



On effect of rhenium on mechanical properties of a high-Cr creep-resistant steel



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ABSTRACT

9–12%Cr martensitic steels are perspective materials for critical components of new high-efficiency power plants working at ultra-supercritical parameters of steam. Addition of 0.2% rhenium in the experimental steel improved the short-term creep strength at 650 °C. Comparison of kinetics of tungsten depletion from the matrix in different high-Cr martensitic steels showed that 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 both aging and creep at 650 °C. At the same time, the precipitation of the high fraction of the fine Laves phase particles provided the effective particle strengthening.

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1. Introduction

The heat-resistant steels with 9–12%Cr like a TOS series are used for critical components of boilers, steam main pipes and turbines of fossil fuel power plants with increased thermal efficiency [1–7]. TOS203 steel was developed by Toshiba in 1980's for high-temperature blade [2,4–6] which had the increased W and decreased Mo contents and an addition of Re, comparing with the TOS202 and TOS110 rotor steels [2]. Rhenium has been suggested an effective contributor to creep strength of nickel-base superalloys [8]. In the TOS203 steel, rhenium acts as a solid solution strengthener and maintains an increased amount of solute tungsten in the matrix during creep or thermal aging at 600 and 650 °C [2,4–6,9]. Moreover, Re significantly suppresses the W diffusion in Fe-15 mol.%Cr-based alloy [10].

It is worth noting that experimental data on the Re effect on creep behavior were obtained during creep at 550–650 °C for high-chromium martensitic steels with standard N content (0.03–0.05 wt%), high Ni content (about 0.6 wt%) and low Co content (about 1 wt%) [2,4–6,9]. However, the recent investigations of alloy design [11–15] showed that modification of the TOS110 steel by reducing nitrogen and increasing boron demonstrated an improved creep resistance up to 40,000 h at 650 °C/120 MPa. Rhenium addition to this modification of the TOS110 steel may further

improve the creep strength. The aim of the present work is to report the positive effect of rhenium on the creep strength of 10 wt%Cr-3%Co-3%W martensitic steel containing 0.002%N and 0.008%B during creep and aging at 650 °C.

2. Material and experimental

100 kg steel ingot containing rhenium, denoted here as 10Cr-3Co-3W-0.2Re, was prepared by vacuum induction melting. The steel was normalized at 1050 °C for 1 h, air quenched and tempered at 770 °C for 3 h. The Re-free 9Cr-3Co-3W-0Re steel [16,17], Re-free 10Cr-3Co-2W-0Re steel with high B and low N contents (modified TOS110 steel) [12–15] and TOS203 steel containing 0.2%Re [2–6] were used for comparison to clarify the rhenium effect on the mechanical properties and microstructural changes. The chemical compositions and heat treatments of the steels are listed in Table 1.

Tensile tests were carried out on the specimens having a cross section of $1.5 \times 3 \text{ mm}^2$ and a 16 mm gauge length using an Instron 5882 testing machine at temperatures of 20, 500, 600 and 650 °C with a strain rate of $2 \times 10^{-3} \text{ s}^{-1}$. Flat specimens with a gauge length of 25 mm and a cross section of $7 \times 3 \text{ mm}^2$ were subjected to creep tests until rupture at 650 °C under initial stresses ranging from 100 to 200 MPa. The structural characterization of ruptured creep specimens was carried out using a JEM-2100 transmission electron microscope (TEM). Phase analysis of the precipitated particles extracted from the steel samples by electrolysis was carried

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Table 1
Chemical compositions of the steels studied (in wt%) and their heat treatments.

	C	Cr	Co	Mo	W	V	Nb	B	N	Ni	Re
10Cr-3Co-3W-0.2Re	0.11	9.85	3.2	0.13	3.2	0.2	0.07	0.008	0.002	0.03	0.17
9Cr-3Co-3W-0Re [16,17]	0.12	9.5	3.2	0.45	3.1	0.2	0.06	0.005	0.05	0.2	–
Mod. TOS110 [12–15]	0.10	10.0	3.0	0.70	2.0	0.2	0.05	0.008	0.003	0.17	–
TOS203 [2–6]	0.11	10.5	1.0	0.1	2.5	0.2	0.1	0.01	0.03	0.6	0.2

10Cr-3Co-3W-0.2Re: Normalized at 1050 °C for 1 h, air quenched and tempered at 770 °C for 3 h.

9Cr-3Co-3W-0Re [16,17]: Normalized at 1050 °C for 0.5 h, air quenched and tempered at 750 °C for 3 h.

Mod. TOS110 [12–15]: Normalized at 1060 °C for 0.5 h, air quenched and tempered at 770 °C for 3 h.

