Effect of Boron on Creep Characteristics in 9Cr-1.5Mo Alloys

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Abstract. For thick-section components such as headers and pipes of the power plants, high creep rupture strength and oxidation resistance are required. It is known that the addition of boron can improve the creep strength and oxidation resistance through the stabilization of M₂₃C₆ carbides in the vicinity of prior austenite grain boundaries. In this study, the effect of boron addition with the range of 0.0033–0.0133 wt% on the creep behavior of 9Cr-1.5Mo steel was investigated. Small punch creep tests were carried out to investigate the effect of boron addition on creep properties. Microstructure observation was performed to analyze the effect of boron addition on creep strength and rupture life. Also, the relationship between the minimum creep rate and the amount of boron addition were analyzed. The addition of boron is beneficial in lowering the steady-state creep rate.

1. Introduction
The rapidly increasing world-wide demand for electrical power brings to attention constructing new power plants with high reliability and performance. To achieve such highly reliable power plants, materials with the excellent mechanical properties at elevated temperature and corrosion resistance in water vapor are required. The 9% Cr ferritic - martensitic steels are widely used for the large component materials in the steam turbine power plants [1]. Such components include main steam pipe, turbine header and blade. Even with their long-term creep resistance at elevated temperatures (600 – 650°C), a number of research projects are being carried out for the purpose of enhancing the mechanical properties at the elevated temperatures [2-4]. One of the efforts is adding small amount of boron into 9 to 12% Cr steels [5].

The 12% Cr steels with boron showed the long-term stability of the martensitic microstructure during creep through the stabilization of M₂₃C₆ carbides in the vicinity of prior austenite grain boundaries. The stabilization of the martensitic microstructure by an enrichment of boron in the M₂₃C₆ carbides causes improvement in the creep strength and oxidation resistance. However, the effect of boron on creep rupture strength in 9Cr-1.5Mo steels and the strengthening mechanism are not yet fully understood. In this study, the creep deformation behavior with boron addition in 9Cr-1.5Mo steel was investigated. The amount of boron addition is varied with the range of 0.0033–0.0133 wt%. Small punch creep tests were carried out to investigate the creep characteristics with boron addition at 600°C. Metallurgical observation was performed to analyze the effect of boron addition on creep strength
and rupture life. Also, the relationship between the minimum creep rate and the amount of boron addition were analyzed.

2. Experimental Procedure

2.1. Material
Using a vacuum induction melting (VIM) furnace, 1 ton of a Cr-Mo steel ingot was melted. The ingot was remelted into a cylindrical shape with a diameter of 200 mm using an electro-slag remelting (ESR) to control the composition, cut to 5 kg lumps, heated at 1150°C for 2 hr followed by hot forging to 60 mm in thickness, then heated at 1100°C for 1 hr followed by hot rolling to 12 mm in thickness with a reduction ratio of 76%. The rolled plate was normalized at 1150°C for 2 hr, and tempered at 700°C for 2 hr to make a tempered martensitic structure. The chemical composition of the prepared 9Cr-1.5Mo steel samples that are designated as B1~B3 is listed in Table 1. The alloy composition was designed to have optimum mechanical properties.

| Table 1. Chemical composition of 9Cr-1.5Mo steel series (wt%) |
|------------------|---|---|---|---|---|---|---|---|---|---|---|
| Alloy | C  | Si | Mn | Ni | Cr | Mo | W  | V  | Nb | N  | B  | Al | Co |
| B1   | 0.17 | 0.06 | 0.17 | 0.14 | 9.25 | 1.49 | 0.06 | 0.23 | 0.07 | 0.011 | 0.0033 | 0.003 | 0.17 |
| B2   | 0.17 | 0.08 | 0.15 | 0.14 | 9.22 | 1.45 | 0.06 | 0.24 | 0.09 | 0.012 | 0.0076 | 0.003 | 0.17 |
| B3   | 0.17 | 0.12 | 0.18 | 0.21 | 9.21 | 1.46 | 0.02 | 0.24 | 0.06 | 0.016 | 0.0133 | 0.003 | 0.16 |

2.2. Small punch (SP) creep test
Creep properties of all specimens were evaluated by conducting small punch (SP) creep tests, shown in figure 1. The temperature of the furnace was controlled with the accuracy of 600±1°C. Constant loads of 613N~795N were applied to a thin square shaped specimen (10×10×0.5mm) by a ceramic(Si₃N₄) ball with diameter of 2.4 mm. All tests were performed in the atmosphere. Displacement of specimen was measured by LVDT with an accuracy of 10⁻³mm.

