STRUCTURAL CHANGES IN A RE-CONTAINING 10 %Cr-3 %Co-3 %W STEEL UPON LONG-TERM AGEING AT 650 °C

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Abstract

The application of new materials in the power units of new generation, which are able to work at ultra-supercritical parameters of steam (T ≥ 620-650 °C, P = 25 - 35 MPa), can increase their efficiency up to 41-44 % and decrease the amount of harmful emissions. The aim of the present research was to investigate the major structural changes in new Re-containing steel during ageing at temperature of 650 °C. Structural changes in martensitic 10%Cr-3 %Co-3 %W-0.2 %Re steel during long-term ageing at 650 °C for about 13,600 h were investigated. This steel was solution treated at 1050 °C for 1 h, cooled in air, and subsequently tempered at 770 °C for 3 h. High thermal stability of tempered martensitic/ferritic lath structure is provided by a dispersion of fine $M_{23}C_6$ carbides precipitated during tempering and the Laves phase particles precipitated after 110 h of 650 °C aging. The precipitation of the Laves phase particles is accompanied with depletion of W atoms from the ferritic matrix. Moreover, decreasing W content in the ferritic matrix have a good correlation with increasing volume fraction of the Laves phase particles in the structure of the 10 %Cr-3 %Co-3%W-0.2 %Re steel during long-term ageing at 650 °C. The effect of Re addition on the kinetic of depletion of W from the solid solution and kinetic of precipitation Laves phase will be discussed.

Keywords: Martensitic steel, phase transformation, ageing, particles, microstructural evolution, precipitation

1. INTRODUCTION

9 - 12 % Cr martensitic steels are promising materials for critical components of boilers, steam main tubes and turbines of the fossil fuel power plants, having a low coefficient of thermal expansion and good creep resistance at temperatures up to 620 °C [1,2]. 10 %Cr-3 %Co martensitic steel with low N content of 0.003 wt.% and high B content of 0.008 wt.% demonstrates time to rupture of ~40,000 h at 120 MPa and 650 °C [3]. Suggested [4,5] that the addition of Re in the 10 %Cr-3 %Co martensitic steel with low N content and high B content enhances their creep resistance at the expense of increasing of solute W in the ferritic matrix at elevated temperatures. In the previous study [6], authors reported on the improved short-term creep strength at 650 °C in the Re-containing 10 %Cr-3 %Co-3 %W steel with low N content and high B content. Note [6] that the precipitation of the high fraction of the fine Laves phase particles provided the effective particle strengthening, but rhenium in the experimental 10Cr-3Co-3W-0.2Re steel did not lead to retaining an increased amount of solute W in the ferritic matrix during creep at 650 °C. There are limited experimental data about the effect of Re on the mechanical properties and the stability of tempered lath structure of the high-Cr martensitic steels during ageing and creep at elevated temperatures in the open literature [7-10]. The aim of the present study is to investigate the stability of the structure of the 10Cr-3Co-3W-0.2Re steel during long-term ageing for 13,670 h as well as to report on the major structural changes during ageing and their effect on softening of the steel.

2. EXPERIMENTAL PROCEDURE

The steel denoted here as 10Cr-3Co-3W-0.2Re with chemical composition of (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 as 100 kg ingot. The 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 temperature 770 °C for 3 h, then air cooled. The tempered samples was aged at 650 °C for 8, 40, 83, 110, 254, 440, 1000, 2000, 10,987 and 13,670 h. The structure was analysed using an optical microscope an Olympus GX7, transmission electron microscope JEOL-2100 (TEM) with an INCA energy dispersive X-ray spectrometer (EDS) and scanning electron microscope (SEM) Quanta 600. For the optical metallography, the specimens were ground, polished and etched in a solution of 2 pct HNO_3 and 1 pct HF in 97 pct H_2O. The foils for TEM and SEM analyses were subjected to electrolytic polishing in a solution of 10 % perchloric acid in a glacial acetic acid with Struers "Tenupol-5" machine. Hardness was measured under a load of 750 N using a Wolpert 3000BLD device at ambient temperature. To estimate the effect of Re on the microstructural changes during long-term ageing, the structural parameters in the 10Cr-3Co-3W-0.2Re steel was compared with those in the Re-free steel with a chemical composition of (in wt.%): 0.10C-0.06Si-0.1Mn-10.0Cr-3.0Co-0.70Mo-2.0W-0.2V-0.05Nb-0.17Ni-0.008B-0.003N, denoted here as 10Cr-3Co-2W-0Re [3].

