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Change in microstructure and hydrogen embrittlement resistance with low temperature aging of drawn pearlitic steel and its proposed mechanism

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Abstract: When the strength level of steels becomes very high, hydrogen embrittlement tends to occur. In this study, we investigated the change in microstructure and hydrogen embrittlement resistance of drawn pearlitic steel with low temperature aging. Using a high carbon drawn pearlitic steel wire (SWRH82B), the change in hydrogen embrittlement sensitivity with low temperature aging was investigated. Low temperature aging at 100 °C and 300 °C increased yield strength and simultaneously improved the hydrogen embrittlement resistance. In order to elucidate the mechanism, TEM (Transmission Electron Microscopy) observation and crystal orientation analysis by nano-beam precession electron diffraction method (TEM orientation mapping) were conducted for as-drawn and subsequently low temperature aged pearlitic steel wire. The low temperature aging, in particular 300 °C aging, revealed that recovery was accelerated in a heterogeneously deformed area. When specimen was aged at 400 °C, recrystallization clearly commenced. Meanwhile, the low temperature aging as low as 300 °C significantly increases yield stress by locking dislocation movement due to carbon segregation. Moreover, hydrogen, initially trapped in dislocation core, is inferred to be replaced by carbon during aging. Therefore, low temperature aging is considered to lead to both the increase in strength and the improvement of hydrogen embrittlement resistance.

1. INTRODUCTION

Drawn pearlitic steel shows excellent resistance to hydrogen embrittlement [1]. However, the mechanism through which its hydrogen-embrittlement resistance is improved remains unclear. Pearlitic steel drawn to large strains has a lamellae structure oriented in the drawing direction. Since a high-density of dislocations are introduced in the ferrite, it is important to clarify the relationship between these microstructural factors and the hydrogen-embrittlement resistance.

Thermal desorption analysis (TDA) is a well-known experimental technique for analyzing the state of hydrogen in steel [2]. Although TDA of the as-patented pearlitic steel shows only hydrogen peak near 100 °C, the drawn pearlitic steel shows a second peak near 300 °C in addition to this near 100 °C peak. The observation of two peaks means that there are multiple hydrogen trapping sites in the structure [3]. Many studies on the relationship between aging and the hydrogen-embrittlement susceptibility of drawn pearlitic steel have been conducted [3-5], and have focused on microstructural changes in severely worked pearlitic steel [7-9]. However, changes in the microstructure, mechanical properties, and hydrogen-embrittlement resistance of such steel with aging at a relatively low temperature of 100–300 °C for a relatively short time of 10 min after wire drawing with a strain of ~2, as done in the present study, have not yet been elucidated. Especially, a detailed microstructural analysis has not been

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conducted regarding the manner of recovery and carbide precipitation to dislocations, among other things.
Therefore, the present study endeavors to deepen the understanding of the effect of aging on the mechanical properties and hydrogen-embrittlement susceptibility of drawn pearlitic steel from the viewpoint of microstructural change. More specifically this study was designed to allow the observation of dislocation structures and carbides in as-drawn and subsequently aged pearlitic steel specimens using transmission electron microscopy (TEM) and to perform grain orientation analysis [10] of small regions using the nanobeam precession electron diffraction method.

2. EXPERIMENT

2.1. Material

SWRS82B, a high-carbon steel (0.8 mass% C steel), was used as the experimental material. First, a 122 × 122 mm^2 billet of SWRS82B was heated to 1100 °C and hot-rolled into a rod with diameter ϕ = 13.0 mm. The microstructure of the as-rolled material was pearlite. The chemical composition is given in Table 1.
The pearlitic steel rod was then heated at 880 °C for 10 min and held at 530 °C for 120 s to induce the pearlitic transformation. The heat-treated rod was pickled, zinc-phosphated, and dry-drawn to ϕ = 5.0 mm at room temperature. Some of the drawn wires were examined in the as-drawn state. The rest were aged at 100 °C for 10 min (BL100) or at 300 °C for 10 min (BL300). Table 2 shows the tensile strength of the specimens. For tensile testing, a ϕ = 5 mm round-bar specimen with a gauge length (GL) 90 mm was used at a tensile speed of 1 mm/min. It is clear that the 100 and 300 °C aging treatments significantly increased the yield strengths of the BL100 and BL300 specimens.