![Figure 1. Schematic illustration of SP creep test apparatus](image-url)
2.3. Metallurgical investigation
After the creep rupture tests, the microvoids/cavities on the samples were investigated by the SEM at the cross section of the creep rupture part. The creep rupture samples were mounted in resin and ground and polished according to standard methods (ASTM/E93). The microstructure was revealed by using an etching solution of HCl, picric acid, and ethanol suitable for 9-13% Cr steels (ASTM/E407-80). The samples were then observed with an optical microscope and with the scanning electron microscope (ESEM: Model-PHILIPS-XL30ES-EM-EFG).

3. Results and Discussion

3.1. Creep test results
Figure 2 shows the SP creep rupture test results in various load conditions. The longest life was found in B3 sample which has the most boron content. At the same load conditions, creep rupture life increased with increasing boron contents. The samples with more amount of boron always had the better creep rupture lives regardless of the loading conditions, which ranged from 613N to 795N. The B1 sample exposed to 613N loading experienced the creep rupture life of 45 hours whereas the B3 sample experienced 87 hours, which is approximately doubled from that of the B1 sample in the same loading condition. In fact, for all the load ranges, the B3 samples exhibited about 2:1 creep rupture life improvement as compared with the B1 samples. Even with the drastic changes in the creep rupture lives among the B1, B2 and B3 samples, the creep curves of the primary creep region were almost identical among three sample types at the same loading conditions. However, note that the slope of creep curves with higher boron contents became lower in the steady creep region. The minimum displacement rate in the steady state creep region became slower with the addition of boron. As results, the creep rupture lives could be increased on the samples with addition of more amount of boron. According to Abe et al [2], the addition of boron on 9Cr steels improved the stability of the lath martensitic microstructure and the creep rupture strength through the stabilization of M23C6 carbides in the vicinity of prior austenite grain boundaries by an enrichment of boron in M23C6 carbides. The data presented in this study agree with the previous results.

Figure 3 presents the results on the minimum displacement rates with three different samples types, B1 to B3. In the SP creep tests, the relationship between displacement rate, \( \dot{\delta} \) (mm/hr) and load, P(N) can be established by the following equation,

\[
\dot{\delta} = AP^n
\]  

where \( A \) is a constant and \( n \) is load exponent [6].

![Figure 2. Creep strain vs. rupture time](image1)

![Figure 3. These Displacement rate vs. applied load.](image2)
The minimum displacement rates for the B1 sample with 33ppm boron were about 47% higher in average than those for the B3 samples with 133ppm boron. Load exponent of the B1 sample was 5.9 while that of the B3 sample was 4.7. With increasing the boron contents, load exponent decreased and this means the samples with higher boron contents are less sensitive to the load conditions than those with lower boron contents. Figure 4 shows creep cavities of creep ruptured B1 and B3 samples by the load of 613N. Creep cavities of B1 sample were widely spread on the ruptured region, while in B3 sample, they were rarely found on the same region. Significant difference between B1 and B3 samples in cavity size and number could be observed. The cavity number of B1 sample increased greatly and the average cavity size of B1 sample was 0.8μm whereas that of B3 sample was 0.5μm. The addition of boron led to suppress the nucleation and growth of cavity through stabilizing carbides in the vicinity of prior austenite grain boundaries.

![Creep cavity distribution at the cross section of the creep ruptured parts of (a) B1 specimen and (b) B3 specimen.](image)

**Figure 4.** Creep cavity distribution at the cross section of the creep ruptured parts of (a) B1 specimen and (b) B3 specimen.

### 4. Conclusion

In this study, the effect of boron addition with the range of 0.0033–0.0133 wt% on the microstructure and creep rupture behavior of 9Cr-1.5Mo steels was investigated. The addition of boron increased the creep rupture life. With 133ppm of boron, the SP creep rupture life doubled as compared with the results of 33ppm of boron at the load range from 613 N to 795N. Boron was found to be effective in decreasing the minimum displacement rate in the steady state creep region and to stabilize the lath martensite microstructure and suppress the growth of creep cavity.

### References

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