1. Introduction

Since sheet steels are usually press formed to structural parts, both of optimum strength and excellent ductility are required. Quench hardenability and corrosion resistance are also required in some cases. To satisfy the tensile properties and the other performance, carbon and the other alloying elements are added in sheet steels. Although chromium is one typical element to invest steels quench hardenability and corrosion resistance, the effect of chromium on tensile properties of steels has not been made clear completely. For example, it has been reported that steels was softened\(^1\),\(^2\) by chromium addition while stainless steels containing chromium more than 10% has certainly higher strength\(^3\) by solid-solution strengthening of chromium compared with the mild steel.

In this study, the effect of chromium content on tensile properties of cold-rolled and annealed extra low carbon steel sheets was investigated systematically for wide range of chromium of 0% Cr to 23% namely from mild steel to stainless steels.

2. Experimental Procedure

Table 1 shows the chemical compositions of steels used. These steels were laboratory-melt and cast into 50 kg ingots. The content of elements except chromium was reduced as low as possible. 0% Cr steel contained no chromium and was a base extra low carbon steel; 5% Cr to 23% Cr steels contain 5%, 10%, 16%, 20%, 23% chromium, respectively. The steel ingots were reheated at 1200°C and forged to 30 mm thickness bars followed by air-cooling. These bars were used as the slabs for laboratory hot-rolling.

The slabs were soaked at 1200°C for 900 s and hot-rolled with 6 passes. Thickness of the rolled sheet was about 4.5 mm. Air-cooling to room temperature was done after hot-rolling. Finishing temperatures measured by radiation thermometry were 990°C, 860°C and 890°C for 0%, 5% Cr, 10% Cr steels, respectively; those of other steels were 820°C. For 0% Cr steel, hot-rolling in which the temperatures of the fifth and sixth passes were below 900°C, was also carried out to investigate the influence of finishing temperature on tensile properties. The finishing temperature measured was about 780°C. To remove the scale defects, both surfaces of the sheets were grinded to 2.7 mm in thickness. Then the grinded sheets were cold-rolled to 0.7 mm thickness.
with 74% reduction.

Difference of chromium content provides the different ferrite grain diameter in the annealed steels. At first, change in ferrite grain diameter with the annealing temperature was examined to obtain wide range distribution of ferrite grain size. Cold-rolled sheets with 17 mm in the length along rolling direction and 30 mm in the width were prepared and heated at the temperatures from 640 to 880°C in a Al$_2$O$_3$ fluidized bath for 180 s.

Nital was used to etch the microstructure for both 0% Cr and 5% Cr steels; the aqua regia was used for other high chromium steels. The measurement of ferrite grain diameter was performed according to Japan Industrial Standard JIS G0552. Seven lines of 600 μm in the length were located both vertically and horizontally at the intervals of 100 μm on the micrographs of the cross section parallel to rolling direction in the thickness; the intersections with the grain boundary were counted. ASTM nominal grain diameters were calculated by multiplying 1.128 to the segment lengths those were obtained by dividing the total length of the lines by the number of intersections.

Cold-rolled sheets were annealed in the Al$_2$O$_3$ fluidized bath for 180 s and air-cooled. No skin pass rolling was carried out to measure yield point elongations. Tensile specimens JIS NO. 13B (GW: 12.5 mm, GL: 50 mm) with longitudinal direction parallel to the rolling direction were machined from the annealed steels. Capacity of tensile test machine was 25 tonf and cross head speed was 10 mm/min through the testing. Upper yield strength was adopted as yield strength.

Moreover, some annealed sheets were reheated at 150°C for 86.4 ks (24 h) followed by furnace-cooling to make the completely aged specimens by carbon diffusion. Some high chromium steels were reheated at 480°C for 250 h to confirm the influence of $\alpha'$ precipitation. Tensile specimens JIS No. 13B were also machined from these aged sheets and tensile test was performed.

The amounts of cementite in the steels were determined by the chemical extraction method. Precipitates extracted electrolytically using 10% acetyle aceton–tetramethyl ammonium chloride–methanol (10% AA) were filtrated with a mesh of 0.2 μm. The extracted residue was resolved in acid and the amount of iron in the residue was measured by inductively coupled plasma spectrometry.

