



Superior creep resistance of a high-Cr steel with Re additives

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ABSTRACT

Re-containing 10Cr-3Co-3W martensitic steel with low nitrogen and high boron contents exhibited a rupture time of 10,987 h at 650 °C/140 MPa. This superior creep resistance was caused by partially saved tempered martensite lath structure due to precipitation of $M_{23}C_6$ carbides and Laves phase chains on lath boundaries as well as their high resistance to coarsening. $M_{23}C_6$ carbides were characterized by decreased interfacial energy that resulted in the retention of the orientation relationship between $M_{23}C_6$ carbides and ferritic matrix. Re slowed down diffusion of W, Mo and Cr atoms.

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1. Introduction

Creep resistant 9–12%Cr martensitic steels are widely used as materials for fossil power plants [1–2]. New generation of the 9–12%Cr-3%Co martensitic steels with low N and high B contents demonstrates enhanced creep resistance up to 650 °C because of the combination of strengthening effects from the lath structure, high dislocation density, supersaturated solid solution and precipitation of the $M_{23}(C,B)_6$ phase and Laves phase [3–17]. These dispersoids provide stability of tempered martensite lath structure (TMLS) under creep and contribute to dispersion strengthening exerting high threshold stress [3,14]. Dudova et al. [14] indicated the creep strength of the 10%Cr steel with low N and high B contents approaches 100 MPa for 100,000 h at 650 °C. Re additives to this 10%Cr steel provide additional improvement of its creep strength [16–18]. Re slows down diffusion rate [1,18]. Re atoms should contribute to stable dislocation substructure [16]. However, the exact origin of excellent creep resistance of Re-containing high-Cr martensitic steel is poorly known [16–18]. The aim of the present work is to consider microstructural aspects of improved creep resistance of a martensitic 10Cr-3Co-3 W-0.2Re steel under creep condition of 650 °C/140 MPa in comparison with the Re-free steel, which is denoted here as 10Cr-3Co-2W-0Re [3,12,14,15].

2. Material and experimental

A Re-containing steel, which is denoted here as 10Cr-3Co-3W-0.2Re, was prepared by vacuum induction melting as 100 kg ingot. The steel was homogenized at 1150 °C and forged at 1150–950 °C. Chemical composition and heat treatment of this steel are listed in Table 1. The 10Cr-3Co-3W-0.2Re steel was solution treated at 1050 °C for 1 h, cooled in air, and 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 140–200 MPa. The structural characterization was carried out using a transmission electron microscope JEOL-2100 (TEM) and scanning electron microscopy Quanta 600 3D (SEM) on ruptured creep specimens. The TEM specimens were prepared by electropolishing at room temperature using Struers «Tenupol-5» machine. The precipitates were identified from both the chemical analysis and the selected-area diffraction method on at least 200 particles. Other details of mechanical and structural characterization were reported in [3,8,9,13–15,17]. Analysis of $\dot{\epsilon}$ vs ϵ curves was performed by techniques described in [3,19].

3. Results and discussion

Normalizing followed by tempering (Table 1) produced TMLS with a high dislocation density of $\sim 2 \times 10^{14} \text{ m}^{-2}$ within laths with a thickness of 300–400 nm in both steels [3,12,14,15,17]. Cr-rich $M_{23}C_6$ carbides with a mean size ranging from 60 to 70 nm precipitated on boundaries of prior austenite grain (PAG), packets, blocks and martensitic laths. The feature of the 10Cr-3Co-3W-0.2Re steel

