Effects of Precipitate Shape on High Temperature Strength of Modified 9Cr–1Mo Steels

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A dispersion of precipitates introduces a threshold stress which opposes deformation. The effect of precipitate shape on dispersion strengthening at elevated temperature has been examined. Three kinds of Mod.9Cr–1Mo steels without Nb(C,N), with spherical Nb(C,N) and with complex Nb(C,N) + V(N,C) "V-wing" were designed to have the same microstructures except for the shape of precipitates. The threshold stresses were measured by tensile and creep tests at 600°C. Two sorts of effects have been observed. The first is that complex precipitates restrain dislocation from climbing even in a condition in which dislocation climbs over a spherical precipitate. Mobile dislocations are considerably trapped at the concavity of the V-wings during deformation. The second effect is that the probability of dislocation trapping at V-wing is larger than that at spherical Nb(C,N). These trapping effects play important roles in the strengthening effect of precipitate.

KEY WORDS: dispersion strengthening; dislocation climbing; Orowan mechanism; attractive interaction; threshold stress; tensile test; creep; V-wing; Mod.9Cr–1Mo steel.

1. Introduction

Heat resistant ferritic steels with high chromium and molybdenum are widely used in the power generating and chemical industries, operating under creep conditions.¹⁾ Nippon Steel Corporation also manufactures Mod.9Cr–1Mo steel plates with 0.055–0.065% nitrogen.²⁾ The steel plates are strengthened by wing-shaped vanadium–nitrides, V-wings adhere to spherical niobium–carbonitride³⁾ as shown in Fig. 3b. The precipitates may give an additional threshold stress to the following constituent creep equation⁴⁾ through interaction with mobile dislocations.

$$\dot{\epsilon} = K(\sigma - \sigma_{th})^n \dots\dots\dots(1)$$

where $\dot{\epsilon}$ is the creep rate, σ the applied stress, σ_{th} threshold stress, n the stress exponent and K the function of temperature, diffusion coefficient and shear modulus.

There are three kinds of interactions between dislocation and precipitate. These are Orowan mechanism,⁵⁾ local climb mechanism⁶⁾ and attractive interaction.⁷⁾ Each mechanism gives a threshold stress of 0.84 Gb/ λ

for Orowan,⁶⁾ 0.3 Gb/ λ for local climb⁶⁾ and 0.65 Gb/ λ for attractive interaction.⁸⁾ Previous works^{7,9)} determined which mechanism dominated the deformation by comparing the time required for a dislocation to bypass a precipitate. Goto¹⁷⁾ showed by using tensile test that the complex shaped particle gives higher threshold stress through Orowan mechanism even in the condition in which climbing should occur on spherical particle in Nickel–SiO₂ systems.

The purposes of this research was to determine the dominant mechanism of the interaction between dislocation and complex shaped precipitate in the case of commercial steel.

2. Experimental Procedure

2.1. Materials

Three kinds of Modified 9Cr–1Mo steels, without niobium and vanadium (mark: Base), with Nb (mark: Nb), and with Nb and V (mark: NbV) were used. Table 1 shows chemical compositions of these steels. These steels were melted in a 50 kg vacuum high-frequency

Table 1. Chemical compositions of materials used. (wt%)

	C	Si	Mn	P	S	Cr	Mo	V	Nb	N
Base	0.087	0.25	0.44	0.003	0.003	9.02	1.02	0.05	0.001	0.0168
Nb	0.086	0.22	0.44	0.003	0.003	9.04	1.02	0.05	0.097	0.0216
NbV	0.090	0.24	0.44	0.003	0.003	9.15	1.01	0.21	0.086	0.0620

furnace and hot-rolled to 25 mm thick plates. Heat treatments included the following:

- (1) Normalizing at 930°C for 1 h (Base-steel)
at 1060°C for 1 h (Nb- and NbV-steels)
- (2) Tempering at 760°C for 1 h (all)

These steels were designed to have the same microstructures except for the shape of precipitates. Microstructural features, especially grain size, precipitate size, precipitate shape and solute concentrations, are important for high temperature strength. Prior austenite grain size was measured by optical microscopy. Shape and size distribution of precipitates were investigated for extraction carbon replicas by using 400 kV analytical transmission electron microscopy (TEM). The solute concentrations of chromium, molybdenum, niobium, vanadium and nitrogen in ferrite matrices were determined by quantitative chemical analysis of residue.

