Roles of Solute C and Grain Boundary in Strain Aging Behaviour of Fine-grained Ultra-low Carbon Steel Sheets

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The roles of solute C and the grain boundary in the strain aging phenomenon of polycrystalline ferritic steel were investigated using Nb-bearing ULC steel sheets with a relatively low solute C content of 1–3 ppm and ferrite grain sizes of 9.5 μm and 183 μm at aging temperatures from 70 to 400°C. The steels exhibited two definite hardening stages. The 1st hardening stage appeared in both fine- and coarse-grained specimens, in which the increase in YP (ΔYP) became saturated at around 30 MPa. From the apparent activation energy and hardening kinetics, the hardening mechanism was assumed to be dislocation pinning by solute C atoms. The 2nd hardening stage, significantly appeared in fine-grained specimens accompanying a large increase in the Hall-Petch coefficient; ΔYP was quite large, reaching 90 MPa. Fine precipitates were not detected in aged specimens observed by TEM and 3DAP. Segregation of solute C to the grain boundaries and diffusion of Fe atoms in the grain boundaries were proposed as possible mechanisms of this 2nd hardening. Grain-boundary hardening was assumed to be one of the hardening mechanisms in the strain aging in polycrystalline ferritic steel.

KEY WORDS: strain aging; grain boundary; segregation; solute C; 3DAP; precipitation; activation energy; Nb-bearing steel; Hall-Petch coefficient; k_y .

1. Introduction

Several mechanisms have been proposed for the strain aging phenomenon of steels that contain solute C and N. The major mechanisms currently accepted are dislocation pinning by solute C or N atoms^{1–4)} and precipitation hardening.^{5–8)} Steels with a trace amount of solute C tend to exhibit a single hardening stage; the mechanism is assumed to be dislocation pinning by solute C atoms.⁴⁾ Low carbon and ultra-low carbon steels with large amount of solute C often exhibit a second hardening stage after the first one; the mechanism is assumed to be precipitation of carbides.^{4–7,9)}

This phenomenon is also known to be influenced by the ferrite grain size,^{3,9–13)} the site of solute atoms,¹¹⁾ the dislocation density and the deformation path.^{14–16)} For example, hardening behaviour is enhanced by grain refinement^{3,9–13)} and the Hall-Petch coefficient, k_y , increases during aging.^{3,9,10,13)} The effect of grain refinement hardly appears at room temperature but dominantly appears at elevated temperatures around 170°C.¹¹⁾ This means that the grain boundary affects strain aging under a specific aging condition. Two possible mechanisms which explain the

effect of grain size and the change in k_y have been proposed to date. One is a change in the dislocation density¹²⁾ and the other is segregation of solute elements to the grain boundary during aging.^{10,13)}

Recently, effects of the segregated interstitials in the grain boundary on YP were focused on.^{17–19)} The amount of solute C in the grain boundary greatly affects k_y and is assumed to be one of the essential factors defining YP of polycrystalline ferritic steels.^{17–19)} Strain aging at 170°C is also well known to be chiefly affected by the solute C embedded in the grain boundary.¹¹⁾ These results indicate that the segregated solute C and the grain boundary themselves play essential roles in the strain-aging phenomenon.

In this study, the strain-aging mechanisms of polycrystalline ferritic steel were reconsidered focusing on the roles of solute C and the grain boundary, using Nb-bearing ultra-low carbon steel sheets which had largely different ferrite grain sizes and contained small amounts of solute C.

2. Experimental Procedure

The chemical composition of the steel used was 0.0019%C-0.37%Mn-0.015%Nb (mass%). This material is a commercially-produced 340 MPa grade bake-hardenable steel sheet with the ferrite grain diameter of 9.5 μm and

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thickness of 0.75 mm, and is a ferritic single-phase steel containing a small amount of solute C. N is fully stabilized as AlN or Nb(C,N) during hot rolling and annealing process. **Figure 1** shows a schematic diagram of the experimental procedure. The as-received steel sheets were skin-pass rolled with the elongation of 3.6% and annealed at 850°C for 10 min to obtain a large-grained microstructure by utilizing strain-induced grain growth. The cooling rate was set to $-15^{\circ}\text{C}/\text{sec}$ to retain some amount of solute C. The steel sheets were then skin-pass rolled again with the elongation of 1.4% and subjected to the following experiments. As-received steel sheets were also annealed at 830°C for 30 sec to evaluate the mechanical properties in the as-annealed condition.

