Improvement of High Temperature Strength by Addition of Vanadium Content of Ni–Cr–Mo Steel for Brake Discs

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Improvements in the high-temperature strength are desired for the ferritic Ni–Cr–Mo steels used for the brake discs in mechanical brake systems on railway. The objective of this paper is to construct a constitutive equation for the high-temperature deformation in Ni–Cr–Mo steels containing small amounts of V. The examined steels were obtained by varying the addition of V from 0 mass% to 0.27 mass% in the steel. The flow stress of Ni–Cr–Mo steels was increased significantly by the addition of V. It was found that the creep mechanism of examined Ni–Cr–Mo steels was climb-controlled dislocation creep controlled by the lattice diffusion. Owing to the increase in the number of vanadium carbide (VC) particles with increasing the concentration of V, the threshold stress increased due to the Orowan mechanism and as a result, the high-temperature strength also increased. The constitutive equation for the high-temperature deformation of Ni–Cr–Mo steels containing small amounts of V was constructed. The constructed equation is useful in modeling the high-temperature strength under similar heat conditions in brake discs.

KEY WORDS: low alloy Ni–Cr–Mo steels; constitutive equation; high-temperature strength; Orowan stress.

1. Introduction

Ferritic Ni–Cr–Mo steels such as A4340 has been used widely for the brake discs in mechanical brake systems on railway.1–3) In recent years, running speed of railway vehicles, which provide superior transport efficiency, has been increasing. Energy in brake discs during braking has increased with the speed up of vehicle. The brake discs for railway vehicles are subjected to repeated frictional heat that is generated during braking. Therefore, improvements in the heat shock resistance and high-temperature strength are desired for the brake discs.1)

Recently the authors improved heat shock resistance of the Ni–Cr–Mo steel used for the brake discs by decreasing the hardenability.2) The hardenability of Ni–Cr–Mo steel was improved by decrease of Ni content, increase of Mo content and 0.1% V additive.2) The concentration of Ni, Cr, and Mo in this improved Ni–Cr–Mo steel was low at approximately 0.8%.2) In contrast to the improvement of the heat shock resistance in authors’ previous study,2) the high-temperature strength of this improved Ni–Cr–Mo steel has not been investigated.

In ferritic heat-resistant steels, alloys containing a high Cr concentration have often been used to improve the oxidation resistance of the material. Hence, the effect of alloying elements for high-temperature strength has been studied extensively in high Cr ferritic heat-resistant steels.4–16) For example, Zhang et al.4) investigated that creep behavior such as stress and temperature dependence of creep rate in two-phase alloy of Fe-15Cr-25Ni. Hamada et al.7) examined that the effect of precipitate shape of Nb(C, N) in 9Cr-1Mo steel on dispersion strengthening at elevated temperature. As the result, it is well known that nano-sized precipitation of carbides of microalloying elements such as V and Nb, is effective in improving the high-temperature strength.11–13,16,17) Therefore, an improvement in the high-temperature strength is expected in the improved Ni–Cr–Mo steel due to the addition of V. However, there are few reports concerning the effect of V addition on the high-temperature strength in the low Cr alloys.18,19) Thus, the high-temperature strength of low alloy Ni–Cr–Mo steels containing small amounts of V was focused in this study. As described above, it is of technical importance of the high-temperature strength in low alloy Ni–Cr–Mo steels containing small amounts of V when these steels are used for the brake discs.

The objective of this paper is to construct a constitutive equation for the high-temperature deformation in the Ni–Cr–Mo steels containing small amount of V. Because the constructed equation can be used in modeling the high-temperature strength under similar heat conditions in brake discs.