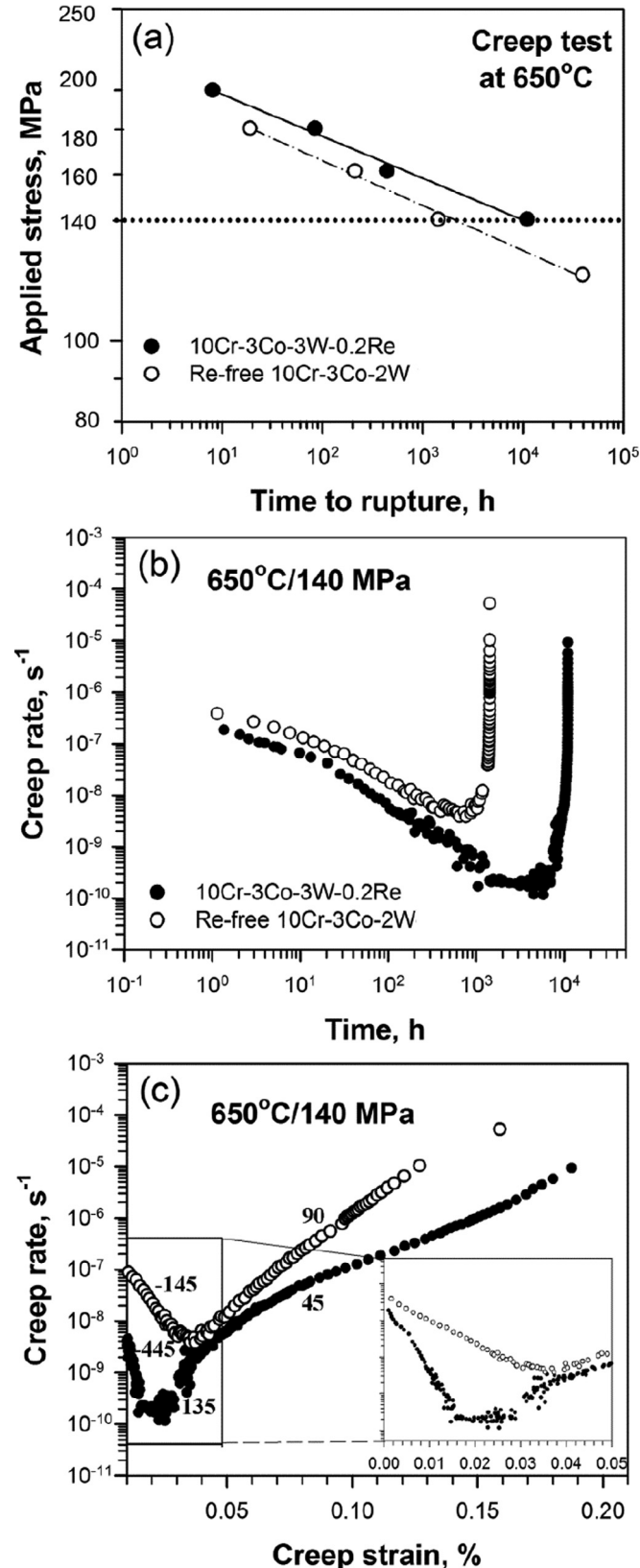
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Table 1
Chemical compositions of the steels studied (in wt.%) and their heat treatments.

Steel	C	Cr	Co	Mo	W	V	Nb	B	N	Re
10Cr-3Co-3W-0.2Re	0.11	9.85	3.2	0.13	3.2	0.2	0.07	0.008	0.002	0.17
Re-free 10Cr-3Co-3 W-0Re	0.10	10.0	3.0	0.70	2.0	0.2	0.05	0.008	0.003	-

HT: Normalization at 1050–1060 °C for 1 h, air cooling, and tempering at 770 °C for 3 h



is high density of $M_{23}C_6$ carbides on lath boundaries. Nb-rich MX carbonitrides with a mean size ranging from 30 to 40 nm randomly distributed in the ferritic matrix in both steels. On the other hand, the 10Cr-3Co-3 W-0.2Re steel had +70% larger PAG size (59 μm) [17] as compared to the 10Cr-3Co-2 W-0Re steel (35 μm) [3,12,14,15].