Table 1. Chemical compositions of the steel used (mass%).

	C	Si	Mn	P	S	N	O
SWRS82B	0.82	0.19	0.78	0.017	0.015	0.0035	0.0015

Table 2. Mechanical properties of the as-drawn and subsequently aged wire for 10 min at 100 °C (BL100) and 300 °C (BL300).

Sample	0.2% Yield strength (MPa)	Tensile strength (MPa)
As-drawn	1530	1943
BL100	1700	2029
BL300	1920	2038

2.2. Evaluation of dislocation stability

To investigate the influence of aging conditions on the stability of dislocations, a stress relaxation test was performed using a smooth, round bar specimen with ϕ = 5 mm. An initial stress of 0.7 σ_B (σ_B: ultimate tensile strength) was applied at a test temperature of 30 °C, and the decrease in the stress was measured in a constant grasping interval. The ratios of stress relaxation (relaxation stress/initial stress) were compared for the as-drawn and subsequently aged specimens at different aging temperatures.

2.3. Methods for evaluating hydrogen embrittlement of drawn pearlitic steel

To investigate the effect of aging treatment on hydrogen embrittlement, the prepared ϕ = 5 mm specimens, described in Section 2.1, were tested using a constant-load test. These specimens were prepared by cutting a round rod to a length of 300 mm and then notching the rod circumferentially at 140 mm from the end to a depth of 0.4 mm, an angle of 60 °, and a radius of curvature of 0.12 mm. These were polished with emery paper to remove the oxide film and then pre-charged with hydrogen and immediately loaded the specimen, and the time to fracture was then measured. To keep the hydrogen concentration constant during testing, tests were conducted under continuous hydrogen charging conditions, using a solution of 0.1 N NaOH + 5 g/L NH_4SCN, a current density of 2 A/m^2, and a temperature of 30 °C.

2.4. Method for analyzing hydrogen in steel

Hydrogen analysis was conducted using gas chromatography. The specimens were ultrasonically washed in acetone before measurement. Each specimen was dried and placed in the quartz tube of a heating chamber. After the atmosphere in the quartz tube was replaced by argon carrier gas, the measurement was started. The heating rate was 100 ºC/h, and the measurement was performed at temperatures of up to 600 °C.

2.5. Microstructural observation using TEM and the grain-orientation mapping method

The drawn and subsequently aged specimens were observed using TEM to investigate the changes in their microstructures with aging. Both the as-drawn and subsequently aged specimens were cut to ϕ 5.0 mm × 10 mm and punched into ϕ = 3.0 mm disks, with the disk center located at a depth of 1.5 mm from the outer circumference to observe from the direction perpendicular to the drawing direction. Thin-film specimens were prepared via mechanical polishing and twin-jet electrolytic polishing. The nanobeam precession electron diffraction method was used to obtain grain orientation maps of the α-Fe phase. In this method, an electron beam is precessed on the specimen (beam-irradiation diameter of ~10 nm and incident angle of 0.6°). That is, an electron beam with a spot size of 10 nm was automatically scanned at a step size of 10 nm to obtain electron diffraction spots representing grain orientations. The TEM observation surface included the longitudinal drawing direction.

2.6. Measurement of dislocation density using X-ray diffraction

The dislocation density was measured at the quarter depth of the specimens cut longitudinally using the Williamson–Hall method.

3. EXPERIMENTAL RESULTS

3.1. Effect of the aging temperature on the stress–strain curve and dislocation stability

Fig. 1 shows the results of the tensile test. The 0.2% yield stress increased with the aging temperature up to 300 °C. Furthermore, the largest total elongation was recorded for the specimen with an aging temperature of 300 °C (BL300 °C).