2. Experimental Procedure

In this study, four kind of ferritic steels, namely 00V, 11V, 20V and 27V were investigated. Four kind of ferritic steels which were obtained by varying the addition of V from 0 mass% to 0.27 mass% in the steel were used in this test. A basic composition were summarized in Table 1. The
steels were melted by radio frequency induction furnace in SiO₂ crucible and cast using 27 mm×27 mm×80 mm cuboid sand mold in air. Cast bars were homogenized at 1 233 K for 3 h in air, followed by furnace cooling to room temperature. Then, the materials were heat-treated at 1 223 K for 3 h in air for austenitization and solution treatment, followed by water quenching. After quench, tempering is done immediately at 903 K for 3 h in air to obtain ferrite structure with precipitation of nano-sized vanadium carbide (VC) particles, followed by air cooling.

The cylindrical bars were machined as tensile test specimens with a gage length of 30 mm and a parallel portion diameter of 6 mm. Table 2 shows the mechanical properties

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Yield strength (MPa)</th>
<th>Tensile strength (MPa)</th>
<th>Elongation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>00V</td>
<td>977</td>
<td>1 143</td>
<td>11.0</td>
</tr>
<tr>
<td>11V</td>
<td>1 076</td>
<td>1 159</td>
<td>11.2</td>
</tr>
<tr>
<td>20V</td>
<td>1 131</td>
<td>1 257</td>
<td>9.2</td>
</tr>
<tr>
<td>27V</td>
<td>1 157</td>
<td>1 280</td>
<td>9.0</td>
</tr>
</tbody>
</table>

at room temperature of 00V, 11V, 20V and 27V. Strain-rate-change tensile tests were carried out at strain rates ranging from ~1×10⁻⁵ to ~1×10⁻³ s⁻¹ and at temperatures of 923, 973 and 1 023 K in air.

The prior austenite grain size was measured by optical microscopy at ×200 magnification in accordance with JIS G 0551 using picric acid reagent. The volume fraction of retained austenite was determined by x-ray diffraction (XRD) using RINTO2100 (Rigaku Co., Ltd.) from the integrated intensities of diffraction peaks (200)γ, (220)γ, (311)γ, (200)α, and (220)α. The austenite start (Ac1) and finish (Ac3) temperatures of the steel samples measured by dilatometry using FTM-100 (Fuji Electronics Industrial Co., Ltd.).

Sold solution V in the matrix was dissolved in 10% AA electrolyte (10% acetylacetone-1% tetramethylammonium chloride-methanol) by using electrolytic extraction. Then, the residual amount of V was analyzed by using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES). The residual amount was assumed as the concentration of V in precipitates. The concentration of V in the solid solution was calculated from the difference between the total concentration of V and the concentration of V in precipitates.

The carbides on a carbon film supported by Cu-mesh grids by using the extraction replica method were observed at ×50 000 magnification using JEM-ARM200F TEM (JEOL Co., Ltd.). The chemical compositions of the carbides were examined by using Noran System 7 EDS (Thermo Fisher Scientific K.K.) that was equipped in the TEM. The particle size distribution of the carbides was examined by using ULV-SEM ULTRA PLUS (Carl Zeiss) at ×15 000 magnification.

**Table 1.** Chemical composition of 00V, 11V, 20V, and 27V ferritic steels (mass%).

<table>
<thead>
<tr>
<th>Symbol</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Ni</th>
<th>Cr</th>
<th>Mo</th>
<th>V</th>
<th>Al</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>00V</td>
<td>0.24</td>
<td>0.82</td>
<td>0.46</td>
<td>0.79</td>
<td>0.76</td>
<td>0.80</td>
<td>0.00</td>
<td>0.03</td>
<td>bal.</td>
</tr>
<tr>
<td>11V</td>
<td>0.22</td>
<td>0.74</td>
<td>0.49</td>
<td>0.79</td>
<td>0.81</td>
<td>0.81</td>
<td>0.11</td>
<td>0.05</td>
<td>bal.</td>
</tr>
<tr>
<td>20V</td>
<td>0.23</td>
<td>0.81</td>
<td>0.51</td>
<td>0.79</td>
<td>0.85</td>
<td>0.79</td>
<td>0.20</td>
<td>0.02</td>
<td>bal.</td>
</tr>
<tr>
<td>27V</td>
<td>0.21</td>
<td>0.87</td>
<td>0.52</td>
<td>0.78</td>
<td>0.77</td>
<td>0.79</td>
<td>0.27</td>
<td>0.04</td>
<td>bal.</td>
</tr>
</tbody>
</table>