Two steels exhibited a linear dependence of applied stress on rupture time (Fig. 1a). Such alloying distinctions of the Re-containing steel as the 0.2% Re additives, +1% increase in W content and -0.4% decrease in Mo content provided 4.6, 2.1 and 7.7 time increases in rupture times at 180, 160 and 140 MPa, respectively. Inspection of the $\dot{\epsilon}$ vs t and $\dot{\epsilon}$ vs ϵ curves (Fig. 1b and c) showed that at 650 °C/140 MPa, the Re-containing steel exhibited the minimum creep rate, $\dot{\epsilon}_{\text{min}}$, at $2 \times 10^{-10} \text{ s}^{-1}$ that was 20 times lower than that in the 10Cr-3Co-2W-0Re steel ($\sim 4 \times 10^{-9} \text{ s}^{-1}$) [15]. In addition, time to minimum creep rate shifted up to 8,000 h for the Re-containing steel instead of 700 h for the Re-free steel and the offset strain, at which the minimum creep rate is attained, decreased to 1.8% instead of 3.5% (Fig. 1b and c). Elongation to rupture was similar for both steels (Fig. 1c).

Under the transient creep, magnitude of strain rate dropped by a factor of ~ 10 due to a strong increase in the parameter $d \ln \dot{\epsilon} / d \epsilon \sim 445$, which was higher by a factor of ~ 3 than that of the Re-free steel [15] (Fig. 1c). The $d \ln \dot{\epsilon} / d \epsilon \sim 445$ is close to the rate of kinetic reactions in the Re-free steel at 120 MPa, at which a superior rupture time of $\sim 40,000$ h was attained [3]. The Re-containing steel exhibited unusual tertiary creep behavior with two distinct stages. The $d \ln \dot{\epsilon} / d \epsilon$ values of ~ 135 and ~ 45 were calculated for first stage from $\dot{\epsilon}_{\text{min}}$ to 5% and second stage from 5% to rupture, respectively (Fig. 1c). Therefore, the rate of acceleration of tertiary creep decreased with increasing time/strain.

After creep test at 650 °C/140 MPa, TMLS of the 10Cr-3Co-3 W-0.2Re steel was partially transformed into the subgrain structure with a mean subgrain size of 1.1 μm (Fig. 2a, b). Dislocation density decreased to $1.7 \times 10^{13} \text{ m}^{-2}$. It was recently shown [17] that W content in the ferritic matrix approached 1.24 wt% in both steels after 500 h of creep; all differences between the crept structures in the Re-containing and Re-free steels after 500 h of creep can be related only to Re additives. The constant growth rate K_g of subgrains was $4.29 \times 10^{-8} \mu\text{m}^3 \text{ s}^{-1}$ (Fig. 2c) for the 10Cr-3Co-3W-0.2Re steel that was similar with that of the 10Cr-3Co-2 W-0Re steel. Extensive coarsening of $M_{23}C_6$ carbides located on boundaries of PAG and packets increased their size up to 120 nm (Fig. 2a and b), while some $M_{23}C_6$ carbides located on lath boundaries retained size ranging from 50 to 70 nm (Fig. 3). The constant growth rate K_g of $M_{23}C_6$ carbides was $4.49 \times 10^{-12} \mu\text{m}^4 \text{ s}^{-1}$ (Fig. 2d) for the 10Cr-3Co-3 W-0.2Re steel that was significantly lower than that of the Re-free steel. The decrease in the constant growth rate K_g of $M_{23}C_6$ carbide was described by a 2-fold decrease in the interfacial energy from 0.1 J m^{-2} for the 10Cr-3Co-2W-0Re steel [15] to 0.05 J m^{-2} for the 10Cr-3Co-3W-0.2Re steel (Fig. 3g). Fine $M_{23}C_6$ particles located on

Fig. 1. Creep behavior of the 10Cr-3Co-3W-0.2Re steel: applied stress vs. time to rupture (a), creep rate vs. time (b) and creep rate vs. strain (c) in comparison with the Re-free steel [15].