Fig. 2 shows the results of the stress-relaxation test. The ratios of stress relaxation were 3.4% for the as-drawn material, 3.2% for the specimen aged at 100 °C (BL100 °C), and 1.6% for the BL300 °C sample. These results suggest that the dislocations were stabilized by the aging treatment.

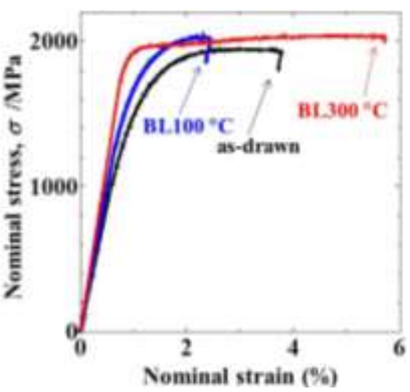

Figure 1. Stress–strain curves of the as-drawn, BL100°C, and BL300 °C specimens.

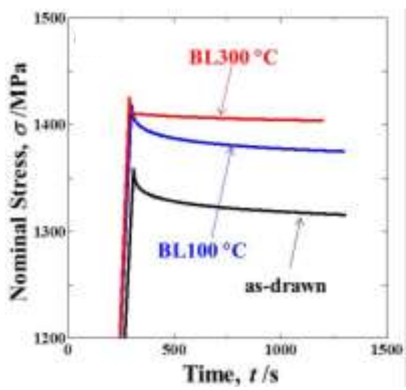

Figure 2. Stress-relaxation curves of the as-drawn, BL100 °C, and BL300 °C specimens.

3.2. Change in the hydrogen-embrittlement characteristics of drawn pearlitic steel with aging treatment

Fig. 3 shows the hydrogen-embrittlement characteristics evaluated using a constant-load tensile test. Applied stress ratio (σ_a/σ_B) is plotted as a function of time to fracture in the constant-load tensile test of specimens as-drawn and as-aged at 100 ºC and 300 ºC. σ_B is fracture stresse without hydrogen charging, and σ_a is applied stress in the constant-load tensile test. It shows that aging treatment at temperatures as high as 300 °C improves hydrogen-embrittlement resistance [11].

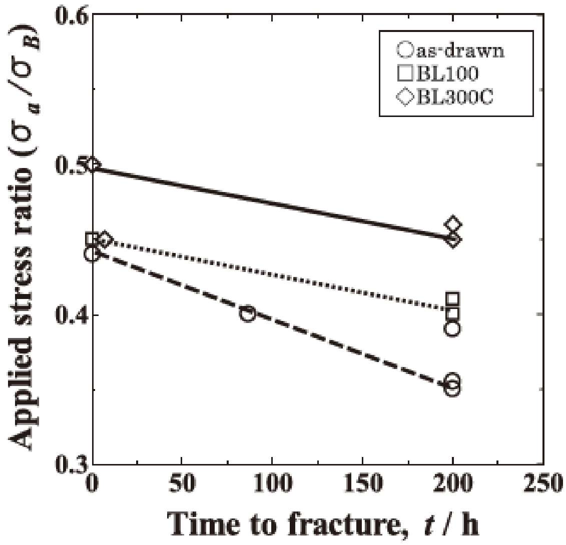

Figure 3. Result of constant load test of the as-drawn, BL100°C, and BL300 °C specimens charged with hydrogen for 144 h.

3.3. Change in the hydrogen trapping state of drawn pearlitic steel with aging treatment

Fig. 4 shows the TDA profiles of the specimens subjected to hydrogen charging for 144 h. Fig. 5 shows the relationship between charging time and hydrogen content of peak 1. The hydrogen concentration is expected to reach an equilibrium value up to the sample center. Two desorption peaks at 100 °C and 300 °C were observed, where the first peak, near 100 °C, corresponds to the hydrogen trapped in the stress field of dislocations, the second peak, near 300 °C, corresponds to hydrogen trapped in dislocation cores [12]. As the aging temperature increased, the height of both peaks decreased, indicating a decrease in trapped hydrogen content.