3. RESULT AND DISCUSSION

3.1. Tempered structure

Figure 1 shows the microstructure of the 10Cr-3Co-3W-0.2Re steel after normalization at 1050 °C, air cooling, and tempering at 770 °C for 3 h, air cooling. The average size of prior austenite grains (PAGs) was 59 μm that significantly exceeds the PAG size of 35 μm in the 10Cr-3Co-2W-0Re steel [3]. These steels differ in the W and Mo contents and the Re addition in the 10Cr-3Co-3W-0.2Re steel; the molybdenum equivalent (about 1.7) is the same for both steels. The results of the structural investigations after tempering and long-term ageing at 650 °C are summarized in **Table 1**.

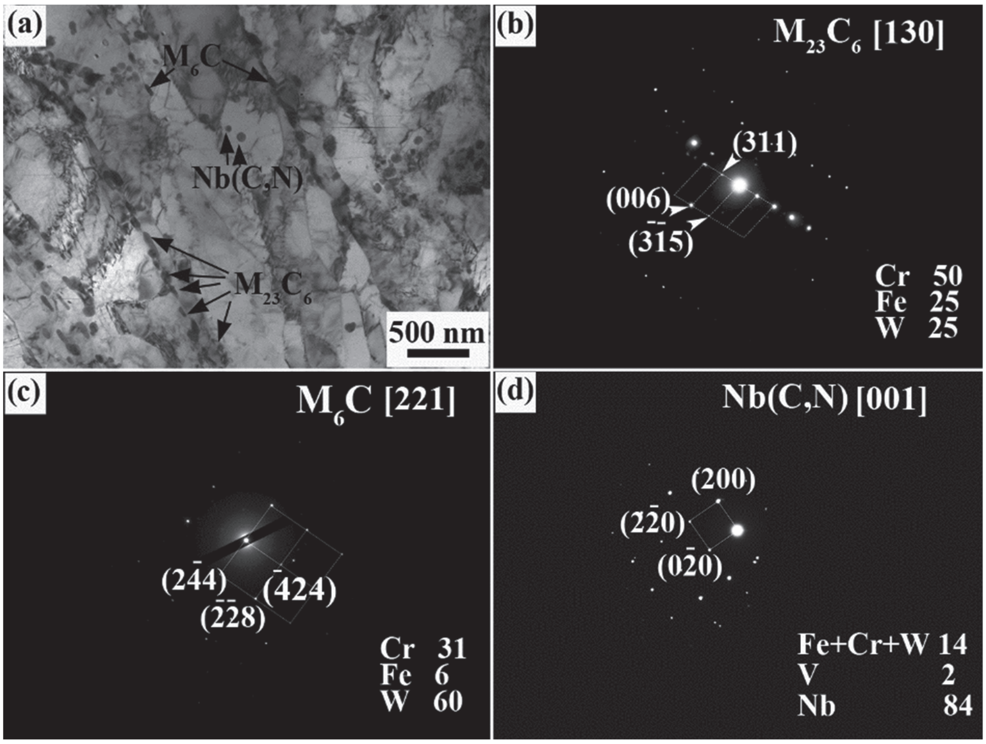

Figure 1 Microstructure of the 10Cr-3Co-3W-0.2Re steel after normalizing at 1050 °C and tempering at 770 °C for 3 h, air cooling (a) and diffraction patterns from secondary particles (b-d) obtained by TEM of foil (a) and carbon replicas (b-d). The amount of main elements in the particles is indicated in wt.% measured from extraction carbon replicas by EDS with TEM.