**Table 2.** The mechanical properties at room temperature of 00V, 11V, 20V and 27V.

**Fig. 1.** The optical microscopy images of 00V, 11V, 20V and 27V.
3. Results

3.1. Microstructures

Figure 1 shows the optical microscopy images of 00V, 11V, 20V and 27V. The prior austenite grain etched by picric acid was revealed. The grain size of the prior austenite is around 26, 20, 18 and 20 μm for 00V, 11V, 20V and 27V, respectively. The volume fraction of retained austenite was lower than the detection limit or less than 1% in each sample. Ac1 temperatures of 00V, 11V, 20V, and 27V were 1 045, 1 041, 1 038 and 1 035 K, respectively. Ac3 temperatures of 00V, 11V, 20V, and 27V were 1 144, 1 167, 1 170 and 1 196 K, respectively. It should be noted that the temperatures of strain-rate-change tensile tests (923, 973 and 1 023 K) were below the Ac1 temperatures in each sample.

3.2. Strain-rate Change Tensile Test

Figure 2 shows the relationship between the strain rate and the flow stress at (a) 923, (b) 973 and (c) 1 023 K. The flow stress of Ni–Cr–Mo steels was increased significantly along with the increase in concentration of V. The stress exponent, $n$, which was estimated from the slope of the curve, exhibited values of 7.4, 10.3, 13.1 and 15.4 at 923 K, 6.6, 7.9, 9.0 and 9.1 at 973 K and 5.2, 5.2, 6.4 and 6.9 at 1 023 K for 00V, 11V, 20V and 27V, respectively.

3.3. Measurement of Mass of Vanadium

Figure 3 shows the relationship between the total concentration of V and the concentration of V in solid solution for 11V, 20V and 27V.

![Fig. 3. Total concentration of V and concentration of V in solid solution for 11V, 20V and 27V.](image)

3.4. Bright-field TEM images of carbon extraction replicas showing the distribution of carbides for (a) 00V, (b) 11V and (c) 27V. EDS analysis of particles assigned with a number in red in these figures is shown in Fig. 5. (Online version in color.)

![Fig. 4. Bright-field TEM images of carbon extraction replicas showing the distribution of carbides for (a) 00V, (b) 11V and (c) 27V. EDS analysis of particles assigned with a number in red in these figures is shown in Fig. 5. (Online version in color.)](image)

Fig. 2. Strain rates for 00V, 11V, 20V and 27V as a function of flow stress at (a) 923 K, (b) 973 K and (c) 1 023 K.
tration of V and the concentration of V in the solid solutions for 11V, 20V and 27V. Regardless of the total concentration of V, the concentration of V in the solid solution was less than 0.03 mass%. All the alloys used in this study contain about 0.23 mass% carbon. Therefore, a major part of V had hardly dissolved in the matrix as the solid solution and formed carbides in 11V, 20V and 27V. The reason for the increase in high-temperature strength along with the increase in concentration of V can be attributed to the precipitated carbides containing V.

3.4. Composition of Carbides

Figure 4 shows the bright-field TEM images of carbon extraction replicas of 00V, 11V and 27V. The number of fine carbides increased when the concentration of V increased. We chosen the equivalent circle diameter as the measure for particle size because of a roughly equiaxed morphology of the carbide particles. Figure 5 shows the relation between the equivalent circle diameter and the ratio of Fe, V, Mo, Cr, Mn, Ni and Si concentrations of the particles that are assigned with a number in red in Fig. 4. The ratio of Fe, V, Mo, Cr, Mn, Ni and Si concentrations indicates the proportion when the sum of concentrations of these elements was taken as 100%, and does not include the concentration of carbon. Cr, Mn, Ni and Si are almost not included in all the carbides. There were three kinds of carbides, namely, the carbide rich in Fe, carbide rich in Mo and carbide rich in V. From the electron diffraction pattern analysis, the structures of three carbides were identified to be orthorhombic Fe₃C, hexagonal Mo₂C, and cubic VC types, respectively. Figure 6 shows the electron diffraction pattern for the carbides rich in Fe, Mo and V, respectively. These carbides are usually observed as precipitates in ferritic steels that contain Mo⁵⁵ and V.¹⁹