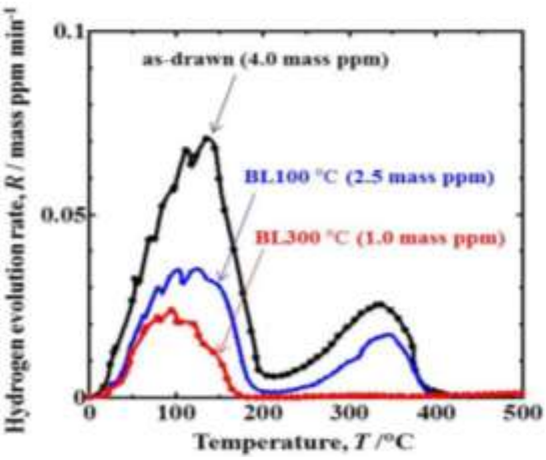

Figure 4. Thermal desorption profiles of the as-drawn, BL100°C, and BL300 °C specimens charged with hydrogen for 144 h.

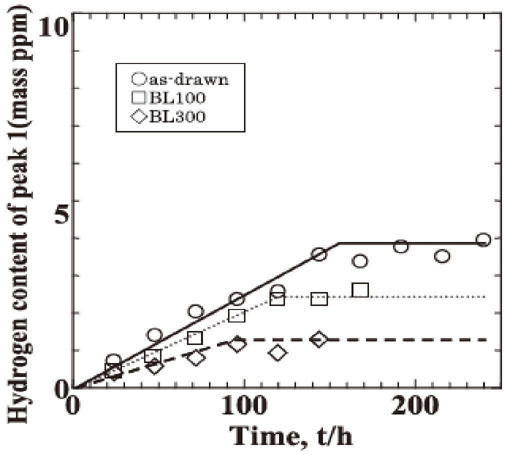

Figure 5. Effect of aging treatment on the hydrogen content of peak 1 in the TDA test as a function of the hydrogen charging time.

3.4. Microstructural changes in drawn pearlitic steel with aging treatment

Fig. 6 shows the bright-field TEM images of the as-drawn specimen as well as of specimens subsequently aged at 100 °C and 300 °C. The drawing direction is indicated by white arrows. Dislocations were observed in the lamellar ferrite in each specimen. The width of the lamellar ferrite was 50–100 nm in each specimen. No clear changes were observed either in the ferrite-phase width or the cementite structure as a result of the aging treatments. The specimens aged at 300 °C, however, yielded images suggesting some dislocation rearrangement in lamellar ferrite, as indicated by the white dashed-line circles in Fig. 6(c). A contrast suggesting the precipitation of carbides was also observed, as indicated by black arrows in Fig. 6(c). Strain contrast arising from the localized presence of high-density dislocations was also observed, as indicated by red circles in Figs. 6(a)–(c).

Fig. 7 shows the detailed information of cementite in the as-drawn specimen and in the specimen subsequently aged at 300 °C. The dark-field image in Fig. 7(d) indicates the commencement of spherodization of very fine carbides at an aging temperature of 300 °C.

Fig. 8 shows the ferrite-phase orientation maps of the as-drawn specimen and the specimens subsequently aged at 100 °C, 300 °C, 400 °C, 500 °C and 600 °C by means of the precession electron diffraction method. In the grain-orientation map of each specimen, grains with the same color are elongated in the drawing direction. A region with the same color is inferred to correspond to an initial block with a width of approximately 1–2 μm. The gradation in the grain orientation in a block is inferred to reflect a packet. In this way, the inhomogeneity of the microstructure of the drawn pearlitic steel is related to the grain orientations of the blocks before the drawing operation. It is worthwhile to note that the specimen aged at 300 °C revealed a region with a fine clear microstructure having high-angle boundaries (Fig. 8(c)). This suggests that the aging treatment at 300 °C locally decreased the dislocation density through the rearrangement of dislocation, resulting in subgrain formation. When specimen was aged at 400 °C, recrystallization commenced and recrystallization further proceeds with increasing aging temperature.