The strain aging behaviours of former two steels were evaluated using JIS No. 5 specimens perpendicular to rolling direction. The specimens were pre-strained with elongations from 0 to 10% in tensile strain, and aged at from 70 to 400°C. They were subjected to the tensile test, microstructural observations by SEM-EBSD (electron backscatter diffraction) and TEM and atomic distribution analysis by 3-dimensional atom probe (3DAP) tomography. Increase in YP during aging, ΔYP , was evaluated as the increase in upper YP against the pre-strained stress. Bake hardening, BH, was evaluated as the increase in upper YP after aging at 170°C for 20 min against 2% pre-strained stress. Aging index, A.I., was evaluated as the increase in lower YP after aging at 100°C for 1 hr against 8% pre-strained stress. The tests were carried out with a crosshead speed of 10 mm/min.

Fig. 1. Schematic illustration showing experimental procedure.

TEM analysis was carried out by the thin-foil technique using a Philips CM200 with the accelerating voltage of 200 kV. 3DAP analysis was carried out using an Ametek LEAP 4000XHR in a voltage mode, *i.e.*, without using a laser, to minimize the diffusion of solute elements. In order to investigate the segregation behaviour of solute C to the grain boundary, AES analysis was carried out using a Philips SAM650. The specimens were skin-pass rolled by 1.8%, aged at 170°C for 30 sec to 20 days and deep-drawn to a cylindrical cup with the diameter of 33 mm. Test specimens were then cut from the flange of the cylindrical cup specimens. The test specimens were fractured in a cooled chamber and more than 30 points of the fractured surfaces were analysed expeditiously under a vacuum of less than 10^{-10} torr. The dislocation density of the pre-strained specimen was evaluated by the X-ray diffraction method using a Rigaku RU300 and Co radiation source by measuring the half-value widths of the profiles of the (110), (211), (220) reflections.^{20,21)}

3. Experimental Results

3.1. Strain Aging Behaviour of Steel Sheets with Different Ferrite Grain Sizes

Figure 2 shows the cross-sectional EBSD-IPF maps of the as-received and the subsequently annealed specimens. The average ferrite grain diameters are 9.5 μm and 183 μm , respectively, and from 80 to 85% of the grain boundaries are high-angle boundaries with a misorientation of more than 15° . **Table 1** shows the mechanical properties of each specimen. A.I. of the as-received (fine-grained) and subsequently annealed (large-grained) specimens are 12 MPa and 29 MPa, respectively. The amounts of solute C within the

Table 1. Mechanical properties of steel sheets before aging.

	YP (MPa)	TS (MPa)	El (%)	2%WH (MPa)	BH (MPa)	A.I. (MPa)
As-received	234	359	41	37	34	12
Subsequently annealed	168	281	—	27	31	29

Fig. 2. Cross-sectional EBSD-IPF maps of (a) as-received and (b) subsequently annealed steels. The orientations of the normal direction to the cold-rolled surface are shown.

grains are estimated to be around 1 and 3 ppm, respectively, from a previous study.²²⁾ Although A.I. of the as-received specimen is smaller, its BH is larger than that of the subsequently annealed specimen. This means that grain refinement contributes to age-hardening at a high temperature of around 170°C, as previously reported.¹¹⁾

Figure 3 shows the strain-stress curves of the fine-grained specimens aged at 170°C after applying 2% pre-strain. YP increases only after 15 seconds of aging and increases drastically after 20 minutes of aging accompanying the clear yield point. **Figure 4** shows the change in ΔYP during aging for specimens with different ferrite grain sizes. Two distinct hardening stages (stage I, II) and a subsequent softening stage (stage III) can be seen in the fine-grained specimen, whereas only a single hardening stage occurs in the large-grained specimen. The ΔYP of the 1st hardening becomes saturated at around 30 MPa for both steels, while that of 2nd hardening reaches around 90 MPa. This large 2nd hardening is exhibited at over 100°C and continues up to 400°C. Lower YP also increases as upper YP increases. The change in TS during aging was less than ± 3 MPa.