2.2. Tensile Test

Interaction between precipitate and dislocation should depend on strain rate.¹⁰⁾ Tensile tests were carried out at strain rates ranging from 10^{-5} to 10^{-2} sec^{-1} at 600°C. The specimen had a 30 mm gauge length and 6 mm diameter. The load accuracy was within $\pm 0.5\%$ and the temperature accuracy $\pm 2^\circ\text{C}$. The elongations of specimens were measured by an extensometer attached to a small rim on the specimen gauge in order to exclude the influence of the machine's rigidity on elongation data. The threshold stress of steel having precipitates should nearly equal to the increment in yield stress from that of the Base-steel (ΔYS). The yield stress was defined at proportional limit on the stress-strain curve to exclude work hardening.

2.3. Creep Test

Creep data were measured at 600°C by single-type lever arm creep machines. All the creep testings were carried out within a load accuracy of $\pm 0.5\%$. The temperature fluctuation along the gauge length of the specimen was controlled to be less than $\pm 2.0^\circ\text{C}$. The elongation of specimens was measured by an exten-

someter attached to a small rim on the specimen gauge. The dial gauge had a resolution of $1 \mu\text{m}$. A minimum creep rate was obtained from the data of specimens elongated more than 2%. The interactions between precipitate and dislocation in the crept specimen were observed by TEM.

3. Result

3.1. Microstructures

The microstructures revealed tempered-martensite as shown in Fig. 1. Prior austenite grain sizes were 15 to $22 \mu\text{m}$. $M_{23}C_6$ of less than $0.2 \mu\text{m}$ diameter mainly precipitated along the grain boundary. The average martensite lath spacing was approximately $0.5 \mu\text{m}$.

Transgranular precipitate can effectively work to restrain dislocation gliding. Figure 2 shows the extraction replica images of transgranular precipitates. The radius of the precipitate was defined as the radius of a sphere having the same volume as the precipitate. The base-steel included a few rod-like $\text{Cr}_2(\text{C}, \text{N})$ of $0.026 \pm 0.008 \mu\text{m}$ radius. Nb-steel included many spherical $\text{Nb}(\text{C}, \text{N})$ of $0.021 \pm 0.012 \mu\text{m}$ radius and a few rod-like $\text{Cr}_2(\text{C}, \text{N})$. NbV-steel included many niobium and vanadium complex carbonitrides of $0.027 \pm 0.010 \mu\text{m}$ radius and a few rod-like $\text{Cr}_2(\text{C}, \text{N})$. The distribution of precipitate radius in Nb-steel was not different from that of NbV-steel. Figure 3 shows higher magnification images of extraction replicas from Nb- and NbV-steels. NbV-steel has peculiarly shaped precipitate "V-wing" adhering to spherical $\text{Nb}(\text{C}, \text{N})$. The average spacing between adjacent precipitates on a glide plane was calculated by following the equation⁵⁾ for extraction replica.

$$\lambda = 1.25n_s^{-1/2} - 2r_s \dots\dots\dots(2)$$

Where n_s is the number density of precipitates, r_s the mean radius of circular section of precipitate in any plane as in the following equation.

Fig. 1. Optical microstructures of materials used.
(a) Base steel (b) Nb-steel (c) NbV-steel

Fig. 2. Extraction replica images of transgranular precipitates.
(a) Base steel (b) Nb-steel (c) NbV-steel

Fig. 3.

