Effect of tungsten on creep properties of martensitic 9Cr steel

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Abstract. The effects of tungsten on the creep behavior and microstructure of tempered martensite 9Cr steel with different W concentrations ranging from 0–2.5 wt% were studied. The matrix consisted of tempered lath martensite structure and M23C6 located along the grain boundary or inside the grain. As the W concentration increased, the number of M23C6 increased while the particle size decreased. Also, with the increasing W concentration, the minimum creep rate and elongation decreased while the time to rupture increased. The rise in W concentration led to the refinement of M23C6, which enhanced the creep strength but reduced the creep plasticity.

Keywords: M23C6, the minimum creep rate, tungsten, the creep strength

1. Introduction

The 9–12% Cr tempered martensite ferritic steels are important high-temperature materials for fossil-fired power plants [1-4]. The excellent creep properties of these steels can be attributed to the stability of the grain boundaries and the martensite lath. The martensite lath is wrapped in the prior austenite grains (PAG) and contain high density of dissociated dislocations and dispersion of secondary phase particles [3,5,6,7]. M23C6 carbide is a chromium-rich compound, and the primary elements are Fe, C, Cr, Mo, and W [7]. M23C6 carbides mainly exist in the raw materials and are located along the grain boundaries and subgrain boundaries [7]. M23C6 carbides exert high zener resistance to inhibit the coarsening of martensite laths and dislocations movement. Also, they hinder the reaction between the dislocations and subgrain boundaries; thereby, can effectively enhance the creep strength [8-11]. However, M23C6 carbides tend to become coarser in long-term service, which may lead to decrease in long-term creep strength [7]. Therefore, long-term creep strength can be improved by slowing the coarsening rate of M23C6 carbide. The studies [12-17] have shown that component diffusion can control the growth and coarsening of M23C6 carbide in the ferritic heat-resistant steel. The addition of B to 9Cr heat-resistant steel can improve the high temperature stability of M23C6 [12-14]. Addition of Co can inhibit the coarsening of M23C6 during tempering [15-16]. Abe [17, 18] suggested that the coarsening speed of tungsten-containing M23C6 carbide is slower due to the low diffusion coefficient of W and the creep behavior is also affected by the W concentration. In this work, the effect of W...
content on the creep properties of 9%Cr ferritic heat-resistant steel was investigated to optimize the W content in 9%Cr ferritic steel.

Table 1. Chemical composition (wt.%) of 9% Cr steel.

|       | Mn | C   | Si  | Cr  | Mo | V   | Ni  | Fe  | P     | S     |
|-------|----|-----|-----|-----|----|-----|-----|-----|-------|-------|
| 0W    | 0.4| 0.10| 0.28| 9.02| 0.5| 0.2 | 0.2 | 89.3 | <0.001 | <0.005 |
| 1.5W  | 0.4| 0.10| 0.21| 8.95| 0.5| 0.2 | 0.2 | 87.8 | <0.001 | <0.005 |
| 2.5W  | 0.4| 0.11| 0.20| 9.02| 0.5| 0.2 | 0.2 | 89.3 | <0.001 | <0.005 |

2. Experimental

The chemical composition of the examined steels is presented in Table 1. Only concentration of W was varied from 0 to 2.5 wt% in the steels, while the other alloying elements were kept constant (9%Cr, 0.1%C, 0.2Si, and 0.4Mn). These three steels are referred to as 9Cr0W, 9Cr1.5W, and 9Cr2.5W steel, respectively, depending on the W concentration. The required raw materials were melted in a vacuum induction furnace and then forged into three cylindrical materials of 50 mm in diameter and 160 mm in height. A 5 mm cube was cut and normalized at 1050°C for 165 min and 760°C for 136 min. The sample for microstructure observation was mechanically polished with a sandpaper and polishing agent, and then, etched with 10 ml of hydrochloric acid and 1 g of picric acid solution in 100 ml of ethanol. Optical microscope (OM, OLYMPUS-BX51M), Scanning electron microscope (SEM, ZEISS Gemini500), and Electron backscatter diffraction (EBSD) were utilized for the microstructural observation. The crystal morphology, M\(_{23}\)C\(_6\) basic morphology, volume fraction, and dimensional change were studied. Coil spring specimens and conventional rectangular specimens were prepared using machine tooling (see Figure 1, 2). The tensile creep tests (RJ-50, 923 K, 120MPa) were conducted on the samples with different compositions of W, namely 0%, 1.5%, and 2.5%. Considering the low strain resolution of the traditional uniaxial creep experiments, the short-term creep experiments were carried out at 30 MPa and 923 K using the spiral spring creep test method [19-22]. The spiral spring creep test piece is shown in figure 2. In the spiral spring creep test method, torsion is the dominant factor in deformation [23]. As the stress or strain of the coil spring is essentially the shear component, it can be converted to an equivalent parameter using the Von-Mises equation [19]. The short-term creep experiment time was 270 ks.