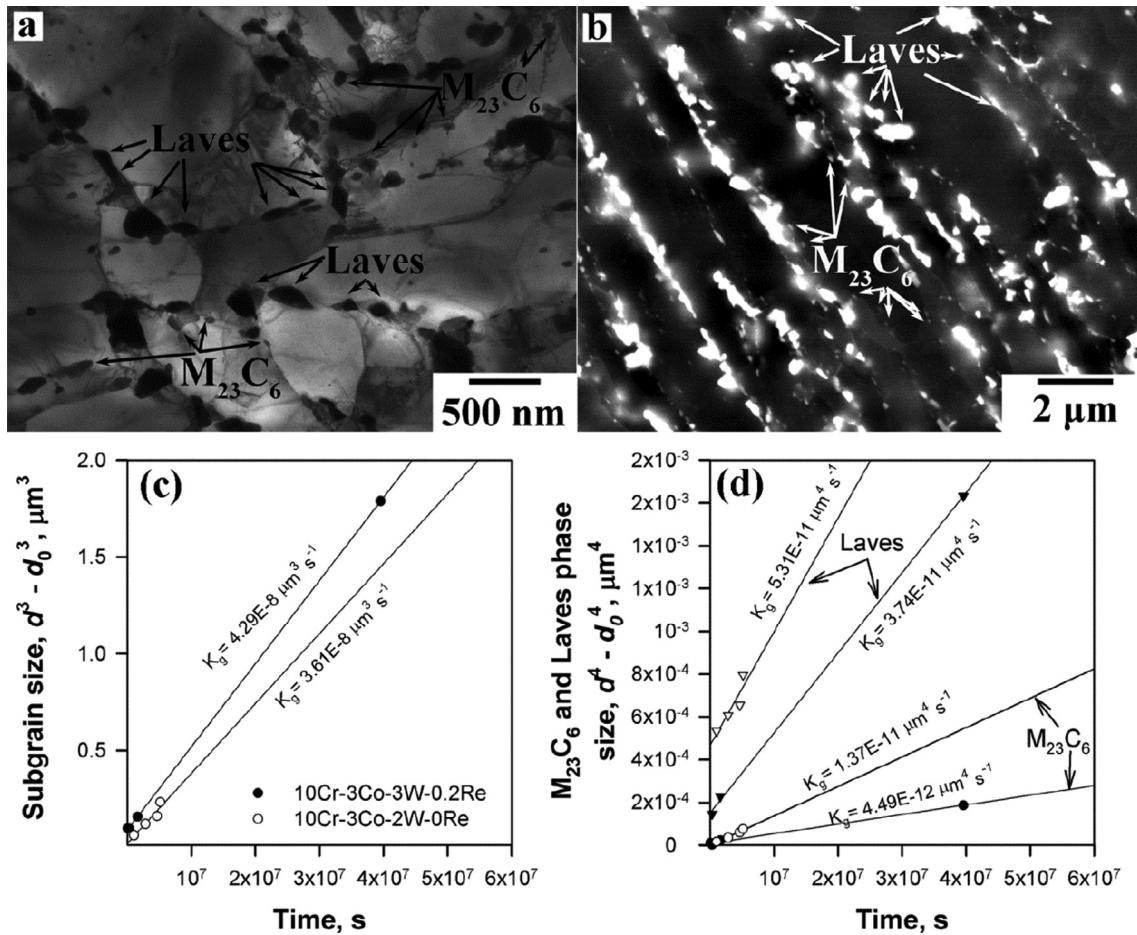


Fig. 2. TEM (a) and SEM (b) images of the 10Cr-3Co-3W-0.2Re steel after creep test at 650 °C/140 MPa; the time dependence of subgrain size (c) and grain boundary particle size (d) in comparison with the Re-free steel [15]. Numbers indicate the coarsening rate constant.