TOS203 [5]: Normalized at 1120 °C for 3 h, oil quenched and tempered at 680 °C for 5 h.

out by X-ray diffraction (XRD) using a Rigaku Ultima IV diffractometer.

3. Results and discussion

An average size of prior austenite grains (PAGs) in the 10Cr-3Co-3W-0.2Re steel was 55 μm after final heat treatment. An average lath thickness was approximately 0.3 μm . The high dislocation density of approximately $2 \times 10^{14} \text{ m}^{-2}$ was observed within the lath interiors. The fine M_{23}C_6 carbides with a mean size of 70 nm were located on the boundaries of PAGs/packets/blocks/laths, and the NbX carbonitrides with a mean size of 40 nm were uniformly distributed within the martensitic laths.

Ultimate tensile strength (UTS) (Fig. 1a) and yield strength (YS) (Fig. 1b) of the 10Cr-3Co-3W-0.2Re steel continuously decrease as testing temperature increases. UTS and YS of the 10Cr-3Co-3W-0.2Re steel correspond to those for the Re-free 9Cr-3Co-3W-0Re [16] and modified TOS110 [12,14] steels, whereas UTS of the TOS203 steel [5] is higher at all testing temperatures and YS is higher only at ambient temperature. Remarkably higher UTS and YS values of the TOS203 steel as compared to other steels are attributed to lower tempering temperature (Table 1). Thus, rhenium in

the 10Cr-3Co-3W-0.2Re steel does not affect an overall strengthening at temperatures of 20, 600 and 650 °C (Fig. 1a and b).

Fig. 1c shows the creep rupture data for the steels at 650 °C. At short-term creep tests with rupture time <5000 h, the 9Cr-3Co-3W-0Re [16,17] and TOS 203 [5] steels had the significant advantage, whereas appearance of creep strength breakdown dramatically reduced their creep resistance at long-term creep. Both steels showed the same creep strength after 10,000 h due to the high nitrogen content. On the other hand, the modified TOS110 steel with lower N content demonstrated an improved creep strength during long-term creep up to 40,000 h [15]. The 0.2% Re addition and increase in W content up to 3% in the experimental 10Cr-3Co-3W-0.2Re steel led to significant increase in the short-term creep strength in comparison with the modified TOS110 steel. Long-term creep tests of the 10Cr-3Co-3W-0.2Re steel are in progress.

For all steels, the W content in the matrix reaches values of 1.3 and 1.2 wt% after ~ 1000 h of thermal aging or ~ 500 h of creep at 650 °C, respectively (Fig. 2). Creep accelerates the tungsten depletion from the matrix. Depletion of tungsten, $f(W)$, is independent of steel alloying and could be described as