Thin foil specimens were prepared from both the annealed and 150°C aged sheets of 0% and 23% Cr steels to observe carbides by using the transmission electron microscope. The foils cut from the center area in the thickness were made by wet-polishing to 0.1 mm followed by twin-jet polishing.

3. Experimental Results

3.1. Change in Ferrite Grain Diameter with Annealing Temperature

The relationship between ferrite grain diameter in completely recrystallized sample and annealing temperature is demonstrated in Fig. 1. Ferrite grains in 0% Cr steel coarsened significantly at temperatures over 800°C as shown in Fig. 1(b). Ferrite grains in both 5% Cr and 10% Cr steels also coarsened under 840°C while the ferrite grains became finer over 840°C. For 16% Cr, 20% Cr and 23% Cr steels, ferrite grains coarsened remarkably over 800°C and significant difference in coarsening behavior was not observed.

In order to clarify the reason of grain refining in 5% Cr and 10% Cr steels at higher temperatures, microstructures were observed in detail. Figure 2 shows the optical micrograph and scanning electron micrograph of 5% Cr steel annealed at 860°C. In Fig. 2(a), fine massive black contrasts were observed at ferrite grain boundaries as indicated by arrows in the micrograph. The massive grains will be martensite since the chromium content of 5% makes $A_1$ temperature down to around 850°C and promotes quench hardenability enough to form martensite under the air-cooling condition. On the other hand, the microstructures of the steels containing chromium more than 10% were ferrite at the higher temperatures since austenite transformation did not occur. These results confirm that the observation of finer grains in 5% Cr and 10% Cr steels is attributed to
martensite appearing by $\alpha \rightarrow \gamma$ transformation during the annealing. As described above, the upper limit of annealing temperature of 5% Cr and 10% Cr steels is 840°C to obtain ferrite microstructure without martensite.

Consequently, annealing temperatures in Table 2 were employed for tensile test samples.

3.2. Relationship between Annealing Temperature and Mechanical Properties

Figure 3 shows the optical micrographs of annealed sheets: (a), (b), (c), (d), (e) and (f) show 0% Cr steel annealed at 780°C, 5% Cr steel annealed at 820°C, 10% Cr steel annealed at 820°C, 16% Cr steel annealed at 820°C, 20% Cr steel annealed at 800°C and 23% Cr steel annealed at 820°C, respectively. Microstructures of all sheets were homogeneous polygonal ferrite. Microstructures of steels annealed at other temperatures were also homogeneous polygonal ferrite.

Figure 4 shows the relationship between tensile properties and annealing temperature. Upper yield strength (YP; MPa) decreased with the increase in annealing temperature as shown in Fig. 4(c). The slope of YP was higher in the 0–10% Cr steels compared with 16–23% Cr steels. It must be noted that the YP of 5% Cr steel was lower than that of 0% Cr steel while the higher YP was exhibited in the other Cr-bearing steels. Pickering showed softening by chromium addition in low carbon steel with about 30 MPa in yield strength per 1 mass% chromium although Leslie showed hardening by up-to-6% chromium in extra low carbon steel. In this study, softening by chromium addition even in 5% Cr steel was observed while the decrease in yield strength per 1 mass% chromium was much smaller than the case of Pickering.

Tensile strength (TS; MPa) slowly decreased with the increase in annealing temperature as shown in Fig. 4(b) and the slope became gradual with the increase in chromium content. The higher chromium steel contained, the higher tensile strength was obtained. Binder and Spendelow have showed that tensile strength increased monotonously with chromium content; the tensile strength of 0% Cr steel was over 300 MPa and that of 20% Cr steel was over 500 MPa. While the same tendency is confirmed in the results of this study, the amount of the increase in tensile strength was lower than that of Binder’s results. This may be attributed to the purity of steel investigated.

Elongation (EL; %) did not change significantly against annealing temperature as shown in Fig. 4(a). Elongation of steel having higher tensile strength was lower; in low chromium steel, elongation decreased significantly against the increase in chromium content.