Table 1 Structural parameters of the 10Cr-3Co-3W-0.2Re steel in the tempered state and aged for different times at 650 °C

Ageing time, h	Lath size, nm	Subgrain size, nm	ρ_{disl}, $\times 10^{14}$ m^{-2}	The mean size of particles, nm			
				$M_{23}C_6$	Nb(C,N)	M_6C	Laves phase
tempering	293 ± 30	270 ± 30	1.98 ± 0,1	67 ± 7	37 ± 4	~40 ± 4	-
8	338 ± 50	389 ± 55	1.39 ± 0,1	65 ± 10	30 ± 5	84 ± 10	-
83	225 ± 50	317 ± 70	1.53 ± 0,1	65 ± 10	36 ± 5	50 ± 5	122 ± 15
440	348 ± 60	363 ± 65	1.37 ± 0,1	73 ± 10	45 ± 5	-	136 ± 20
13670	350 ± 20	310 ± 9	1.04 ± 0.4	80	-.	-	198

After tempering at 770 °C, the average transverse size of martensitic laths was 293 ± 30 nm, and a high dislocation density in the lath interior was about 1.98 × 10^{14} m^{-2} (**Table 1**). Finer martensitic lath structure in the steel studied was observed in the comparison with the 10Cr-3Co-3W-0.2Re steel (a mean size of martensitic lath of 380 nm) [3]. Analysis of the chemical compositions and diffraction patterns showed Cr-rich $M_{23}C_6$ carbides with a chemical composition of (in wt.%) 50 %Cr-25 %Fe-25 %W (**Figure 1b**), W-rich M_6C carbides with a chemical composition of 31%Cr-6 %Fe-60 %W (**Figure 1c**) and Nb-rich M(C,N) carbonitrides with a chemical composition of 14 %(Fe+Cr+W)-2%V-84%Nb (**Figure 1d**). The $M_{23}C_6$ and M_6C carbides are located on low- and high-angle boundaries, whereas Nb(C,N) carbonitrides are randomly distributed in the ferrite matrix (**Figure 1a**). A mean sizes of $M_{23}C_6$ carbides, M_6C carbides and Nb(C,N) carbonitrides were 65, 40 and 37 nm, respectively (**Table 1**). The sizes of secondary particles in the 10Cr-3Co-3W-0.2Re steel are similar with those in the 10Cr-3Co-2W-0Re steel [3].

3.2. Hardness and structure after ageing

In the aged specimens, the hardness retains the value of 221 ± 3 HB with increasing in exposure time up to 13,670 h (**Table 2**).

Table 2 Hardness of the steel studied after ageing

Ageing time, h	8	83	110	254	440	10,987	13,670
Hardness, HB	221 ± 3	224 ± 4	217 ±3	225 ± 2	222 ± 4	217 ± 3	221 ± 3

Figure 2 illustrates the microstructure of the 10Cr-3Co-3W-0.2Re steel after ageing at 650 °C for 13,670 h. After ageing at 650 °C for 13,670 h, tempered martensitic/ferritic lath structure remains in the 10Cr-3Co-3W-0.2Re steel; the martensitic lath width increases by 20 % compared to tempered state (**Table 1**). A slight increase in the martensitic lath width correlates with an insignificant decrease in the dislocation density during the ageing at 650 °C; the dislocation density decreases to 1.04 × 10^{14} m^{-2} after ageing at 650 °C for 13,670 h (**Table 1**). During ageing, a slight coarsening of Cr-rich $M_{23}C_6$ carbides and Nb-rich MX carbonitrides takes place (**Table 1**). Moreover, the chemical compositions (in wt%) of Cr-rich $M_{23}C_6$ carbides and Nb-rich MX carbonitrides are 57 %Cr-17 %Fe-26 %W and 10 %(Fe+Cr+W)-2 %V-88 %Nb, respectively, that correspond to their equilibrium values obtained by Thermo-Calc prediction. Increasing Cr and W content in $M_{23}C_6$ carbides as well as increasing Nb content in NbX carbonitrides do not lead to significant coarsening of these particles. The effect of Re on structural changes is insignificant; the sizes of structural parameters in the 10Cr-3Co-3W-0.2Re steel are similar with those in the 10Cr-3Co-2W-0Re steel [3]. The transverse width of martensitic lath and the size of subgrains are 27 % and 30 % less than those in the 10Cr-3Co-2W-0Re steel after 10,000 h of ageing [3].

