New Type of IF-High Strength Steel with Superior Anti-secondary Work Embrittlement

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(Received on May 18, 2001; accepted in final form on July 3, 2001)

High strength cold-rolled steel sheets (HSS) with sufficient formability have been developed for the IF steel-bases in the last decade, in which the major strengthening method was solid-solution hardening with silicon, manganese and phosphorous. When the IF steel is strengthened with the high amount of solid-solution elements, it becomes susceptible to the secondary work embrittlement because of the lack of grain boundary strength, which is the essential drawback of interstitial free steel. Although the grain refinement is an effective method to improve the toughness of steel, this method has not been taken into consideration in view of press-formability because it leads the steel to higher yield ratio, lower n-value and lower r-value.

A new type of IF-HSS was strengthened by hybridizing the grain refinement and the supplemental solid-solution hardening. The grain refinement was achieved by means of the fine distribution of carbide under the appropriate combination of the relatively higher carbon content near 60 ppm with a suitable carbide-forming element. While this steel has the fine grain structure, yield strength hardly increases due to the formation of unique microstructure containing PFZ, and the γ fiber texture sufficiently develops. As a result, a new type of grain-refined IF-HSS has been successfully developed to reach a higher r-value and a superior secondary work embrittlement as compared with the conventional IF-HSS.

KEY WORDS: IF steel; high strength steel; grain refinement; precipitation; texture; secondary work embrittlement.

1. Introduction

In the last decades, high strength cold-rolled steel sheets (HSS) with excellent formability have been developed as the interstitial free (IF) steel-bases mainly strengthened by solid-solution elements such as silicon, manganese and phosphorous. When IF steel is strengthened by the high amount of solid-solution elements, it becomes susceptible to the secondary work embrittlement because of the lack of grain boundary strength, which is the intrinsic drawback of interstitial free steel. Although the grain refinement is an effective method to improve the toughness of steel, this method has not been taken into consideration in view of press-formability because it leads the steel to higher yield ratio, lower n-value and lower r-value.

A new type of IF-HSS was strengthened by hybridizing the grain refinement and the supplemental solid-solution hardening. The grain refinement was achieved by means of the fine distribution of carbide under the appropriate combination of the relatively higher carbon content near 0.060 mass% with niobium. Effects of the balance between carbon and niobium contents on the grain refinement, the mechanical properties and secondary work embrittlement are investigated in view of the texture formation and the precipitation behavior.

2. Experimental Procedures

Chemical compositions of steels investigated are shown in Table 1. Steel A is the conventional niobium bearing IF steel with niobium higher than stoichiometry for ultra low carbon content, where manganese and phosphorous are added for solid-solution hardening. In Steel B, carbon and niobium contents are much higher than those in Steel A for the purpose of the grain refinement and precipitation hardening.

These steels were melted and cast into 50 kg ingots. They were hot-rolled to 30 mm thick slabs. A sequence of the experimental procedures is schematically shown in Fig. 2. After soaking at 1 473 K for 3.6 ks, they were hot-rolled to 2.8 mm thick at the finishing temperature of 1 173 K followed by soaking at 913 K for 3.6 ks and furnace cooling as a simulation of the hot-coiling. Hot-bands were pickled and cold-rolled to 0.56 mm thick with the rolling reduction of 80%. Subsequently, they were annealed at 873 to 1 143 K.
for 50 s in a salt bath. The annealed sheets at 1 103, 1 123 and 1 143 K were skin-pass rolled with the elongation of 0.7%.

Recrystallization behavior during hot deformation was evaluated by measuring softening ratio with the stress strain curve obtained in consecutive twice compression test at 1 173 K with the intervals of 0.1 to 500 s using cylindrical specimens (8 mm in a diameter, and 12 mm in a height) as schematically shown in Fig. 3.

Recrystallization behavior during annealing was investigated by measuring Vickers hardness at the center of thickness in the cross-sections of both cold-rolled samples and annealed samples at 873 to 1143 K.

Tensile tests were carried out in transverse direction using JIS No. 5 specimens (25 mm in the gauge width and 50 mm in the gauge length) of sheets annealed at 1 103, 1 123 and 1 143 K. Lankford values (r-values) were measured in three directions, 0°, 45° and 90° to rolling direction using the above specimens with 15% tensile strain and mean r-values were calculated by the following Eq. (1).

\[ \text{Mean-}r = \left( \frac{r_0 + 2r_{45} + r_{90}}{4} \right) \]  

(1)

Texture changes during recrystallization were assessed by the normalized relative values of X-ray integrated intensities for \{111\}, \{100\} and \{211\} planes. Hence, all of the textures were measured in the middle of the thickness. The \( \phi_x = 45^\circ \) sections of orientation distribution functions, ODFs were evaluated in hot-bands, cold-rolled samples and annealed samples at 1 123 K, which were calculated by the series expansion method (lmax. = 22) from the complete pole figures of \{111\}, \{100\} and \{211\} planes.