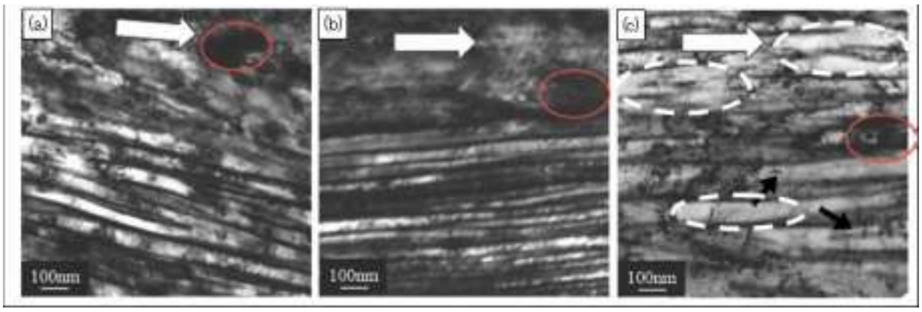

Figure 6. TEM images showing the dislocation structure in (a) the as-drawn specimen and in the specimens subsequently aged at (b) 100 °C and (c) 300 °C.

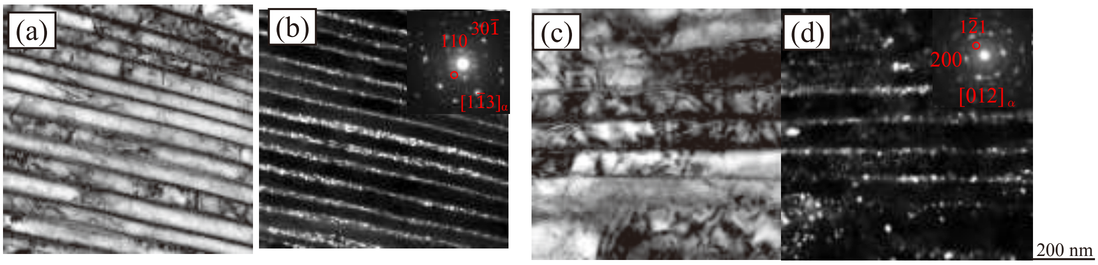

Figure 7. TEM images showing the lamellar cementite structure (a) the bright field image of the as-drawn specimen, (b) dark field image of the as-drawn specimen, (c) bright field image of the specimen aged at 300 °C, and (d) dark field image of specimen aged at 300 °C.