![Figure 1](image1.png) Rectangular specimens for uniaxial creep test.

![Figure 2](image2.png) Helical spring specimens for creep testing under low stresses.
3. Results and discussion

Fig. 3 Optical microscopy (OM) images of 9%Cr Heat-resistant Steel without aging. (a) 9Cr-0W, (b) 9Cr-1.5W, and (c) 9Cr-2.5W, and (d) partial enlarged drawing, 9Cr-1.5W.

Fig. 4 Scanning electron microscope (SEM) images of 9%Cr heat-resistant steel at 650°C. (a) 9Cr-0W; (b) 9Cr-1.5W, (c) 9Cr-2.5W, (d) 9Cr-1.5W-partial enlarged drawing, and Energy Dispersive Spectrometry (EDS) (e) and (f).

Figure 3 displays the optical microstructure of tempered and normalized martensitic without aging containing different contents of W element ((a) 0W; (b) 1.5W, and (C) 2.5W). The matrix primarily
consisted of lath martensite structure in prior austenite grain (PAG). With the increase in W content, the martensite lath and austenite grains were refined.

For the analysis of morphology and phase of the precipitates, the microstructure of the specimen was observed using Scanning electron microscope (SEM) images (see figure 4 (a-d)), Energy Dispersive Spectrometry (EDS) analysis (see figure 4(e, f)), and X-ray diffraction (XRD) measurements (see figure 5). The results demonstrated that the precipitates were M23C6 while no other types of precipitates were identified. The average particle size and density of carbides in the SEM images were measured using Image-Pro-Plus software. The results are presented in figure 6. As the concentration of W element increased, the number of M23C6 gradually increased and the size of M23C6 decreased; namely, the W element induced the refining of M23C6. Through EDS measurements, the primary components of M23C6 were Fe, Cr, C, Mo, and W, and the W element in the precipitate was much higher than that in the matrix. These results suggest that W was mainly enriched in M23C6 during normalizing and tempering.

As shown in figure 7 (a) and figure 8 (a), the creep curves at a high stress, 120 MPa, can be divided into three stages; the primary creep stage in which the creep strain decreases gradually with time, the secondary creep stage in which the creep strain basically stays unchanged, and the accelerated creep stage in which the creep strain increases rapidly with time until fracture. At the initial stage of creep of 1000 s, the creep rates of 9Cr steels with different W concentrations were approximately the same. For a longer period of time above 1000 s, with the increasing in W
concentration, the minimum creep rate and elongation decreased while the time to fracture increased (see figure 9). These results are consistent with the previous conclusions [18]. For a low stress 30 MPa (see figure 7 (b) and 8 (b) ), the creep curves included only primary creep stage. With the increasing in W concentration, strain rate gradually decreased. These results show that W can enhance the creep strength of 9Cr steel under high stress and low stress conditions but reduce the plasticity.

Fig. 7 (a) Creep curves of 9%Cr heat-resistant steel as the function of W concentration with different stress contents at 650°C and 120 MPa

Fig. 7 (b) Creep curves of 9%Cr heat-resistant steel as the function of W concentration with different stress contents at 650°C and 30 MPa

Fig. 8 (a) Creep rates in log scale versus time curves for 9Cr steels as the function of W concentration with different stress at 650°C and 120 MPa

Fig. 8(b) Creep rates in log scale versus time curves for 9Cr steels as the function of W concentration with different stress at 650°C and 30 MPa.

Fig. 9(a) Dependence of the minimum creep rate on W concentration in 9Cr steel creeping at 650°C, 120 MPa and 30 MPa.

Fig. 9(b) Dependence of elongation and time to rupture on W concentration in 9Cr steel creeping at 650°C, 120 MPa.
Schematic drawings of the effects of W concentration on the creep properties are presented in figure 10. With the increase in W concentration, the concentration of W in both the matrix and M$_{23}$C$_6$ carbides increased, stabilizing the M$_{23}$C$_6$ carbides, which led to the refinement of M$_{23}$C$_6$ and prevention of the migration of lath boundary. The phenomenon provided a significant hindrance to the dislocation movement, leading to an improvement in the creep strength.

![Fig. 10 Schematic drawings of the effects of W concentration on creep properties [18]](image)

4. Conclusion
The microstructure and creep properties under different tungsten concentrations in 9%Cr ferritic heat-resistant steel were investigated to study the effect of W content on the creep properties. The primary results are summarized as follows:

1. With the increase in tungsten concentration, the number of M$_{23}$C$_6$ increased while the particle size decreased.
2. With the increasing in W concentration, the minimum creep rate and elongation decreased, while the time to fracture increased.
3. The increase in W concentration led to the refinement of M$_{23}$C$_6$, which enhanced the creep strength but reduced the creep plasticity.

5. References
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Acknowledgments
This project was supported by the National natural science foundation of China (Grant No.51605330), Natural science foundation of tianjin (No.18JCYBJC88700)