The higher magnification extraction replica images of transgranular precipitates from (a) Nb-steel and (b) NbV- steel. Spherical Nb(C,N) in Nb-steel and Wing-like V(N,C) “V-wing” adhering to Nb(C,N) in NbV-steel.

Table 2. Microstructural features.

Mark	Macro		Precipitates							
	γ dia. (μm)	Lath spa. (μm)	G. B.		Transgranular					
			I.D.	$\langle r \rangle$ (μm)	I.D.	n_s (μm^{-2})	$\langle r \rangle$ (μm)	$\langle r^2 \rangle$ (μm^2)	r_s (μm)	λ (μm)
Base	22	0.5	M_{23}C_6	0.2	Cr_2C	0.69	0.026	0.00075	0.021	1.456
	15	0.5	M_{23}C_6	0.2	NbC	5.94	0.022	0.00060	0.019	0.479
NbV	16	0.5	M_{23}C_6	0.2	Cr_2C V-wing Cr_2C	6.23	0.027	0.00084	0.021	0.458

$$r_s = \frac{\pi \langle r^2 \rangle}{4 \langle r \rangle} \dots\dots\dots (2-a)$$

It is noted that r_s does not equal the mean radius of precipitate; $\langle r \rangle$. Table 2 shows the microstructural features; n_s , $\langle r \rangle$, $\langle r^2 \rangle$, r_s and λ .

Table 3 shows solute concentrations of chromium, molybdenum, vanadium, niobium and nitrogen. Vanadium and nitrogen solute concentrations in NbV-steel were higher than those in Nb-steel, while niobium solute concentration in NbV-steel was 0.012% lower. These differences are negligible, because the solution hardening by 0.012% Nb in 19% Cr ferritic stainless steel is less

Table 3. Solution concentrations. (wt%)

	Cr	Mo	V	Nb	N
Base	8.02	0.89	0.038	<0.001	0.0134
Nb	8.12	0.89	0.039	0.023	0.0159
NbV	8.13	0.88	0.070	0.011	0.0243

than 0.5 MPa at elevated temperature,¹⁸⁾ the solution hardening by 0.031% V in ferrite matrix is almost zero at room temperature¹⁹⁾ and the solution hardening by 0.0084% N in low Carbon steel is estimated to be less than 2.0 MPa at 600°C.²⁰⁾

3.2. Tensile Test

The ΔYS of Nb-steel strongly depends on strain rate. However, the ΔYS of NbV-steel slightly depended as shown in Fig. 4. In case of Nb-steel ΔYS at lower strain rate was less than a half of ΔYS at higher strain rate.

3.3. Creep Test

Figure 5 indicates the relations between minimum creep rate and applied stress. Every steel showed large n -value of 8 to 9 as dispersion strengthening alloy generally shows.¹¹⁾ In case of Nb-steel, the relation was divided into two parts at the minimum creep rate $2 \times 10^{-9} \text{ sec}^{-1}$. While the relation of NbV-steel consisted of one part.

4. Discussion

4.1. Tensile Test

A dislocation/precipitate interaction which dominates for shear loading is determined as the minimum time required for a dislocation to pass the precipitate, when applied stress is higher enough than the threshold stress. Assuming that successive dislocations make a Orowan loop after a previous loop disappears, Ashby's model¹⁰⁾ gives the time; t_o required for Orowan bypass as

Fig. 4. Relationships between yield stress increment from YS of base-steel " ΔYS " and strain rate at 600°C.