Microstructures were observed using the optical microscope and the ferrite grain sizes were measured by the point-counting method. Distributions of fine precipitates in the annealed samples were observed using transmission electron microscope, TEM with both replica and thin foil.

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### Table 1. Chemical compositions of steels. (mass%)

| Steel | C | Si | Mn | P | N | Nb | Nb/C |
|-------|---|----|----|---|---|----|------|
| A     | 0.0020 | 0.02 | 0.66 | 0.043 | 0.0029 | 0.022 | 1.42 |
| B     | 0.0062 | 0.01 | 0.62 | 0.040 | 0.0032 | 0.068 | 1.69 |

\( \text{Nb/C: Atomic ratio of niobium and carbon contents} \)

3. Results and Discussion

3.1. Effects of Carbon and Niobium Contents on Recrystallization Behavior

Figure 4 shows the effects of carbon and niobium contents on the austenite recrystallization softening behavior during hot compressions at 1 173 K. The time when softening ratio of Steels A and B reaches to 100%, that is, austenite recrystallization completes are 30 s and 500 s, respectively and it is much longer in Steel B than in Steel A. This indicates that recrystallization of austenite in Steel B with higher amount of carbon and niobium is considerably retarded comparing with that in Steel A.
Figure 5 shows the optical micrographs in cross-sections of the hot-bands of Steels A and B. The mean ferrite grain size of Steel B, about \(11 \mu m\) is smaller than that of Steel A, about \(14 \mu m\). It is inferred that the fine ferrite structure of hot band of Steel B is caused by the \(\gamma \to \alpha\) transformation from both the deformed austenite and the fine recrystallized austenite grains accompanied with the retardation of austenite recrystallization during hot rolling.

Figure 6 shows the effects of carbon and niobium contents on the ferrite recrystallization behavior during annealing. Recrystallization of Steel B starts at higher temperature than that of Steel A. Recrystallization finishing temperatures, \(T_R\) of Steels A and B are 953 K and 1013 K, respectively and it is 60 K higher in Steel B. Optical micrographs of annealed samples at 1123 K in both steels are shown in Fig. 7. The ferrite grain is refined from about \(13 \mu m\) (Steel A) down to about \(9 \mu m\) (Steel B), which become 30% smaller by increasing in carbon and niobium contents. Figure 8 shows the effects of annealing temperature on the mean ferrite grain sizes of both steels. Although the grain size of Steel A tends to increase through grain growth with elevation of annealing temperature, the grain growth in Steel B is suppressed compared with Steel A.

3.2. Effects of Carbon and Niobium Contents on Mechanical Properties

Figure 9 shows mechanical properties of the annealed samples at 1103, 1123 and 1143 K. Increment of tensile strength in Steel B against Steel A, \(\Delta TS\) is approximately 30 MPa at each annealing temperature. The increase in tensile strength of Steel B is inferred to be caused by both the precipitation hardening and grain refinement. However, yield ratio of Steel B is 10% lower than that of Steel A. If
tensile strength of Steel B is increased by these two strengthening mechanisms, its yield ratio is also expected to be increased with increase in yield stress. Therefore, it is implied that this inconsistent behavior in Steel B arises from different yielding mechanism.

Mean $r$-value of Steel B is over 2.0 at each temperature, which is 0.2 higher than that of steel A. Figure 10 shows the correlations between mean $r$-value and grain size No. in Steels A and B overlayed with the conventional steels. Mean $r$-value increases with decrease in grain size No. in each conventional steel. In particular, titanium bearing IF steel has higher mean $r$-value under the same grain size No. In Steel A, which is a conventional niobium bearing IF steel, the correlation between mean $r$-value and grain size No. corresponds to that in titanium bearing IF steel (Ti: C+N=12). However, Steel B has higher mean $r$-value despite of smaller grain size comparing with other steels. Therefore, it is inferred that the IF steel containing higher amounts of carbon and niobium leads to the improvement of recrystallization texture for $r$-value.

3.3. Texture Changes during Hot-rolling, Cold-rolling and Recrystallization Annealing

Figure 11 shows the $\phi_2=45^\circ$ sections of ODFs in hotbands of Steels A and B, respectively. Steel A has the fairly randomized orientations, whereas Steel B has the relatively developed RD//\{110\} orientations ($\alpha$-fiber texture), of which the main component is \{112\}(110). It has been reported that the development of \{112\}(110) orientation is caused by the $\gamma$ to $\alpha$ transformation from the unrecrystallized austenite due to high amount of niobium in low carbon steel. The austenite recrystallization of Steel B is evidently retarded comparing with that of Steel A as shown in Fig. 4. Therefore, it can be considered that recrystallization of austenite is strongly suppressed in Steel B, which leads to the development of \{112\}(110) orientation through the $\gamma$ to $\alpha$ transformation. Figures 12 and 13 show the $\phi_2=45^\circ$ sections of ODFs in cold-rolled samples and annealed samples at 1 123 K of Steels A and B, respectively.