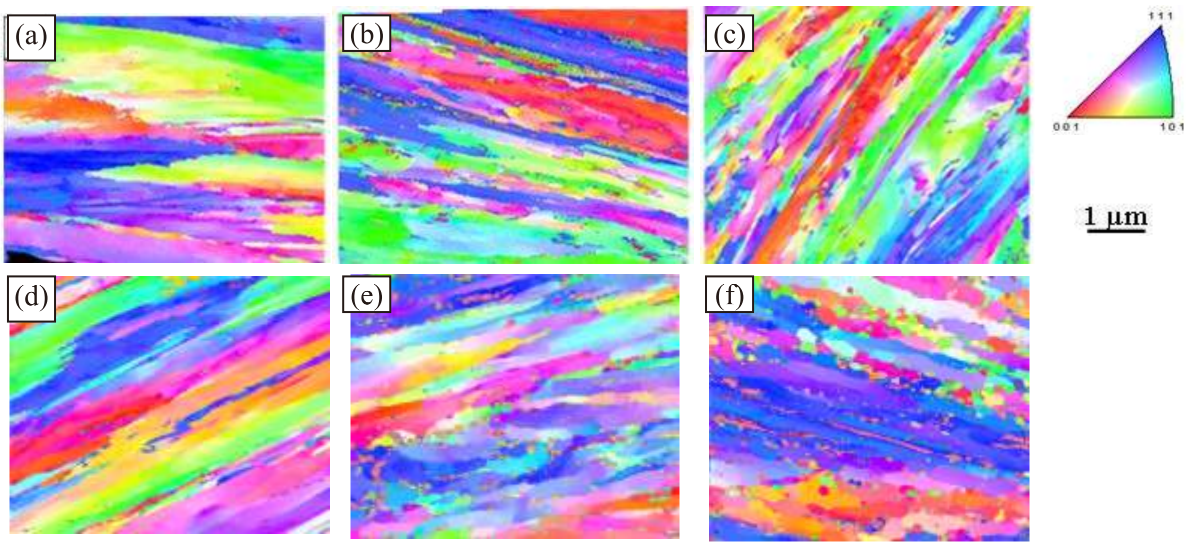

Figure 8. TEM grain-orientation maps of specimens: (a) as-drawn, subsequently aged at (b) 100 °C, (c) 300 °C, (d) 400 °C, (e) 500 °C and (f) 600 °C.

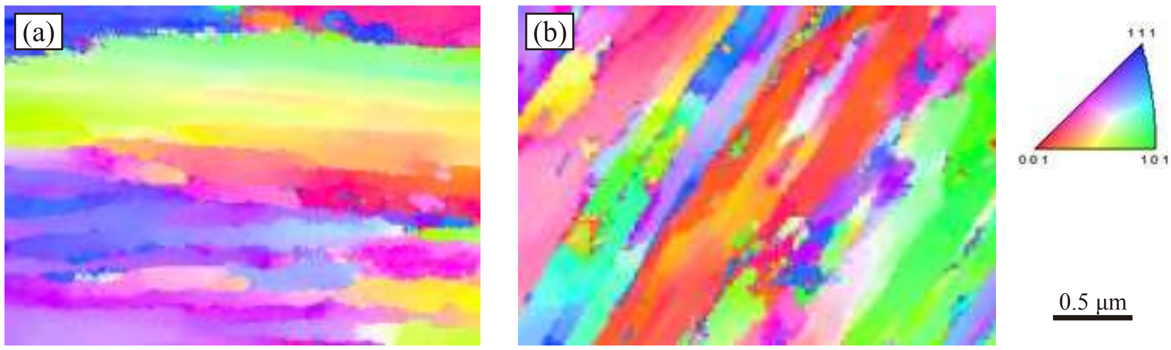

Figure 9. Magnified TEM grain-orientation maps of specimens: (a) as-drawn and (b) subsequently aged at 300 °C.

The magnified TEM grain-orientation maps shown in Fig. 9 evidently imply that dislocation rearrangement proceeds during aging at 300 °C.

4. DISCUSSION

4.1. Change in the yield strength and relaxation-stress ratio with aging treatment

The yield strength increased upon the application of the aging treatment, more significantly at 300 °C than at 100 °C. Dislocations during the relaxation test were also stabilized by the aging treatment in a similar manner to that observed in the tensile test, where again, the aging treatment at 300 °C had a stronger effect than that at 100 °C. During the drawing process for pearlitic steel at room temperature, lamellar cementite is expected to be partly dissolved as solute carbon in the ferrite matrix together with an introduction of dislocations. These dislocations are supposed to be locked or pinned by segregated carbon or by very fine carbides formed during the aging treatment. Taking into account the fact that recovery simultaneously occurs during aging at 300 °C, the increment in the pinning force for dislocation movement by segregated carbon or very fine carbides is postulated to be much larger than the softening effect by recovery.

4.2. Change in hydrogen embrittlement with aging treatment

Takai and Watanuki [3] confirmed the presence of two peaks for hydrogen near 100 °C and 300 °C, respectively, in the TDA curves of drawn pearlitic steel. Doshida and Takai [4] explained that plastic deformation of drawn pearlitic steel increases hydrogen-embrittlement susceptibility and that this condition is correlated to the increase in the magnitude of the lower temperature hydrogen peak. Meanwhile, Chida et al. [6] reported that aging the drawn pearlitic steel results in a decrease in hydrogen content associated with the lower temperature peak. They considered that during aging, carbon is preferentially trapped in dislocations, thereby decreasing the number of hydrogen trapping sites. Fig. 3 in the present study shows results similar to those obtained by Chida et al. The hydrogen content of the lower temperature peak significantly decreased after aging at 100 °C for 10 min, accompanied by a further decrease in size of both peaks after aging at 300 °C. Aging for only a relatively short period of 10 min clearly increased the yield strength. The ultimate tensile strength of the drawn pearlitic steel was, however, barely affected (see Table 2). Simultaneously, aging for a short duration considerably decreased hydrogen-embrittlement susceptibility [11].