Figure 5 shows the yield point elongation (YPel; %) of the annealed sheet. The yield point elongation decreased with the increase in the annealing temperature. The slope of 0% Cr steel was the steepest; the slope became small with the increase in chromium content. This is attributed to the decrease in the amount of solute carbon with chromium carbide precipitation since appearance of YPel requires

Table 2. Annealing temperatures for tensile test specimens.

| Annealing temperature | 0% Cr | 5% Cr | 10% Cr | 16% Cr | 20% Cr | 23% Cr |
|-----------------------|-------|-------|--------|--------|--------|--------|
|                        | 700°C | 740°C | 780°C | 820°C | 780°C | 820°C |
|                        | 700°C | 740°C | 780°C | 820°C | 780°C | 820°C |
|                        | 700°C | 740°C | 780°C | 820°C | 780°C | 820°C |
|                        | 700°C | 740°C | 780°C | 820°C | 780°C | 820°C |
|                        | 700°C | 740°C | 780°C | 820°C | 780°C | 820°C |
|                        | 700°C | 740°C | 780°C | 820°C | 780°C | 820°C |

Fig. 3. Optical micrographs showing typical ferrite grain structure of annealed sheets; (a) 0% Cr steel annealed at 780°C, (b) 5% Cr steel annealed at 820°C, (c) 10% Cr steel annealed at 820°C, (d) 16% Cr steel annealed at 820°C, (e) 20% Cr steel annealed at 800°C and (f) 23% Cr steel annealed at 800°C.

Fig. 4. Change in mechanical properties with annealing temperature; (a) elongation, (b) tensile strength and (c) yield strength.
Figure 6 shows the relationship between ferrite grain diameter and yield strength. The yield strength increased linearly against the reciprocal of square-root of ferrite grain diameter \((d; m)\) obeying Hall–Petch relationship as the following equation;

\[
YP = \sigma_0 + kd^{-1/2} \quad (\sigma_0: \text{MPa}, k: \text{MPa} \cdot \text{m}^{1/2})
\]

where \(k\) is Hall–Petch coefficient and \(\sigma_0\) is friction stress. Hall–Petch coefficient of 0% Cr steel was about 0.6 MPa \cdot m^{1/2}. This value was as large as that of Morrison’s data\(^{10}\) and the slope became small with the increase in chromium content. Especially, it was identified that yield strength of 23% Cr steel did not change remarkably for ferrite grain diameter since \(k\) of 23% Cr steel was very small. Comparing under the same grain diameter, the yield strength of 5% Cr steel was the lowest and that of 23% Cr steel was the highest. The lowest yield strength was caused by the lowest \(\sigma_0\) in this study. Both the increase and decrease in yield strength with chromium addition have been reported as described in introduction.\(^{1,2}\) This can be caused by the difference in grain size and friction term depending on reports.

### 4. Discussion

#### 4.1. Hall–Petch Coefficient of Extra Low Carbon Steel

Wilson\(^{11}\) has showed that Hall–Petch coefficient of extra low carbon steel water-quenched from annealing temperature changed with long-time aging at 90°C. Wilson also discussed that the increase in the Hall–Petch coefficient was attributed to grain boundary segregation of supersaturated solute carbon and nitrogen generated by water-quenching. Takeda and coworkers\(^{12}\) have performed the tensile test of some steels water-quenched from annealing temperature. They reported that Hall–Petch coefficient increased by carbon at grain boundaries and that the coefficient saturated over 60 ppm carbon. Here, it should be noted that the amount of carbon segregated at grain boundaries in their study is less than that in equilibrium. Therefore, the saturated value of \(k\) 0.6 (MPa \cdot m^{1/2}) can be obtained by carbon segregation at grain boundaries even if total carbon content is less than 60 ppm. The amount of carbon segregated at grain boundaries in extra low carbon steel has been reported to be about 6 ppm\(^{11,13}\) at room temperature and the value is smaller than the carbon contents of the steels in this study. Consequently, the reason why \(k\) of 0% Cr steel was 0.6 is the carbon segregation at grain boundaries during air-cooling after annealing. Here, to clarify the discussion above, 0% Cr steel water-quenched from annealing temperature was made.