The grain-size dependency of YS and the change in the Hall-Petch coefficient, k_y , during aging are shown in **Figs. 5** and **6** respectively. As previously reported,^{9,23)} k_y of the as-annealed state is quite large, but it drops sharply after skin-pass rolling or pre-straining. The k_y increases little during the 1st hardening stage, while increases drastically during

Fig. 3. Strain-stress curves of specimen with a ferrite grain diameter of 9.5 μm with 2% pre-strain. Showing the effect of aging at 170°C.

Fig. 5. Grain-size dependency of YS under each condition.

Fig. 6. Change in k_y during aging.

Fig. 4. Aging behaviour of 2% pre-strained specimens with ferrite grain diameters of (a) 9.5 μm and (b) 183 μm . ΔYP is the increment of yield stress by aging treatment.

the 2nd hardening stage, then becomes saturated at around $500 \text{ MPa}\mu\text{m}^{1/2}$, which is close to that of the annealed state.

The previously-reported k_y of the as-annealed, after straining and after aging conditions are listed in **Table 2**. Armstrong²³⁾ reported that k_y of as-annealed 0.1%C steel is $742 \text{ MPa}\mu\text{m}^{1/2}$ and drops to $323 \text{ MPa}\mu\text{m}^{1/2}$ after applying 2.5% plastic strain. Wilson¹³⁾ reported that k_y of quenched ultra-low carbon steel increases during aging from 294 $\text{MPa}\mu\text{m}^{1/2}$ to around 700 $\text{MPa}\mu\text{m}^{1/2}$, which is close to the value of slowly cooled steel. Hanai³⁾ also reported that k_y increases during aging at 170°C for 20 min, and the increment reaches $87 \text{ MPa}\mu\text{m}^{1/2}$ in batch-annealed steel with 5 ppm of solute C and N. Although k_y of the pre-strained state and the increment of k_y during aging at 170°C for 20 min in this work are 283 and 48 $\text{MPa}\mu\text{m}^{1/2}$, respectively, which are slightly smaller than the previously-reported values, they seem to be consistent because they decrease as the amount

of solute C decreases, as reported by Takeda¹⁸⁾ and Hanai.³⁾

Figure 7 shows the effect of pre-strain on ΔYP after aging at 170°C for 9 days, which is near the peak aging condition. The 1st hardening is hardly influenced by the amount of pre-strain. This is because the dislocation density is $1.0 \times 10^{14} \text{ m}^{-2}$ and the amount of solute C is sufficient for the pinning sites of dislocations.⁴⁾ The 2nd hardening, however, decreases as the amount of pre-strain increases. It suggests that the amount of the dislocation density is a negative factor for the 2nd hardening.

4. Discussion

As mentioned, the fine-grained steel sheet exhibits distinct 1st and 2nd hardening stages, and the 2nd hardening reaches around 90 MPa accompanying a great increase in k_y , even though the amount of solute C is quite small. Precipitation hardening⁵⁾ and grain-boundary segregation of interstitial elements¹³⁾ were believed as mechanisms of the 2nd hardening. In this study, essential roles of solute C and grain boundaries to the 1st and 2nd hardenings are discussed in terms of microstructural change, hardening kinetics and segregation behaviours.

4.1. Contribution of Grain Interior and Grain Boundary to Age-hardening

First, the contributions of the grain interior and the grain boundary to the 1st and 2nd hardenings are evaluated in the 2% pre-strained specimens. Yield strength, σ_y , is expressed using strength of the grain interior, σ_0 , the Hall-Petch coefficient, k_y , and the grain size, d , as Eq. (1):

$$\sigma_y = \sigma_0 + k_y d^{-1/2} \dots\dots\dots (1)$$

Strength of the grain interior, σ_0 can be estimated as an extrapolated YS when $d^{-1/2}$ equals zero. The critical grain-

Fig. 7. Relationship between amount of pre-strain and increment of YP after aging at 170°C for 9 days.

Table 2. Previously reported k_y in as-annealed, after plastic deformation and after aging conditions.

