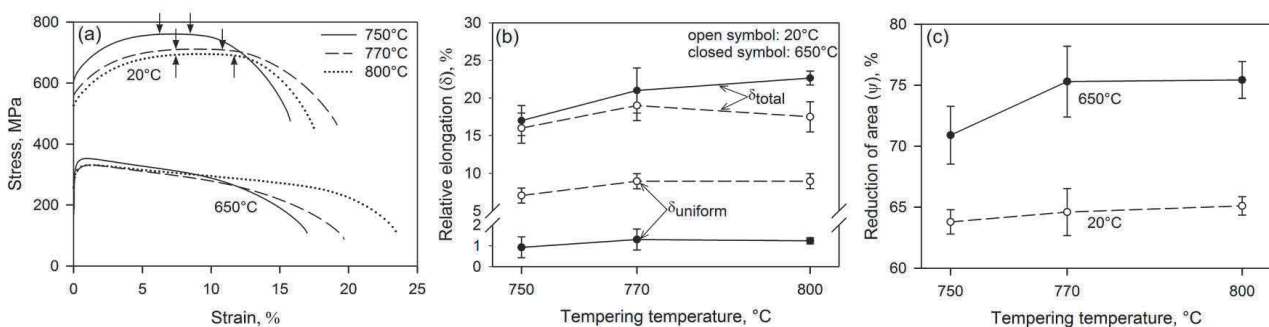


Figure 3 The effect of the tempering temperature on the engineering stress-strain curves (a), relative elongation (b) and reduction of area (c) at 20 and 650 °C testing for the 10Cr-3Co-3W-0.2Re steel

At room temperature, the specimens tempered at 750, 770 and 800 °C showed an extensive strain hardening at the initial stage (**Figure 3a**) which was followed by the apparent steady-state flow up to necking. Post-uniform necking elongation has occurred up to fracture. Increasing the tempering temperature led to an increase in the duration of the apparent steady-state stage and did not affect the relative elongation and reduction of area. At 650 °C, all the engineering stress-strain curves showed the short stage of extensive strain hardening, very short apparent steady-state stage and long stage of necking. Increasing the tempering temperature led to an increase in the total elongation and reduction of area. At 20 °C testing, an increase in the tempering temperature resulted in a decrease in YS from 618 to 530 MPa and UTS from 760 to 695 MPa.

At 650 °C testing, an increase in the tempering temperature led to a decrease in YS from 334 to 315 MPa and UTS from 356 to 330 MPa (**Table 1**).

Table 1 Mechanical properties of the 10Cr-3Co-3W-0.2Re steel after tempering at 750, 770 and 800 °C

T _{tempering} , °C	T _{test} , °C	YS, MPa	UTS, MPa	KCV, J / cm ²	Hardness, HB
750	20	618 ± 5	760 ± 5	164 ± 1	248 ± 7
	650	334 ± 3	356 ± 3	-	-
770	20	558 ± 5	712 ± 5	176 ± 3	223 ± 4
	650	300 ± 8	324 ± 5	-	-
800	20	530 ± 5	695 ± 5	172 ± 13	211 ± 5
	650	315 ± 4	330 ± 2	-	-

Tempering temperature did not affect the impact toughness of the steel studied; impact toughness was ~ 170 J / cm² after tempering at any temperature conditions (**Table 1**). Shear fracture measured according to ASTM 23-5 was 65-70 %. Increasing the tempering temperature from 750 to 800 °C reduces the hardness from 248 to 211 HB. No effect of Re on the mechanical short-term properties was detected [16]. So, increasing in the transverse dimension of the martensitic laths and formation of subgrains together with growth of dispersoids along PAG and lath boundary as well as inside martensitic laths leads to decrease in the strength characteristics (YS and UTS) and hardness but does not affect impact toughness of the steel studied. 770 °C-tempering provides the structure and mechanical properties that satisfies the requirements for boiler steels for power units.

After 770 °C-tempering, the flat specimens were crept until rupture at 650 °C under an applied stress ranging from 140 to 200 MPa with a step of 20 MPa. Creep test under an applied stress of 140 MPa is in progress now. To estimate the effect of Re on the short-term creep properties, the comparison of creep rupture time of the Re-containing steel studied with the 10 % Cr Re-free steel [17] was represented in **Table 2**.

Table 2 Creep rupture time (h) for the 10Cr-3Co-3W-0.2Re and 10 % Cr Re-free steels [17] tempered at 770 °C

Applied stress	200 MPa	180 MPa	160 MPa	140 MPa
10Cr-3Co-3W-0.2Re	8	84	440	>2700 (in progress)
10 % Cr Re-free steel [17]	-	18	211	1425

The steel studied demonstrated improved creep properties in comparison with the 10 % Cr Re-free steel [17]. Times to rupture of steel studied are approximately 4.6 and 2 times higher than those for the Re-free steel at 180 and 160 MPa, respectively [17].

4. CONCLUSION

The effect of heat treatment on the microstructure and mechanical properties of a 10 wt. % Cr-3Co-3W-0.2Re martensitic steel was investigated. An increase in the tempering temperature from 750 to 800 °C leads to a gradual transformation of tempered martensitic lath structure with an average transverse dimension of martensitic laths of 280 nm to a subgrain structure with an average subgrain size of 580 nm, wherein the dislocation density insignificantly decreases. Size of Cr-rich M₂₃C₆ carbides, Nb-rich MX carbonitrides and W-rich M₆C carbides increase with increasing the tempering temperature. An increasing in tempering temperature from 750 to 800 °C results in the decrease in strength characteristics (YS and UTS) and hardness but does not affect impact toughness of the steel studied. 770 °C-tempering provides the structure and mechanical

properties that satisfies the requirements for boiler steels for power units. Alloying by Re improves the short-term creep properties of the 9-10 %Cr martensitic steels.

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