$$f(W) \sim 2.17 \exp(-0.0033t) \text{ during aging} \quad (1)$$

and

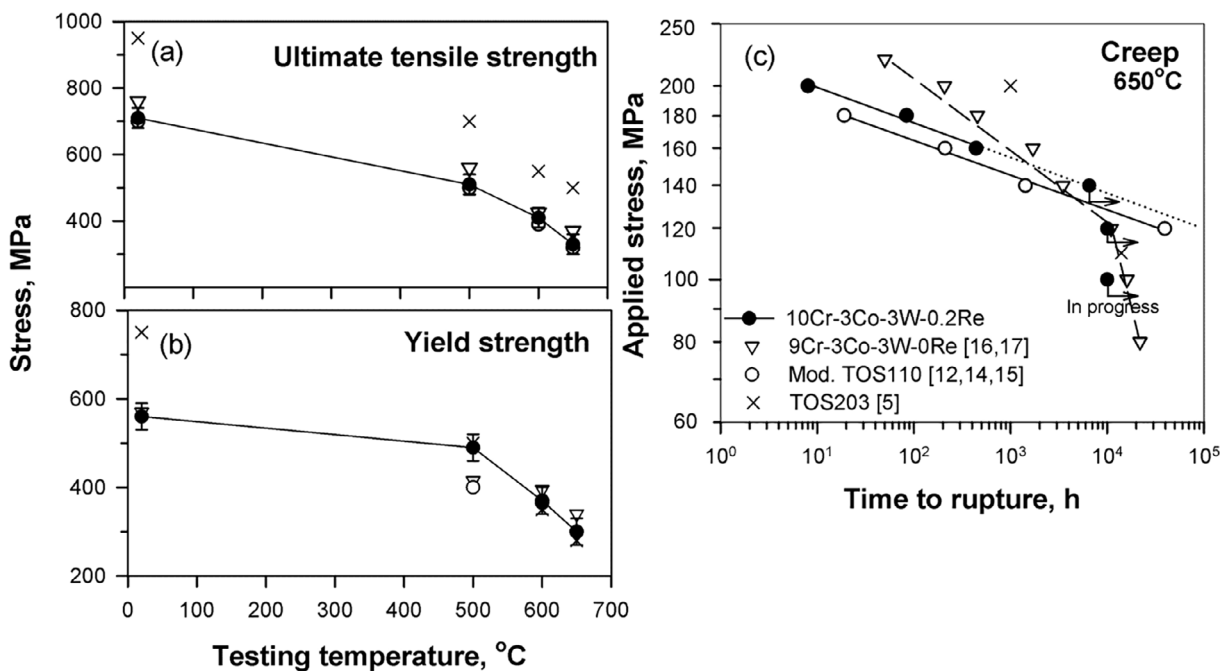


Fig. 1. Ultimate tensile strength (a) and yield strength (b) vs. testing temperature for the 10Cr-3Co-3W-0.2Re steel, creep behavior (c) in comparison with the Re-free 9Cr-3Co-3W-0Re [16,17], modified TOS110 [12,14,15] and TOS203 [5] steels.

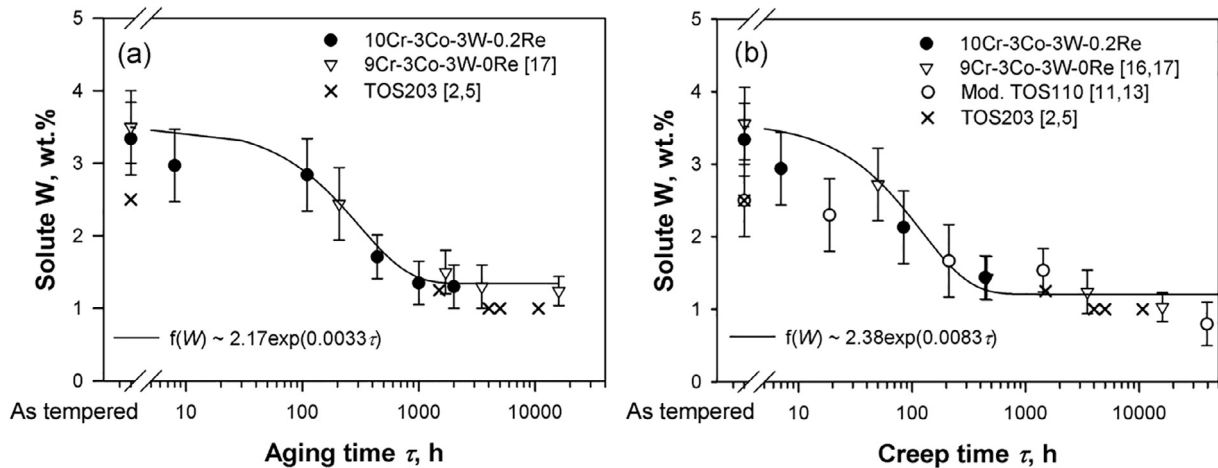


Fig. 2. Change in the tungsten content in the ferritic matrix during aging (a) and creep (b) at 650 °C.

$$f(W) \sim 2.38\exp(-0.0083t) \text{ during creep} \quad (2)$$

Rhenium in the 10Cr-3Co-3W-0.2Re and TOS203 steels did not lead to retaining an increased amount of solute W in the ferritic matrix during both thermal aging and short-term creep at 650 °C that contradicts data represented in [2,4–6]. These relations (1–2) were obtained in the previous investigations [16]. Initially higher W content in the 10Cr-3Co-3W-0.2Re and 9Cr-3Co-3W-0Re steels provides an increment in the solid solution strengthening only during the first 100 h of creep/aging at 650 °C before the precipitation of Laves phase, $\text{Fe}_2(\text{W},\text{Mo})$. The Laves phase particles precipitate along the boundaries of PAGs/laths in the 10Cr-3Co-3W-0.2Re steel during the first 100 h of creep/aging at 650 °C (Fig. 3). The volume fraction of the Laves phase particles increases with increasing the creep/aging time, wherein the average size of these particles increases up to 100 nm after 2000 h of aging or 440 h of

creep (Fig. 3b). In the 10Cr-3Co-3W-0.2Re steel, the average size of the Laves phase particles was significantly less than that (152 nm after 278 h of creep) in the modified TOS110 steel [11] after short-term creep that is related to higher volume fraction of this phase (1.88% in the 10Cr-3Co-3W-0.2Re steel vs. 1.59% in the modified TOS110 steel according to Thermo-Calc prediction). The average sizes of M_{23}C_6 carbides and NbX carbonitrides remain about 70 nm and 40 nm, respectively, during 2000 h of aging or 440 h of creep (Fig. 3b). In the modified TOS110 steel, the average sizes of these phases are 80 nm and 47 nm, respectively, after 278 h of creep [11]. Therefore, rhenium retards the particle coarsening. Together the high volume fraction and the fine size of the Laves phase particles enhanced the stability of lath structure during creep that provided the increment in creep strength.