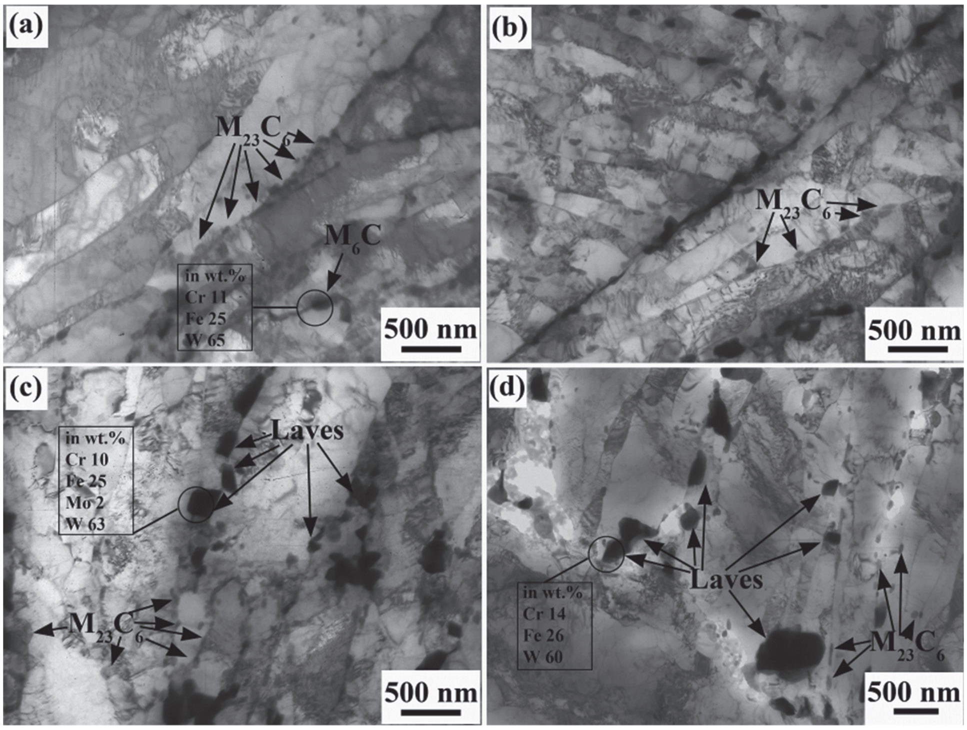

Figure 2 Microstructures of the 10Cr-3Co-3W-0.2Re steel after ageing at 650 °C for (a) 8 h, (b) 83 h, (c) 440 h and (d) 13,670 h obtained by TEM of foils. The amount of main elements in the particles is indicated in wt.% measured from extraction carbon replicas by EDS with TEM.