low-angle boundaries retained their orientation relationships (OR) with ferritic matrix, such as Kurdjumov-Sachs OR: $(110)_{\alpha-Fe} \parallel (111)_{M_{23}C_6}$, $[11\bar{1}]_{\alpha-Fe} \parallel [011]_{M_{23}C_6}$ with lattice misfit 1.1% (Fig. 3a), Pitsch ORs: $(\bar{1}21)_{\alpha-Fe} \parallel (660)_{M_{23}C_6}$, $[11\bar{1}]_{\alpha-Fe} \parallel [3\bar{3}2]_{M_{23}C_6}$ with lattice misfit 7.3% (Fig. 3c), $(\bar{1}01)_{\alpha-Fe} \parallel (600)_{M_{23}C_6}$, $[131]_{\alpha-Fe} \parallel [0\bar{1}5]_{M_{23}C_6}$ with lattice misfit 12.4% (Fig. 3d).

Laves phase precipitated along boundaries after 110 h of creep/aging. Most of Laves phase particles precipitated on lath boundaries retained OR with ferritic matrix of $(\bar{1}\bar{1}2)_{\alpha-Fe} \parallel (302)_{Laves}$, $[1\bar{3}1]_{\alpha-Fe} \parallel [0\bar{1}0]_{Laves}$ with lattice misfit 10.3% even after 10,987 h of creep (Fig. 3f). These particles were smaller than those decorated boundaries of PAGs and packets (Figs. 2b, 3e). The constant growth rate K_g of 3.74×10^{-11} μm⁴ s⁻¹ (Fig. 2d) was insignificantly lower than that of the Re-free steel. The interfacial energy of Laves phase in the 10Cr-3Co-3W-0.2Re steel was higher than that of Re-free 10Cr-3Co-2W-0Re steel; however, this did not lead to a significant increase in its constant growth rate. This fact indicates that Re additives slow down the diffusion of Fe and alloying elements such as W, Mo and Cr comprising the Laves phase according to [13,18].

The coherency of M₂₃C₆ carbides and Laves phase particles precipitated heterogeneously provides retention of chains of these particles on lath boundaries after rupture that is quite unusual. In contrast with the other high-Cr steels [1,8,13,15], Re additives,

which provide coherency of boundary particle interfaces and slowing down diffusion rate, prevent dissolution of the fine particle chains along lath boundaries under creep. These chains stabilize TMLS during 10,987 h of creep under the high applied stress.

4. Conclusions

At 650 °C and an applied stress of 140 MPa, Re additions in the high-Cr steel with low N and high B contents increase creep rupture time by a factor of ~8 due to the formation of dense precipitations of M₂₃C₆ carbides and Laves phase on lath boundaries that leads to strong hardening under transient creep, low $\dot{\epsilon}_{min}$ value and extended steady-state creep stage. These additions decreased the energy of M₂₃C₆/ferrite interfaces and induced nucleation of Laves phase with coherent interfaces. Re also slows down diffusion. As a result, coarsening of M₂₃C₆ carbides and Laves phase occurred with low rates; the chains of these particles on lath boundaries retained up to rupture. Superposition of these factors provided superior creep resistance of Re-containing steel.

Alexandra Fedoseeva, Nadezhda Dudova and Rustam Kaibyshev formulated the original problem, designed the study, developed the methodology and wrote the manuscript. Ivan Nikitin carried out creep tests, collected data and assisted with data analysis. Alexandra Fedoseeva and Nadezhda Dudova performed the TEM investigations, collected data and provided interpretation of data. Rustam Kaibyshev provided direction, guidance and interpretation of data.