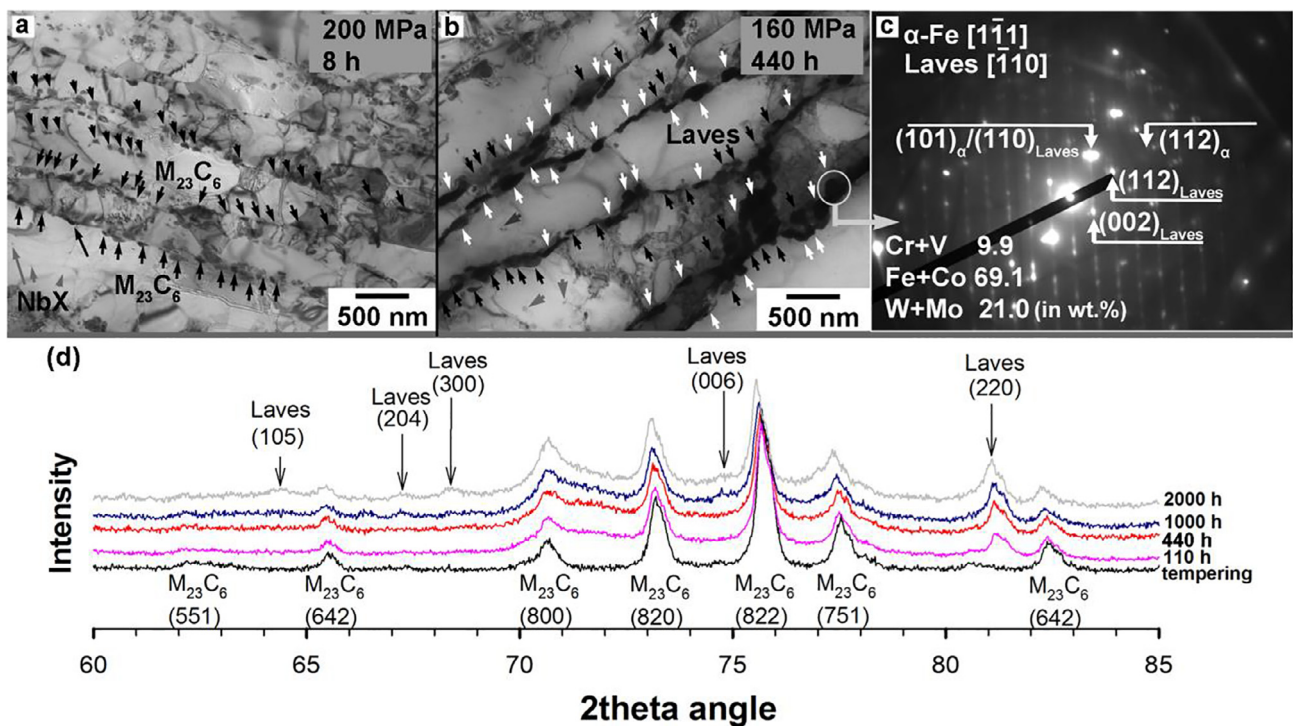


Fig. 3. TEM micrographs of the 10Cr-3Co-3W-0.2Re steel after short-term creep tests at 650 °C: 200 MPa, 8 h (a) and 160 MPa, 440 h (b), black and white arrows indicate M_{23}C_6 and Laves phase particles, respectively, located along the lath boundaries; grey arrows indicate NbX particles precipitated within the laths. Electron diffraction pattern (c) is obtained from the Laves phase particle shown by circle in (b). XRD spectra of the 10Cr-3Co-3W-0.2Re steel after isothermally aging at 650 °C with different durations (d).

4. Conclusions

- 1) Addition of 0.2% rhenium in the experimental 10Cr-3Co-3W-0.2Re steel improves its short-term creep strength, whereas it does not affect UTS and YS at testing temperatures of 20, 600 and 650 °C.
- 2) Addition of 0.2% rhenium did not lead to retaining an increased amount of solute tungsten in the ferritic matrix during both aging and creep at 650 °C. The increment in the creep strength in the experimental 10Cr-3Co-3W-0.2Re steel is related to the precipitation of the high fraction of the fine Laves phase particles and retarding their coarsening.

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