Materials	Conditions	k_y ($\text{MPa}\cdot\mu\text{m}^{1/2}$)	Tested Temp.	Ref.
Al-killed Nb-bearing ULC steel ; sol.C=1–3 ppm (present work)	as-annealed, L.YP/U.YP	503/567	R.T.	–
	after 2% pre-straining	283		
	after aging, 170°C , 1 min, L.YP/U.YP (end of the I stage)	279/283		
	after aging, 170°C , 20 min, L.YP/U.YP	331/331		
	after aging, 170°C , 20 days, L.YP/U.YP (end of the II stage)	463/503		
0.1%C semi-killed steel	as-annealed, L.YP	742	R.T.	23)
	as-annealed, 2.5% flow stress	323		
ULC steel ; sol.C=30 ppm	as-annealed(slowly cooled)	688–710	R.T.	13)
	as-annealed(quenched)	294		
	after aging, 90°C , 10^5 min	672–710		
0.015–0.041% Al-killed steel ; sol.C+N=5 ppm	(Batch-annealed)			
	after 2% pre-straining	127	–	3)
	after aging, 170°C , 20 min, L.YP	214		
	; sol.C+N=10 ppm			
	after 2% pre-straining	115	–	3)
	after aging, 170°C , 20 min, L.YP	285		
; sol.C+N=20 ppm	after 2% pre-straining	93	–	3)
	after aging, 170°C , 20 min, L.YP	319		

boundary strength, τ_c , when the dislocation sources operate at or near grain boundaries, *i.e.*, shear stress acting on the grain boundary when yielding occurs, can be theoretically given from k_y , assuming the pile-up model.^{24,25)} The k_y and τ_c are related in the double pile-up model as Eq. (2):

$$k_y = M \sqrt{\frac{2Gb\tau_c}{\pi k}} \quad \dots\dots\dots (2)$$

where M is the Taylor factor, G is the shear modulus, b is the Burgers vector and k is a constant equal to $(1-\nu)$ for edge dislocation and 1 for screw dislocation, where ν is the Poisson's ratio. τ_c can be estimated by giving the proper values of M , G , b and k in bcc Fe.

Figure 8 shows the estimated σ_0 and τ_c under aging conditions of 70°C and 170°C when M , G , b and k are given as 2, 80 GPa, 0.25 nm and 0.85, respectively. The σ_0 increases during the 1st hardening stage and its increment becomes saturated at around 30 MPa, which is independent of aging temperature. On the other hand, τ_c hardly changes during the 1st hardening stage, but increases drastically after the completion of 1st hardening and reaches 4 GPa, which is close to the value of the as-annealed state.

Thus, the 1st hardening seems to be derived from an increase in the strength of the grain interior, and the 2nd hardening, in the strength of around the grain boundary. One of the authors *et al.* showed that the pop-in load at the grain boundary in the nano-indentation method increased gradually during the 2nd hardening stage,²⁶⁾ which is consistent with the above theory.

Here, there could be two possible processes of increas-

ing τ_c and k_y . One is the previously-predicted additional hardening process due to precipitation hardening⁵⁾ or grain-boundary segregation.¹³⁾ The other is the recovery process of the grain boundary. As shown above, τ_c and k_y drop after deformation and increase drastically during aging. Previously, essential reasons for the drop in k_y when plastic strain is applied was believed to be the distribution of mobile dislocations,^{16,23)} micro-residual stress¹⁴⁾ and inhomogeneous plastic strain.²⁷⁾ The values of τ_c and k_y are, however, still quite small even at the end of the 1st hardening stage. This indicates that the drops in τ_c and k_y are chiefly caused by the decrease in the strength of the grain boundary rather than the distribution of mobile dislocations. Then, τ_c and k_y increase to near the values of the annealed state during the 2nd hardening stage. This implies that τ_c and k_y simply return from the deformed state to the annealed state during aging by the local recovery around the grain boundary.

4.2. Kinetics of Age-hardening

Cottrell and Bilby¹⁾ established a kinetic model for dislocation pinning, in which the number of solute atoms segregated to the dislocations is proportional to the concentration of solute C in the matrix and the 2/3 power of time. Harper²⁾ considered the saturation effect of segregation and obtained the extended model shown in Eq. (3):

$$W = \frac{n_t}{n_0} = 1 - \exp \left[-3L \left(\frac{\pi}{2} \right)^{\frac{1}{3}} \left(\frac{ADt}{kT} \right)^{\frac{2}{3}} \right] \quad \dots\dots\dots (3)$$

where n_t is the number of solute atoms segregated per unit length of dislocation at time t , n_0 is the number of solute atoms per unit volume of matrix, L is the total length of dislocations per unit volume, A is the interaction energy between a dislocation and a solute atom and D is the diffusion coefficient of an interstitial solute. Equation (3) can be rewritten as the following Eq. (4):