Figure 5 indicates that regardless of the concentration of V, the particle size of Fe₃C was coarse with a particle diameter of about more than 80 nm, and that of Mo₂C and VC particles are fine with a particle diameter of about less than 60 nm. In 00V, there were only the coarse Fe₃C particles.

Fig. 5. Relationship between ratio of Fe, V, Mo, Cr, Mn, Ni and Si concentration in the particiles and equivalent circle diameter of the particiles for (a) 00V, (b) 11V and (c) 27V.

Fig. 6. TEM images of the carbide particles and corresponding diffraction patterns for the carbides rich in (a, b) Fe, (c, d) Mo and (e, f) V, respectively.
and the fine Mo$_2$C particles. The number of fine particles of VC increased along with the increase in the concentration of V. Therefore, the reason for the increase in high-temperature strength along with the increase in concentration of V can be attributed to the increase in the number of fine particles of VC.

3.5. Particle Size Distribution

Figure 7 shows the SEM micrographs of microstructures of 00V, 11V and 27V. We measured the equivalent circle diameter of all the particles as much as possible from the three SEM micrographs including Fig. 7 for 00V, 11V and 27V, respectively. The total number of particles in 00V, 11V, and 27V were 1 921, 2 360 and 3 600, respectively. This number of particles corresponds to the density of particles of 13.3, 16.3 and 24.9 particles/μm$^2$, respectively. Figure 8 shows the particle size distributions of 00V, 11V and 27V. The average particle diameters for 00V, 11V and 27V were 75, 68 and 48 nm, respectively. The particle size decreased and the particle density increased along with the increase in the concentration of V. The cause of decrease in the average particle diameters is increase in the number of VC particles. As shown in the previous section, Fig. 5 indicates that the number of fine particles of VC with a particle diameter of about less than 60 nm increased along with the increase in the concentration of V.

4. Discussion

4.1. Mechanism and Constitutive Equation

It is presumable that the flow stress has not been affected dynamically by the changes in the microstructure. Because there were no changes in the microstructure such as growth...
of prior austenite grain size, phase transformation of retained austenite, and growth of the precipitates. The constitutive equation to describe the deformation behavior at the high temperature used for a wide range of metallic materials such as ferritic steels,\textsuperscript{8,21} Al,\textsuperscript{22} Mg,\textsuperscript{23} Sn\textsuperscript{24} and Cu\textsuperscript{25} alloys is generally expressed as\textsuperscript{26,27}

\[
\dot{\varepsilon} = A \left( \frac{G b}{kT} \right) \left( \frac{\sigma - \sigma_0}{G} \right)^n D_0 \exp \left( -\frac{Q}{RT} \right) \tag{1}
\]

where \( \dot{\varepsilon} \) is strain rate, \( \sigma \) is flow stress, \( G \) is the shear modulus, \( b \) is the Burgers vector, \( k \) is Boltzmann’s constant, \( T \) is the absolute temperature, \( n \) is the stress exponent, \( D_0 \) is the pre-exponential factor for diffusion and \( Q \) is activation energy which depends on the rate-controlling process, \( R \) is the gas constant and \( A \) is a material constant. The value of the stress exponent can be used to identify the mechanisms controlling the deformation as either: dislocation glide \((n = 3)\) or dislocation climb \((n = 4–7)\).\textsuperscript{16} Furthermore, \( n = 5 \) suggests the climb-controlled dislocation creep due to the lattice diffusion and \( n = 7 \) suggests low temperature climb of dislocation due to diffusion of dislocation core.\textsuperscript{28}