Figure 7 shows the relationship between yield strength and ferrite grain diameter in 0% Cr steel with the cooling conditions. The slope of water-quenched steel was smaller than that of the air-cooled steel. In Fig. 8, the coefficient \(k\) obtained from Fig. 7 is plotted on Takeda’s result.\(^{12}\) To
compare with Takeda’s result, the amount of solute carbon was determined by the subtracting the amount of carbon composing cementite from the total content. The solute carbon was assumed to be 13 ppm since no cementite was detected in both the 0% Cr steels. The coefficient of the water-quenched steel had a good agreement with Takeda’s result. Therefore, it is concluded that the reason why \( k \) of 0.6 was obtained for 0% Cr steel is carbon segregation at grain boundaries occurring during air-cooling from annealing temperature.

4.2. Influence of Finishing Temperature in Hot-rolling Process on Yield Strength

While austenite region finish rolling in hot-rolling process is conducted to 0% and 5% Cr steels, because of absence of austenite transformation, ferrite region rolling occurs in 16%, 20% and 23% Cr steels. Then, the influence of ferrite region rolling on the relationship between yield strength and ferrite grain diameter was investigated.

Ferrite region rolling was carried out for 0% Cr steel by lowering the fifth and sixth rolling temperatures below 900°C. The cold-rolling and annealing conditions were set to the same as the austenite region rolled steel. Figure 9 shows the optical micrographs of both the ferrite region rolled and austenite region rolled sheets. The microstructures of both sheets were polygonal ferrite. Figure 10 shows the relationship between yield strength and ferrite grain diameter. No influence of hot-rolling condition was exhibited.

Therefore, the difference between austenite region rolling and ferrite region rolling in hot-rolling process does not have something to do with the change in the Hall–Petch coefficient by chromium content.

4.3. Yield Strength of High Chromium Steel and \( \alpha' \) Phase Precipitation

The \( \alpha' \) phase easily precipitates in the steel containing chromium more than 20% by the spinordal decomposition. Then the influence of \( \alpha' \) phase precipitation in the high chromium steels on the Hall–Petch coefficient was investigated to clarify whether precipitation-strengthening of \( \alpha' \) weaken the influence of grain diameter on strength or not. Figure 11 shows the optical micrograph of 20% Cr steel aged at 480°C for 250 h to precipitate \( \alpha' \) phase. Only polygonal ferrite grains were observed. Figure 12 shows the relationship between yield strength before and after aging and ferrite grain diameter. As shown in Fig. 12(c), yield strength of 16% Cr steel aged became about 100 MPa higher than that before aging under the same ferrite grain diameter but the slope did not vary significantly. In the cases of 20% Cr and 23% Cr steels, as shown in Figs. 12(a) and 12(b), respectively, the coefficients of the aged steels were as large as those before aging like 16% Cr steel while...
the amount of an increase in yield strength by aging became larger with the increase in chromium content. Therefore, it is concluded that the $\alpha'$ phase does not affect the Hall–Petch coefficient of high chromium steels.

4.4. Increase in Yield Strength by Quench Aging of Carbon

Change in the relationship between yield strength and ferrite grain diameter with aging at 150°C for 86.4 ks (24 h) was investigated since yield strength increases by quench aging of carbon in solution. Figure 13 shows yield strength of 0%, 5% and 10% Cr steels by the aging. The slopes did not vary significantly compared with those before aging. This is attributed to the saturation of the coefficient by the carbon segregation at grain boundaries as described in Sec. 4.1.

Maruyama and Takahashi\(^\text{(15)}\) have calculated the amount of carbon segregating to dislocations in 2% strained extra low carbon steel to be 2 ppm by 3D-AP. They indicated that hardening occurred by cementite precipitation on dislocations in steel containing solute carbon more than 5 ppm. Since the steels in this study contain about 13 ppm carbon that is enough to segregate on dislocation, the increase in friction term by 150°C aging is attributed to cementite precipitation on dislocation. Figure 14 shows the yield strength of 16% Cr, 20% Cr and 23% Cr steels before and after aging at 150°C. Significant change in the slope was not observed in these steels.