$$\ln(1-W) = -\left(\frac{t}{\tau} \right)^n = -(kt)^n \quad \dots\dots\dots (4)$$

where τ , k are constants depending on the temperature. The parameter W is often equated with the fractional increase in YP during aging, $\Delta\sigma/\Delta\sigma_{max}$, where $\Delta\sigma$ is the increase in YP for time t and $\Delta\sigma_{max}$ is the maximum increase in YP during the aging process.²⁸⁾ **Figure 9** shows the result of an analysis of the kinetics of 1st hardening by Eq. (4). The exponential, n , is from 0.65 to 0.70 for the 1st hardening and is independent of grain size. This is close to the 2/3 given for Cottrell locking.

Figure 10 shows the apparent activation energies of the 1st and 2nd hardening estimated for several ΔYP levels. The apparent activation energy of the 1st hardening is from 83 to 86 kJ/mol, which is independent of grain size and is close to the activation energy of the volume diffusion of C atoms in α -Fe²⁹⁾ shown in **Table 3**. Thus, the dominant mechanism for the 1st hardening would be dislocation pinning by solute C atoms.

The apparent activation energies change discontinuously from 83 to 86 kJ/mol to around 135 kJ/mol over 100°C. This suggests that the mechanism of 2nd hardening is different from that of 1st hardening. Similar values³⁰⁻³²⁾ and the

Fig. 8. Changes in critical grain-boundary strength and strength of grain interior during aging. Gray areas show the 1st and 2nd hardening stages under the aging condition of 170°C.

temperature dependency³²⁾ were mentioned in the previous reports, in which the phenomenon in high temperature was understood as clustering or precipitates, because the activation energy is large and it follows the formation of the Cottrell atmosphere.^{23,25)}

The apparent activation energy of 135 kJ/mol is also close to that of pipe diffusion and grain-boundary diffusion of Fe atoms^{33,34)} and precipitation of η -carbide.³⁶⁾ The activation energies of grain-boundary and pipe diffusion of Mn and P in α -Fe would be close to that of Fe atoms, because those of volume diffusion in α -Fe are close to that of Fe atoms.^{37,38)} They are the candidates of the essential rate-controlling factor of 2nd hardening.

Fig. 9. Hardening kinetics of 2% pre-strained specimens with different grain sizes during 1st hardening stage analyzed by Harper model.²⁾

Fig. 10. Apparent activation energies estimated for several ΔYP levels.

Previously been predicted, however, segregation of solute C to grain boundary may not be a predominant hardening factor, because the obtained apparent activation energy is approximately 1.5 times larger than that of volume diffusion of C atoms which is assumed to be rate-controlling in the grain-boundary segregation. Effect of the grain-boundary segregation during aging is discussed later in more detail as an additional enhancing factor of the age-hardening.

4.3. Microstructural Changes during Aging

Figure 11 shows a TEM micrograph of the fine-grained specimen aged at 170°C for 7 days. Fine precipitates are not observed either in the vicinity of the grain boundaries or within the grains, even under the peak hardening condition. Figure 12 shows the atomic distribution of the chief elements obtained by 3DAP analysis in the specimen aged at 170°C for 20 days. Segregation of solute C, Mn and P in the grain boundary is clearly observed. However, fine precipitates are not observed around the grain boundary. Figure 13 shows a TEM micrograph of the specimen aged at 170°C for 180 days. Similarly, fine precipitates are not observed even in the overaged region. This indicates that the 2nd hardening which significantly appeared in the fine-grained steel is not due to the previously-predicted precipitation hardening. The softening behaviour is also not due to the coarsening of precipitates.

On the other hand, some changes in the dislocation structures are observed during aging. Apparently, two types of dislocations are developed, as shown in Fig. 13. One type of dislocation, which is adjacent to the grain boundary, is linear and is aligned vertical to the grain boundary; the other type

Fig. 11. TEM micrograph of as-received specimen aged at 170°C for 7 days.

Table 3. Activation energies of various mechanisms reported in previous studies.