Fig. 5. Relationships between minimum creep rate and applied stress at 600°C.

$$t_o = \frac{b}{2Mr\dot{\epsilon}} \quad (3)$$

The simple climb model of Ansell and Weertman¹²⁾ gives the time; t_c required for a dislocation to climb over the precipitate when originally on a glide plane nearly intersecting its center as

$$t_c = \frac{bkTr}{D_v\Omega\tau} \quad (4)$$

The diffusional relaxation model of Srolovitz *et al.*⁷⁾ gives the time t_a for attractive interaction to reach the equilibrium state by the volume diffusion as

$$t_a = \frac{3(1-\nu)r^2kT}{2ED_v\Omega} \quad (5)$$

where, b : Burger vector 0.247 nm

M : Taylor factor 2.5

r : Precipitate radius about 0.025 μm in these steel

$\dot{\epsilon}$: Strain rate 2×10^{-5} to 10^{-3} sec^{-1} at this test

k : Boltzman constant $1.38 \times 10^{-23} \text{ J/K}$

T : Absolute temperature 873 K in this test

D_v : Volume self-diffusion coefficient

$4.7 \exp(-40550/T) \text{ m}^2/\text{s}^{16)}$

Ω : Atomic volume 0.041 nm^3

τ : Shear stress 150 MPa in Mod.9Cr-1Mo steel at 600°C

ν : Poisson's ratio 0.35

E : Young's modulus 168 GPa at 600°C in Mod. 9Cr-1Mo Steel.

Substitution in Eqs. (3), (4), (5) of these values gives

$$t_o = 2 \text{ to } 200 \text{ sec}$$

$$t_c = 300 \text{ sec}$$

$$t_a = 45 \text{ sec.}$$

These times suggest that the Orowan mechanism dominates at higher strain rate deformation and attractive interaction dominates at lower strain rate. Because, the time required for Orowan by pass is minimum at higher strain rate and the time for attractive interaction is minimum at lower strain rate. However, local climb is possible to dominate when ΔYS is between climbing stress and Orowan stress.

Scattergood and Bacon give Orowan stress¹³⁾ and attractive interaction stress¹⁴⁾ as per the following equation in case of interaction between a spherical particle and an edge dislocation.

$$\sigma_o = \frac{MEb}{4\pi(1+\nu)\lambda} (\ln(h/r_o) + 0.7) \quad (6)$$

$$\sigma_a = \frac{MEb}{4\pi(1+\nu)\lambda} \left(1 - \frac{1}{1-\nu} \sin^2 19^\circ \right) \cos 19^\circ \times (\ln(h/r_o) + 0.7) \quad (7)$$

Where h is the harmonic mean λ and $2r_s$, r_o the outer cut-off radius $5b$. Arzt and Ashby⁶⁾ give local climb stress as

Climb

$$\sigma_c = \frac{0.3Eb}{2(1+\nu)\lambda} \quad (8)$$

Table 4. Calculated threshold stresses.

Mark	Orowan (MPa)	Attr. (MPa)	Climb (MPa)
Base	12	11	3.2
Nb	50	45	9.6
NbV	55	49	10.1

Table 4 shows each threshold stress.

If attractive interaction dominates the deformation at lower strain rate, instead of Orowan mechanism, ΔYS should decrease to about 80% of ΔYS at higher strain rate. Because, substitution in Eq. (7) of $\nu=0.35$ and Eq. (6) gives $\sigma_a=0.79\sigma_o$. This change is considered to occur in NbV-steel and not in Nb-steel, because ΔYS at strain rate $2 \times 10^{-3} \text{ sec}^{-1}$ is 88 MPa and ΔYS at 2×10^{-5} is 73 MPa in NbV-steel. However 88 MPa and 73 MPa are much larger than the calculated threshold stresses increment from that of Base steel, 43 MPa (Orowan) and 38 MPa (attractive interaction), of NbV-steel in Table 4. These differences are considered to come from the definition of precipitate radius. If V-wings lie in the most efficient direction for dislocation pinning, we had better use half of the V-wing length ($0.09 \mu\text{m}$) as precipitate radius than the radius of sphere having the same volume as the precipitate ($0.027 \mu\text{m}$). Substitutions in Eqs. (2), (6) and (7) of $n_s=6.23 \mu\text{m}^{-2}$ and $r_s=0.09 \mu\text{m}$ give modified threshold stresses increment, 71 MPa (Orowan) and 55 MPa (attractive interaction), which nearly equal experimental values.