The stress exponent obtained in Fig. 2 has high values in the range of 5.2–15.4. These high values of \( n \) for the present steels are higher than that of dislocation glide and dislocation climb. The reason for the difference in values of \( n \) may arise from the presence of threshold stress, due to the interaction of dislocation with second phase particles.\textsuperscript{8,16} Under the presence of threshold stress, \( \sigma_0 \), Eq. (1) can be modified such that the applied stress is replaced by an effective stress, \( (\sigma - \sigma_0) \). This equation when written in the normalized form is given by:\textsuperscript{21}

\[
\dot{\varepsilon} = A \left( \frac{G b}{kT} \right) \left( \frac{\sigma - \sigma_0}{G} \right)^n D_0 \exp \left( -\frac{Q}{RT} \right) \tag{2}
\]

Equation (2) can be rewritten by

\[
\sigma = G \left[ A \left( \frac{G b}{kT} \right) D_0 \exp \left( -\frac{Q}{RT} \right) \right]^{1/n} \dot{\varepsilon}^{1/n} + \sigma_0, \quad \tag{3}
\]

Therefore, in order to estimate \( \sigma_0 \), the data at a single temperature are plotted as \( \sigma \) vs. \( \dot{\varepsilon}^{1/n} \) using a double linear scale. Then, the datum points for each temperature will fit a straight line and the extrapolation of these lines to zero strain rate gives the value of threshold stress, \( \sigma_0 \), at each temperature.

To identify the rate-controlling creep mechanism, the stress exponent was varied from 3 to 7, and a stress exponent of 5 gave the best fit to a straight line. The linearity of the fitting curve was better for \( n = 5 \) than for \( n = 3 \) and 4. In the case of \( n = 6 \) and 7, fitting curves gave the negative values of threshold stress. Recently, Shrestha et al. calculated the threshold stress of 9Cr-1Mo steel in a similar way, and reported that \( n = 5 \) gave the best fit to datum points in the temperature range of 873–1 023 K.\textsuperscript{15} Figure 9 shows the plot of \( \dot{\varepsilon}^{1/n} \) versus \( \sigma \) at three temperatures 923, 973 and 1 023 K. The threshold stress, \( \sigma_0 \), was calculated from the extrapolation of the best fitting line to zero strain rate in Fig. 9.

Figure 10 shows the threshold stress as a function of the concentration of V. Calculated values of Orowan stress, \( \sigma_{OR} \), is also shown in this figure.
The threshold stress is a function of V concentration and increases in proportion to V concentration. Additionally, the threshold stress is decreases with increasing temperature.

Taking the natural logarithm of Eq. (2) and differentiating with respect to \(1/T\), the activation energy for creep can be calculated from

\[
Q = -R \left\{ \frac{d \ln \dot{\varepsilon}}{d(1/T)} \right\}_{\sigma - \sigma_0 = G}.
\]  

In order to calculate the activation energy, the relationship between \(\dot{\varepsilon} kT G b \) and reciprocal temperature at fixed normalized stress, \((\sigma - \sigma_0)/G\), of \(3 \times 10^{-3}\) is illustrated in Fig. 11. The values of the Burgers vector \(29)\) and the shear modulus\(30)\) of \(\alpha\)-Fe that were used for the normalization are shown in Table 3. The activation energies for the creep were 244, 219, 240 and 209 kJ/mol for 00V, 11V, 20V and 27V, respectively. These activation energies are close to 241 kJ/mol\(31)\), of the lattice diffusion in \(\alpha\)-Fe. Therefore, it was demonstrated that the creep mechanism of 00V, 11V, 20V and 27V was climb-controlled dislocation creep controlled by the lattice diffusion.