Volume diffusion of C ²⁹⁾ in α -iron	Self diffusion in α -iron			Precipitation of ϵ carbide ³⁵⁾	Precipitation of η carbide ³⁶⁾	Precipitation of cementite ³⁶⁾
	Pipe diffusion ³³⁾	Volume diffusion ³⁴⁾	G.B. diffusion			
75–84	134	241	241 × (0.5–0.7)	71	124*	176*

*: in martensitic steel

Fig. 12. Element mapping and concentration profile around grain boundary for several elements obtained by 3DAP in the as-received specimen aged at 170°C for 20 days.

Fig. 13. TEM micrograph of as-received specimen aged at 170°C for 180 days. The black arrows show grain-boundary dislocations and the white arrows show dislocations arranged vertically to the grain boundary.

is a cluster of grain-boundary dislocations. These features are hardly observed in the specimen during the 1st hardening stage, but are clearly observed in the specimen aged at 400°C. This indicates that Fe atoms can diffuse locally, in both the grain boundary and the dislocation core, with a long aging duration at over 100°C.

4.4. Effect of Diffusion of Elements around Grain Boundary

Various mechanisms of the 2nd hardening are conceivable if the diffusion of elements around the grain boundary is considered. Previously predicted mechanism is the segregation of interstitial atoms into the grain boundaries.¹³⁾ The others would be segregation of substitutional atoms such as P, Mn and Nb into the grain boundary, and changes in micro-residual stress¹⁴⁾ by dislocation movement, change in the dislocation structure and rearrangement and ordering of Fe or other atoms in the grain boundaries. Here, the effect of grain-boundary segregation of solute C was estimated first, after which the other possibilities were discussed.

McLean³⁹⁾ established a model expressing the velocity of grain-boundary segregation assuming a linear flow of

solutes to the grain boundary as in Eq. (5):

$$2\sqrt{(Dt_{0.5})} / \{(C_{gb}/C_1)\delta\} = 3/4 \quad (5)$$

where D is the diffusion coefficient of solutes, $t_{0.5}$ is the half-completion time, C_{gb} is the equilibrium concentration of solutes in the grain boundary, C_1 is the concentration of solutes in the matrix and δ is the thickness of the grain boundary.

The half-completion time, $t_{0.5}$, at 170°C is shown in **Fig. 14**. C_{gb} and δ are assumed to be 30 at% and 3 atomic diameters, respectively, and the amount of solute C within grains is varied to 1, 3, 10 and 50 wt.ppm. If the amount of solute C is 1 wt.ppm, $t_{0.5}$ is on the order of 10^4 min, which is close to the experimental result. Since the solubility of C in iron⁴⁰⁾ is less than 1 ppm at 170°C, if more than 1 ppm of solute C within a grain is assumed to diffuse to the grain boundary, the result based on the mass balance is an increase of more than 1 at% of solute C in the grain boundary, when the ferrite grain size is set to 9.5 μm and width of the grain boundary is set to 3 atomic layers.

The influence of segregated solute C was analysed experimentally. **Figure 15** shows a SEM micrograph of the fractured surface of an as-received specimen. Both the intergranular and cleavage fractured surfaces were analysed by AES. Since about 3 at% of C was detected even at the cleavage fractured surface, this was subtracted as contamination.

Figure 16 shows the change in the concentrations of C and P at the intergranular fractured surface of aged specimens. Segregation of C seems to occur slightly during aging. The increment of the amount of C during aging is approximately 0.2–0.3 at%, and the increment of k_y is estimated as roughly 40–50 $\text{MPa}\mu\text{m}^{1/2}$ from the experimental data.¹⁷⁾ This accounts for only 1/5 of the total increment of k_y . One reason for this would be that the amount of initial solute C is already large in the grain boundary, because the steel sheet is gas-cooled after annealing and solute C is segregated during cooling.⁴¹⁾ This indicates that the segregation of solute C during aging contributes to age-hardening to some extent as an additional enhancing factor, but it is not a predominant rate-controlling factor.

Tanigawa³²⁾ reported that the cause of large activation energy above 100°C is not the addition of Mn, P and the existence of NbC, because large activation energy is also obtained in Al-killed steel. This indicates that segregation of substitutional elements such as Mn, P and Nb may also have enhancing effects on age-hardening, but cannot be the

dominant rate-controlling factor.