ΔYS at the highest strain rate in Nb-steel, 51 MPa, nearly equals the calculated Orowan stress, increment, 38 MPa, and ΔYS at lower strain rate, 22 MPa, is between the calculated climb stress, increment, 6.4 MPa, and the attractive interaction stress, 34 MPa. This means local climb must partly occur at lower strain rate.

These results suggest two precipitate shape effects. The first is that V-wing can restrain local climb even in the condition in which dislocation climbs over a spherical precipitate. Showfelt and Brown⁹⁾ exactly found the time for a dislocation to climb over a precipitate as

$$t_c = \frac{kT\lambda}{4\pi r D_v \Omega} \int \frac{(dA/dx)^2}{|T_d(dL/dx) - \tau b\lambda|} dx \dots\dots\dots(9)$$

where A is the area of the climbed segment of dislocation projected perpendicularly to the Burgers vector, T_d the line tension of this climbing segment of dislocation, and L the line length of the climbing segment of dislocation. If a dislocation pins at the concavity of V-wings and Nb(C,N), the value of dA/dx increases extremely and t_c increases drastically. The second is that the probability of dislocation trapping at V-wing is larger than that at spherical Nb(C,N).

4.2. Creep Test

When the strain rate was less than 10^{-4} sec^{-1} , the tensile test suggested that local climb partly occurred in Nb-steel and attractive interaction occurred in NbV-steel. If the same mechanisms dominate during creep, the increment of applied stress from base-steel at minimum

Fig. 6. Interaction between dislocations and a V-wing during creep deformation for 4 500 h under 180 MPa loading at 600°C.

creep rate 10^{-7} and 10^{-8} sec^{-1} (AB and CD in Fig. 5) should equal ΔYS at strain rate 10^{-5} sec^{-1} (22 and 73 MPa). AB of 20 MPa and CD of 80 MPa correspond well with ΔYS s. **Figure 6** shows interaction between a dislocation and a V-wing in the crept specimen after 4 500 h under 180 MPa loading at 600°C. The dislocation line, which core has smarted-out on the surface of the precipitate, is perpendicular to the surface of V-wing the same as Herrick *et al.*¹⁵⁾ showed an attractive interaction in Oxide Dispersion Strengthening Alloy.

Base- and Nb-steel change the slopes at creep rate 10^{-8} and 10^{-9} sec^{-1} , respectively. It is considered that grain boundary sliding occurs at applied stress level less than 120 MPa.²¹⁾ While in NbV-steel this change has not occurred yet, even in the creep rate $10^{-10} \text{ sec}^{-1}$. V-wing would act to delay the change from transgranular dislocation sliding to grain boundary sliding. Because V-wings are sure to pin mobile dislocations more strongly than spherical precipitates, and to restrain dislocation pile-up on grain boundary, which lead to grain boundary sliding.

5. Conclusion

The effect of precipitate shape in Mod.9Cr-1Mo steel on dispersion strengthening has been examined. Two types of effect have been observed. The first is that complex precipitates, V-wing, restrain dislocation climbing even in a condition in which dislocation climbs over a spherical precipitate. Mobile dislocations are considerably trapped at the concavity of the V-wings during deformation. The second effect is that the probability of dislocation trapping at V-wing is larger than that at spherical Nb(C,N). Because V-wing grown to effective direction for dispersion hardening. Calculated threshold stresses in Nb-steel with spherical Nb(C,N) corresponded well with experimental values. Also, in NbV-steel with V-wing, experimental threshold stresses were nearly equal to the values calculated by using V-wing length.

V-wing would act to delay the change of creep deformation mechanism from transgranular dislocation sliding to grain boundary sliding.

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