Figure 15 shows the transmission electron micrographs of carbides in 0% Cr and 23% Cr steels. Sparsely distributed cementites of some nanometer in diameter were observed in 0% Cr steel before 150°C aging. Although cementite was not detected by the chemical extraction method, cementite was observed by the transmission electron microscopy. This should be caused by the reason that the cementite in 0% Cr steel was not collected by filtration since the amount of the cementite was small and the size of the cementite was much smaller than the diameter of hall on the mesh. In aged 0% Cr steel, cementites were also observed more easily. On the other hand, large chromium carbides were observed in 23% Cr steel before aging as shown in Fig. 15(c). The large chromium carbides are generated and grow through hot-rolling and annealing process since austenite does not appear in 23% Cr steel. After aging.
large chromium carbides were also observed as shown in Fig. 15(d). In 0% Cr steel, friction term increased with cementite precipitation by 150°C aging. In high chromium steels, friction term slightly decreased. This can be attributed to coarsened chromium carbides by the aging.

4.5. Change of Hall–Petch Relationship with Chromium Content

Figure 16 shows the correlation of the coefficient $k$ with the chromium content. The coefficient decreased linearly and the slope per 1 mass% chromium was 0.02 MPa·m$^{1/2}$. Sawatani et al. \cite{16} have studied the relationship between ferrite grain diameter and yield strength of 0.005%C–16.5%Cr steel containing titanium to scavenge carbon and nitrogen. They have reported lower value of $k$ (0.19 MPa·m$^{1/2}$) than the present study. This is attributed to the scavenging effect of carbon and nitrogen by titanium.

According to the pile up model,\cite{27} which assumes that dislocation pilli up to grain boundary until yield stress, the coefficient $k$ is described as the following equation\cite{18}:

$$k = \frac{G b \tau^*}{\alpha}$$

where $G$ is the shear modulus (MPa), $b$ is Burgers vector (m), $\tau^*$ is the activation stress of dislocation source (MPa) and $\alpha$ is a constant. The equation indicates that lowering of $G$ or $b$ or $\tau^*$ causes decrease in $k$. Shear modulus measured by the oscillation method was about 87 GPa independently on chromium content. Moreover, Leslie\cite{8} has reported that Burgers vector increased with chromium content. These results suggest that the decrease in $k$ with the increase in chromium content is caused by lowering $\tau^*$.

In this study, chromium and interstitial element can be mentioned as factors to influence $\tau^*$. However, interstitial element has a large effect to $\tau^*$ because the atomic radius of chromium is as large as that of iron.\cite{19} Then decrease in $\tau^*$ can be caused by the decrease in the amount of carbon segregated at grain boundaries. Grain boundary misfit segment\cite{20} is considered to be the dislocation source but further analysis technique and progress are necessary to analysis of carbon segregation to grain boundary ledge.

Figure 17 shows the relationship between friction terms $\sigma_0$ of steel annealed or aged at 150°C and chromium content. The minimum of $\sigma_0$ was exhibited at 5% Cr and $\sigma_0$ increased for chromium content more than 5%. This increase in $\sigma_0$ is attributed to solid-solution strengthening of chromium. In aged steels, $\sigma_0$ of the low chromium steels increased and $\sigma_0$ became to show linear relationship against chromium content. Morrison\cite{10} has reported that $\sigma_0$ in Hall–Petch equation for 50 ppm–0.2% carbon steels recrystallized at 550°C was about 100 MPa. Since the air-cooling after annealing did not progress aging insufficiently in this study, $\sigma_0$ is lower than that was obtained by Morrison and approach Morison’s value by 150°C aging. When the increase in $\sigma_0$ of the aged steels regarded to be solid-solution strengthening, the amount of solid-solution strengthening per 1 mass% chromium become about 5.6 MPa. Sawatani et al.\cite{16} have reported that friction term of 0.005%C–16.5%Cr steel containing titanium is 225 MPa. The value of the friction term in the present study shows the good agreement of Sawatani’s data. Lewis and Pickering\cite{21} have reported that the amount of solid-solution strengthening of chromium is 8.5 MPa per 1 mass% chromium by using 0.02%C–17%Cr and 0.02%C–24%Cr steel sheets. The calculation result of solid-solution strengthening of chromium using the data of 15% Cr and 23% Cr steels before 150°C aging in this study was 8.9 MPa per 1 mass% chromium. The calculation result shows the good agreement of Lewis and Pickering’s data. Considering the change in the friction term by aging, the amount of solid-solution strengthening of chromium can be exactly estimated by using data of aged steels in this study.