Figure 3 demonstrates the evolution of microstructure of the 10Cr-3Co-3W-0.2Re steel during ageing at 650 °C for 8 h, 40 h, 210 h, 1000 h, 2000 h and 13,670 h obtained by SEM of foils**.** Two types of particles could be clearly distinguished by their bright contrast in the back scattered electron image. Bright white particles are W-rich precipitates, and gray particles are Cr-rich $M_{23}C_6$ carbides. When ageing time increases, the amount of W-rich precipitates increases. The precipitation of W-rich particles is accompanied by W depletion from the solid solution (**Figure 4**). After the first 8 h of ageing, the amount of the W-rich particles is insignificant (~0.17 %). The particle fraction increases up to 2.9 % for next 500 h and further does not change for 13,670 h (**Figure 4a**). At the same time, W content decreases in the ferritic matrix to 1.2 wt.% for 2000 h of long-term ageing (**Figure 4a**). The W-rich phase particles precipitated along the boundaries of prior austenite grains and martensitic laths/subgrains in the vicinity of $M_{23}C_6$ carbides (**Figure 3**). In other studies [11-15] was reported that M_6C carbides are able to grow up to very large particles at the expense of W atoms from segregations in the vicinity of the PAG/lath/subgrain boundaries. On the other hand, some M_6C carbides are isolated from W segregation by other grain boundary $M_{23}C_6$ carbides that lead to the dissolution of M_6C carbides and precipitation of the Laves phase particles ($Fe_2(W,Mo)$). Since the dissolution of M_6C carbides enriches the ferritic matrix by W, the precipitation of the Laves phase particles is a thermodynamically-favorable reaction. The results of present research are in agreement with the results of previous study [11]. All M_6C carbides were surrounded by $M_{23}C_6$ carbides and were isolated from W segregation that led to absence of very large M_6C particles (about 500 nm) after tempering at 770 °C and ageing for 110 h. M_6C carbide is metastable phase and has to be dissolved with precipitation of the Laves phase, which is stable phase. This process was observed in the present research. Note that the nucleation mechanism of the Laves phase particles is the formation of the nuclei on M_6C/ferrite surface. Moreover, the nuclei of the Laves phase have orientation relationships with M_6C carbides and ferrite matrix. The dissolution of M_6C carbides started after 10 h of ageing and ended after 110 h of ageing. The Laves phase particles start to precipitate after 110 h of ageing and grow up to 200 nm for next 13,670 h of ageing. The chemical composition of the Laves phase is (in wt.%) 14 %Cr-26 %Fe-60 %W.

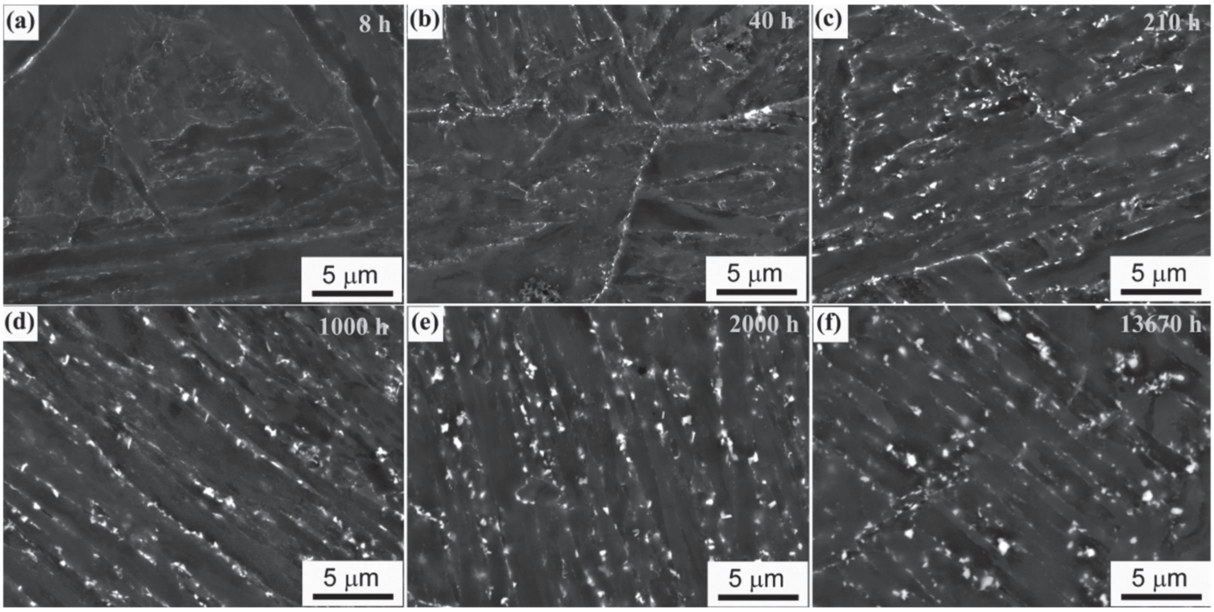

Figure 3 Microstructures of the 10Cr-3Co-3W-0.2Re steel after ageing at 650 °C for (a) 8 h, (b) 40 h, (c) 210 h, (d) 1000 h, (e) 2000 h and (f) 13,670 h obtained by SEM of foils.