Microstructural changes during the aging treatment are considered to have a positive effect against hydrogen embrittlement. The TEM grain-orientation maps of the minute regions of the as-drawn specimen and those of the specimen subsequently aged at 300 °C (Figures. 7(a) and (c), respectively) not only revealed the grains elongated in the drawing direction but also indicated the occurrence of dislocation rearrangement more prominently during aging at 300 °C. Furthermore, the TEM grain-orientation maps revealed for the first time the formation of a fine microstructure with high-angle grain boundaries wherein recovery progressed and subgrain formation apparently proceeded. This microstructural change is expected to soften the material. A slight hardening actually occurred, however, during aging at 300 °C. This is presumably caused by the further strengthening resulting from the segregation of carbon or the precipitation of very fine carbides, as shown in figures. 7(c) and (d). When the aging temperature becomes 400 °C or higher, the recrystallization starts, accompanied by the decrease in strength.

Fig. 10 shows the results of the dislocation-density measurements performed using X-ray diffraction to indirectly evaluate the aging-induced recovery behavior. The dislocation density hardly changed with aging at 100 °C for 10 min, suggesting the occurrence of only the decoration of dislocations with carbon. Meanwhile, aging at 300 °C for 10 min slightly decreased the dislocation density. The results obtained via X-ray diffraction are considered to be in good agreement with the TEM grain-orientation maps.

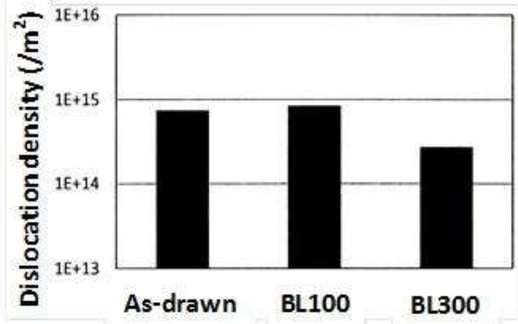

Figure 10. Dislocation density of the following specimens: as-drawn and subsequently aged at 100 °C (BL100) and 300 °C (BL300).

4.3. Proposed mechanism for the change in the microstructure and mechanical properties with aging treatment

Fig. 11 schematically illustrates proposed the mechanism for the change in microstructure and the improvement in mechanical properties upon aging the as-drawn specimen at 100 °C and 300° C .

Pearlitic steel in the as-drawn stage consists of an elongated lamellar structure consisting of ferrite and cementite. Since cementite is considered to be partly dissolved as solute carbon during the drawing process, solute carbon is expected to exist in dislocated lamellar ferrite. When drawn pearlitic steel is aged at 100 °C for 10 min, the solute carbon segregates to the dislocations (Fig. 11 (a)). Therefore, the yield stress is considered to increase as a result of the Cottrell atmosphere. Moreover, hydrogen-embrittlement susceptibility is expected to decrease, because the amount of harmful hydrogen segregated to the dislocations decreases owing to the preferential segregation of carbon to the dislocations. Moreover, the mobility of dislocation, which was initially promoted by the HELP theory owing to the segregated hydrogen, is inferred to be significantly reduced by the presence of segregated carbon in the dislocations.