When the yield strength of Cr-bearing steel is discussed, even if it is extra low carbon steel, thermal history of the steel must be paid attention since the yield strength varies significantly by aging.

5. Conclusion

The mechanical properties of Cr-bearing extra low carbon steel (12–16 ppmC) was investigated. Conclusions obtained are as follows;

(1) Upper yield strength decreases with the increase in annealing temperature. The slope against the annealing temperature is the largest in 0% Cr steel and the smallest in 23% Cr steel.

(2) Tensile strength decreases slowly with the increase in annealing temperature. The higher chromium steel exhibits higher tensile strength. Elongation hardly changes by annealing temperature.

(3) The slope of upper yield strength against ferrite grain diameter is the largest in 0% Cr steel and the coefficient in Hall–Petch equation is about 0.6 MPa·m$^{1/2}$. The co-
efficient decreases with the increase in chromium content. The decrease is attributed to the decrease in the amount of carbon segregated at grain boundary by the scavenging effect of chromium carbide precipitation. The amount of the decrease per 1 mass% chromium is 0.02 MPa · m^{1/2}.

(4) The friction term in Hall–Petch equation shows the minimum at the chromium content of 5% while those of steels containing chromium more than 10% increase with chromium content. The friction terms of low Cr steels increase by 150°C aging and become to show straight line against chromium content by solid-solution strengthening of chromium. The amount of the increase per 1 mass% chromium is about 5.6 MPa.

REFERENCES
1) M. Gensamer: Trans. ASM, 32 (1944), 88.
2) M. Gensamer: Trans. ASM, 36 (1946), 30.
3) Y. Yazawa, Y. Kato and M. Kobayashi: Kawasaki Steel Gihō, 30 (1998), No. 2, 93.
4) ASTM designation, E112-82 (1982).
5) T. Nakazawa, Y. Sato and T. Koseki: Properties of High Purity Fe–Cr Alloy, ISIJ, Tokyo, (1995), 2.
6) E. Baerlecken, W. A. Ficscher and K. Lorenz: Stahl Eisen, 81 (1961), 768.
7) F. B. Pickering and T. Gladman; Iron Steel Inst. Special Report, (1963), No. 81, 10.
8) W. C. Leslie: Metall. Trans., 3 (1972), 5.
9) W. O. Binder and H. R. Spendelow, Jr.: Trans. ASM, 43 (1951), 759.
10) W. B. Morrison: Trans. ASM, 59 (1966), 824.
11) D. V. Wilson: J. Met. Sci., 1 (1967), 40.
12) K. Takeda, N. Nakada, T. Tsuchiyama and S. Takaki: ISIJ Int., 48 (2008), 1122.
13) Y. Yamazaki, S. Okada, S. Sato and T. Kato: Physical Metallurgy of IF Steel, ISIJ, Tokyo, (1993), 217.
14) P. J. Grobner; Metall. Trans., 4 (1973), 251.
15) N. Maruyama and M. Takahashi: Tetsu-to-Hagané, 93 (2007), No. 7, 506.
16) T. Sawatani, K. Shimizu, T. Nakayama and T. Hirai: Tetsu-to-Hagané, 63 (1977), 832.
17) J. C. M. Li and Y. T. Chou: Metall. Trans., 1 (1970), 1145.
18) E. O. Hall: Proc. Phys. Soc. (London), B64 (1951), 747.
19) A. M. Adair, R. E. Hook and R. L. McGaughey: Trans. AIME, (1966), 174.
20) H. Gleiter: Prog. Mater. Sci., 16 (1972), 1.
21) D. B. Lewis and F. B. Pickering: Met. Technol., 10 (1983), 264.