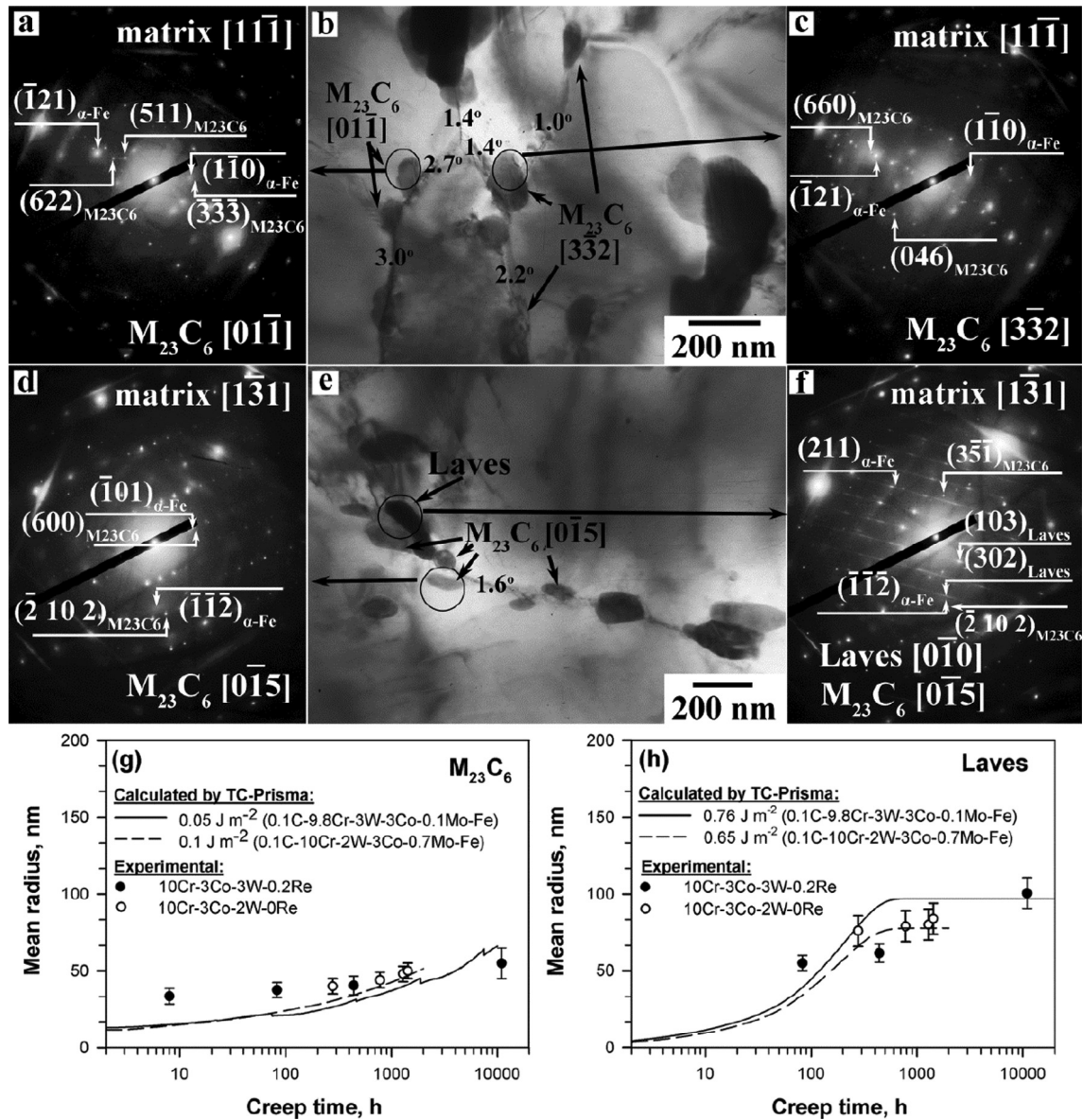


Fig. 3. TEM micrographs of the 10Cr-3Co-3W-0.2Re steel after long-term creep test at 650 °C/140 MPa and composed electron diffraction patterns from $M_{23}C_6$ carbides and the adjacent ferritic matrix (a-e) as well as from Laves phase particle and the adjacent ferritic matrix (f) showing the orientation relationship; the numbers in (b) and (e) indicate the misorientation of low-angle boundaries. The time dependence of the particle size of $M_{23}C_6$ carbides (g) and Laves phase (h) during creep for the 10Cr-3Co-3W-0.2Re and Re-free steels.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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