When drawn pearlitic steel is aged at 300 °C for 10 min, carbon further segregates to the dislocations and very fine carbide precipitation may occur (Fig. 11(b)). On the other hand, aging at 300 °C induces local recovery or subgrain formation (see the regions enclosed with white broken circles in Fig. 6(c) and the circles in the lower part of Fig. 11(b)). Despite the softening effect induced by recovery, the yield strength increased. This significant increase in the yield strength with aging at 300 °C is expected to be caused by the very strong pinning force exerted by fine carbides. As for

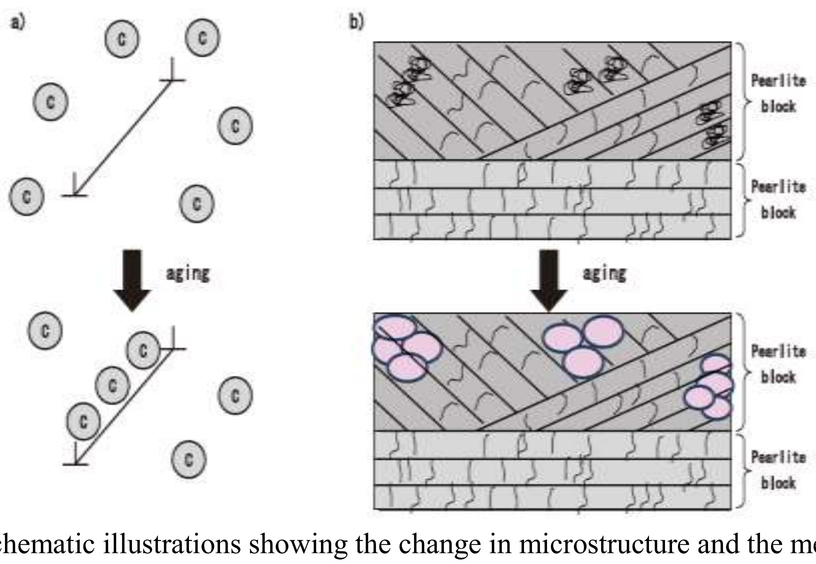

Figure 11. Schematic illustrations showing the change in microstructure and the mechanism of the improvement in mechanical properties upon aging the as-drawn specimen at a) 100 °C and b) 300° C.

hydrogen-embrittlement susceptibility, it should be essentially high after wire drawing, as pointed out by Doshida and Takai [4], owing to the presence of hydrogen segregation at dislocations, and due to the deterioration of toughness associated with the work-hardened structure, particularly in high-strained regions where dislocations are tangled in a complex manner (see Fig. 6 and the upper part of Fig. 11(b)). However, aging at 300 °C improved hydrogen-embrittlement resistance. This presumably occurred because dislocations are strongly pinned by the very fine carbides and the toughness is improved by the recovery.

5. CONCLUSIONS

The changes in the microstructure and mechanical properties, such as strength, stress relaxation, and hydrogen-embrittlement susceptibility, resulting from low temperature aging (at either 100 °C or 300 °C) were investigated for a drawn 0.8 mass% C pearlitic steel. The microstructure was evaluated using the newly developed nanobeam precession electron diffraction technique in the transmission electron microscope to obtain grain-orientation maps. The following findings were obtained:

(1) The yield strength of the specimen increased upon aging, and the increase was more prominent after aging at 300 °C compared to 100 °C.

(2) The stress-relaxation ratio increases with the aging temperature in a manner similar to that observed for yield strength, which implies that the dislocations were stabilized by aging of the drawn wire.

(3) Aging treatment, especially at 300 °C, decreased the hydrogen-embrittlement susceptibility.

(4) The height of the lower temperature peak seen in TDA measurements (associated with hydrogen trapped in dislocation stress fields) decreased with aging. The peak height of this peak and that of the higher temperature peak (associated with hydrogen trapped at dislocation cores) further decreased with aging at 300 °C.

(5) The aging treatment at 300 °C decreased the dislocation density and accelerated localized recovery, leading to the rearrangement of dislocations.

(6) Solute carbon released by dissolution of cementite during wire drawing was assumed to segregate to dislocations and to precipitate as very fine carbides during aging. The microstructural changes in terms of the state of carbon, hydrogen, and the dislocation substructure are concluded to be responsible for improving the balance of strength and hydrogen-embrittlement resistance during low-temperature aging.

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