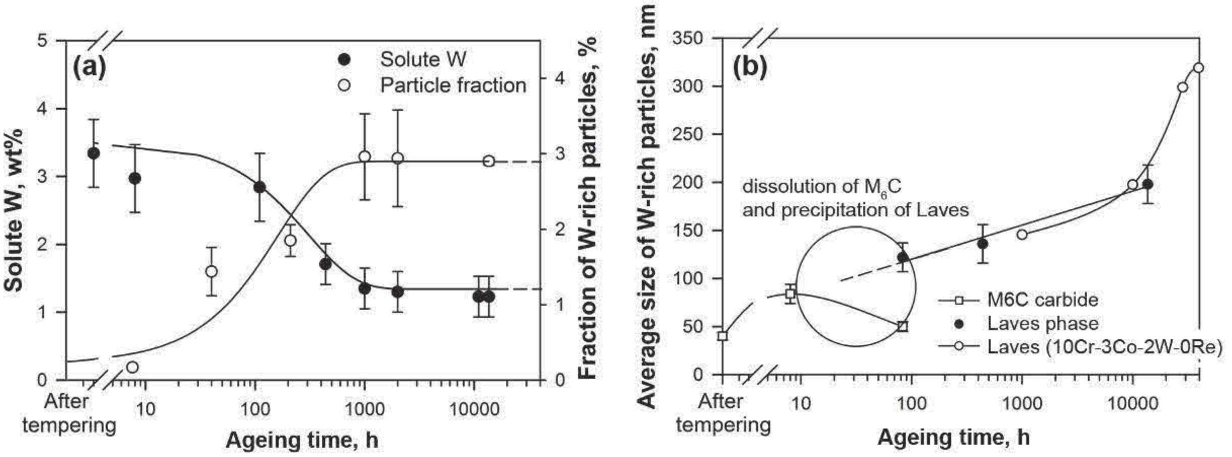

Figure 4 Decreasing W content in the ferritic matrix and increasing fraction of W-rich particles during ageing at 650 °C (a), as well as change of the size of W-rich particles during ageing in comparison with the 10Cr-3Co-2W-0Re steel [3] (b)

The depletion of W from the ferritic matrix corresponds to the precipitation of the Laves phase particles and is not related to increasing W content in $M_{23}C_6$ carbides and Laves phase. The sizes of the Laves phase particles in the steel studied is similar with those in the 10Cr-3Co-2W-0Re steel (**Figure 4b**). So, the increasing W content to 3 % and Re additive do not effect on the coarsening of the Laves phase particles during long-term ageing for 13,670 h. Nevertheless, both $M_{23}C_6$ carbides with size less than 100 nm and Laves phase with sizes less than 200 nm effectively stabilize the tempered martensitic/ferritic lath structure during ageing at 650 °C. So, tempered martensitic/ferritic lath structure has high resistance to thermal exposure without the significant changes in the microstructure and hardness during long-term ageing at 650 °C.

4. CONCLUSION

The tempered martensitic/ferritic lath structure of the investigated 10Cr-3Co-3W-0.2Re steel is thermally stable at a temperature of 650 °C for long time. The major structural change which occurred during ageing is the precipitation of W-rich Laves phase via interim M_6C carbide that is accompanied by the depletion of W from the ferritic matrix. Both $M_{23}C_6$ carbides with size less than 100 nm and Laves phase with sizes less than 200 nm effectively stabilize the tempered martensitic/ferritic lath structure during ageing for 13,670 h at 650 °C. No softening during ageing supports this suggestion.

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