Because of the similarity between the value of \(Q\) and that for the self-diffusivity of \(\alpha\)-Fe, the self-diffusion coefficient of \(\alpha\)-Fe, \(D_L\), was used in normalizing the data of 00V, 11V, 20V and 27V. The relationships between normalized strain rate, \(\dot{\varepsilon}/D_L(kT/G)\), and normalized effective stress, \((\sigma - \sigma_0)/G\), for 00V, 11V, 20V and 27V are shown in Fig. 12. The used material factors\(29-31)\) of \(D_L\), \(G\) and \(b\) for the alloy as a function of temperature are taken as that for \(\alpha\)-Fe and are listed in Table 3. As shown in the figure, the flow behaviors of 00V, 11V, 20V and 27V were represented by straight lines with a slope of 5th power. A constitutive equation of the deformation behavior of the alloy at present experimental conditions can be written as:

\[
\dot{\varepsilon} = 3.9 \times 10^4 \left( \frac{Gb}{kT} \right) \left( \frac{\sigma - \sigma_0}{G} \right)^8 D_L.
\]  

This equation can be used in modeling the high temperature strength of these alloys under similar heat conditions in the disc brakes.

### Table 3. List of material constants in \(\alpha\)-Fe.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Burgers vector, (b) (nm)</td>
<td>0.2465 + 4.4 \times 10^{-6} T</td>
<td>Ref. [25]</td>
</tr>
<tr>
<td>Shear modulus, (G) (MPa)</td>
<td>89 019 – 26.77</td>
<td>Ref. [26]</td>
</tr>
<tr>
<td>Lattice diffusion coefficient, (D_L) (m² s⁻¹)</td>
<td>2.0 \times 10^{-4} exp(240 900/RT)</td>
<td>Ref. [27]</td>
</tr>
</tbody>
</table>

![Fig. 11](image1.png)

**Fig. 11.** Temperature dependence of the normalized strain rate, \(\dot{\varepsilon} kT / G b\), for (a) 00V and 11V and for (b) 20V and 27V.

![Fig. 12](image2.png)

**Fig. 12.** The relationships between normalized strain rate, \(\dot{\varepsilon} / D_L(kT / G)\), and normalized effective stress, \((\sigma - \sigma_0)/G\), for 00V, 11V, 20V and 27V.
calculated considering the particles as spheres by using the average particle diameter and density of particles.

Figure 10 shows the relation between the calculated value of Orowan stress and concentration of V. The calculated Orowan stress is result not only from VC particles but also other particles such as Mo₂C. Because the calculated Orowan stress is based on the average particle diameter of all the particles as much as possible from the SEM micrographs including VC, Mo₂C, Fe₃C, etc. Similar to threshold stress, Orowan stress also increased with the increase in concentration of V. The threshold stress at all temperatures was lower than the Orowan stress. In Eq. (6), the decrease in Orowan stress associated with the increase of temperature caused by a thermal activation is not taken into account. The threshold stress rapidly decreased from Orowan stress along with the increase in temperature. From the above, we elucidated that in Ni–Cr–Mo steels containing small amount of V, owing to the increase in the number of fine VC particles that was associated with the increase in the concentration of V, the threshold stress increased due to the Orowan mechanism and as a result, the high-temperature strength also increased.

5. Conclusion

We investigated the high-temperature strength of Ni–Cr–Mo steels used for the brake discs. The results are summarized as follows.

1) The flow stress of Ni–Cr–Mo steels was increased significantly by the addition of V.
2) A major part of V formed VC in Ni–Cr–Mo steels. The number of fine particles of VC increased along with the increase in the concentration of V. The reason for the increase in high-temperature strength along with the increase in concentration of V can be attributed to the increase in the number of fine particles of VC.
3) The creep mechanism of Ni–Cr–Mo steels containing small amount of V was climb-controlled dislocation creep controlled by the lattice diffusion.
4) Owing to the increase in the number of fine VC particles, the threshold stress increased due to the Orowan mechanism. As a result, the high-temperature strength also increased under the climb-controlled dislocation creep controlled by the lattice diffusion.
5) The constitutive equation under the climb-controlled dislocation creep controlled by the lattice diffusion in the Ni–Cr–Mo steels containing small amount of V was constructed introducing the threshold stress. The constructed equation can be used in modeling the high temperature strength under similar heat conditions in the disc brakes.

REFERENCES
33) M. N. Shetty: Dislocations and Mechanical Behaviour of Materials, PHI Learning, Delhi, (2013), 455.