If segregation of elements during aging is slight, the recovery of the deformed grain boundary might be a candidate for the essential rate-controlling factor. As shown in Figs. 10 and 13, the apparent activation energy for the 2nd hardening is close to that of grain-boundary diffusion of Fe atoms, and the structure of the grain boundary seems to change gradually with increasing temperature. If local diffusion of Fe atoms takes place in the grain boundary, the

Fig. 14. Estimated half-completion time of grain-boundary segregation of C at 170°C.

Fig. 15. SEM micrograph of fracture surface of as-received specimen fractured in vacuum chamber for AES analysis.

structure of the grain boundary would become more stable during aging. Since the segregated solute C in the grain boundary cause a quite large increase in k_y in the annealed state rather than in the deformed state, such a grain boundary recovery process would cause the increase in k_y in steel in which solute C is segregated before and during aging. These combined effects of embedded solute C and diffusion of Fe atoms in the grain boundary might be essential characteristics of the strain aging that appears over 100°C. This is a new proposal, and will be discussed in detail in the subsequent report.

4.5. Strain-aging Behaviour in Fine-grained Steel Containing Small Amount of Solute C

Although the detailed microscopic mechanisms are still unclear, the general strain-aging behaviour of polycrystalline ferritic steel can be illustrated as shown in Fig. 17. The 1st hardening would be due to dislocation pinning by solute C, *i.e.*, suppression of primary slip, and the 2nd hardening would be due to grain boundary hardening, *i.e.*, suppression of secondary slip.

The 1st hardening contributes to strain aging through an increase in σ_0 in Eq. (1). The hardening effect by dislocation pinning by solute C is around 30 MPa at full aging. Since the segregation velocity is proportional to the concentration

Fig. 16. Change in amounts of C and P at intergranular fractured surface of specimens aged at 170°C.

Fig. 17. Presumable mechanisms and their illustrations for 1st and 2nd hardenings in the steel with fine grain and containing small amount of solute C.

of solute C¹⁾ and the pinning sites are fully occupied by the quite small amount of solute C, the amount of solute C affects the hardening rate, but it hardly affects the maximum hardening value.

The 2nd hardening contributes to strain aging through an increase in k_y , if the amount of solute C within the grain is small and precipitation is slight. In the 2nd hardening, the large apparent activation energy of 135 kJ/mol is necessary; the 2nd hardening appears significantly at elevated temperature. Such a hardening effect is enhanced in fine-grained steel from Eq. (1). These points are consistent with the previously-reported features of bake-hardenable steel.^{3,13)} Addition of micro-alloying element such as Nb would contribute to hardening through grain refinement. Many researchers^{16,32,42)} have pointed out the limitation of the applicability of Hundy's equation,⁴³⁾ which is based on the Cottrell's model.¹⁾ One of the reasons for this might be the onset of the increase in k_y because the deviation occurs at over 100°C^{16,32,42)} accompanying the large apparent activation energy of 140 kJ/mol.³²⁾

If the amount of solute C within the grain becomes larger, the amount of segregated solute C in the grain boundary before and during aging would also become larger, and if it exceeds the solubility in ferrite, precipitation would occur. The former would enhance the age-hardening through an increase in k_y and the latter, through an increase in σ_0 .

5. Conclusions

The strain-aging mechanisms of polycrystalline ferritic steel were investigated using Nb-bearing ULC steel sheets with ferrite grain sizes of 9.5 μm and 183 μm , which contained a quite small amount of solute carbon. The major conclusions are as follows:

(1) The fine-grained specimens exhibited two distinct hardening stages, whereas large-grained specimens showed only a single hardening stage. The increase in YP in the 1st hardening stage is around 30 MPa, and the apparent activation energy of this stage is estimated to be from 83 to 86 kJ/mol. The increase in YP in the 2nd hardening stage reaches 90 MPa, and the apparent activation energy is 135 kJ/mol.

(2) The 1st hardening stage progresses proportionally to approximately the 2/3 power of time, and its apparent activation energy is close to that of C diffusion in bcc Fe. Therefore, the predominant mechanism of hardening in this stage is assumed to be dislocation pinning by solute C atoms.

(3) The 2nd hardening stage progresses accompanying a large increase in the Hall-Petch coefficient, k_y . During this process, fine precipitates do not exist. The 2nd hardening is presumed to be associated with grain-boundary hardening. Local diffusion of Fe atoms around grain boundaries where solute C is embedded is proposed as an essential mechanism of the 2nd hardening. The grain-boundary segregation of solute C during aging could promote the primary mechanism.

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