Regarding the cold-rolling texture, significant difference is not observed between both steels, where the $\alpha$-fiber texture are strongly developed and the main orientation is \{223\}(110) as shown in Fig. 12. However, the recrystallization texture in Steel B is significantly improved in view of $r$-value comparing with Steel A. Although the ND/(111) orientations ($\gamma$-fiber texture) favorable for $r$-value are fully developed in both steels and the main orientation is \{111\}(112), its intensity in Steel B is stronger than that in...
Steel A as shown in Fig. 13. The remarkable difference in texture change between both steels is that $\gamma$-fiber texture after recrystallization in Steel B is more strongly developed than that in Steel A despite of the almost same cold-rolling texture. This implies that the growth rate of $\gamma$-fiber texture during recrystallization in Steel B is faster than that in Steel A.

Figure 14 shows the changes in the integrated X-ray intensities for $\{111\}$, $\{100\}$ and $\{211\}$ orientations with the annealing temperature. As it is also evident from ODFs described in Figs. 12 and 13, the recrystallization texture of Steel B is markedly improved comparing with that of Steel A despite of no significant difference in the cold-rolling textures between both steels. That is, the ND/$(111)$ orientation increases and the ND/$(100)$ and the ND/$(211)$ orientations decrease conversely with elevation of annealing temperature. Above all, it is important to note that the growth rate of ND/$(111)$ orientation in Steel B is faster than that in Steel A.

Steel A and B, respectively.

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1406
migration rate as Steel A.

Consequently, it is conceivable that the higher amounts of niobium and carbon contents in Steel B retards the austenite recrystallization followed by the ferrite grain refinement in hot-band, which leads to the increase in favorable nucleation sites of the ND//\text{[111]} grains during annealing followed by the strong development in the $\gamma$-fiber texture.

3.4. Dispersion of Fine Precipitates

As shown in Figs. 7 and 9, Steel B containing higher amounts of carbon and niobium exhibited lower yield ratio despite of the smaller ferrite grains compared to the conventional niobium bearing IF steel, Steel A. It is clear that the balance between the yield ratio and the ferrite grain size in both steels can not be explained only with the Hall–Petch's law. Then, the precipitation behavior after annealing in both steels was investigated by TEM observation to clarify the microstructural effect on this yielding behavior.

Figure 15 shows TEM image with replica and EDS spectra of precipitates observed in the specimen annealed at 1 123 K of Steel B.

Figure 16 shows the distribution of the precipitates observed by TEM with the thin foil of Steel B annealed at 1 123 K. The arrays of precipitates are observed along the grain boundaries 1 and 2 as shown with arrows, which seem to be the traces left by the grain boundary migration. These precipitates are approximately 30 nm larger than the fine intra-granular precipitates. Figure 17 shows the micrograph of precipitates observed by TEM with thin foil of Steel A annealed at 1 123 K. Comparing with these precipitates in Steel B, niobium precipitates in Steel A are homogeneously dispersed in a grain regardless of grain boundary and the precipitates-depleted-zone is not observed.

The increase in tensile strength of Steel B against Steel A is approximately 30 MPa caused by the precipitation hardening and grain refinement as shown in Fig. 9. Therefore, it can be inferred that the regions close to grain boundaries where the precipitates are depleted, PFZ are softened compared to the intra-granular regions with distribution of fine precipitates, which eventually leads to lower yield strength in Steel B as schematically shown in Fig. 18.

3.5. Mechanism of PFZ Formation during Annealing

The niobium carbides in case of Steel B, 0.0052 mass% carbon and 0.068 mass% niobium, must be fully precipitated after the hot-coiling at 913 K according to the solubility of niobium carbide in ferrite derived by Turkdogan. This
higher amounts of fine niobium precipitates is expected to retard the ferrite recrystallization and suppress its grain growth by their pinning effect during annealing. It is inferred that the depletion region of precipitates nearby the grain boundaries is to be formed during the grain growth after recrystallization because the shape of this region is intimate to the grain boundary of recrystallized grains as previously mentioned.

The hypothesis on the formation of this precipitates-depleted-zone during annealing is schematically shown in Fig. 19. At the lower temperature over the recrystallization temperature, $T_R$, the grain boundary migration of recrystallized grains is restrained by the pinning effect of fine niobium precipitates with the diameter of around 10 nm. With elevation of annealing temperature, these fine precipitates are coarsened by the Ostward-ripening on the grain boundaries which are predominant precipitation sites due to larger diffusivity of niobium compared with the volume diffusion, so that the pinning force of grain boundary by precipitates is weakened and the grain boundary starts migration. Therefore, it is inferred that the arrays of coarse precipitates parallel to the grain boundaries as shown in Figs. 15 and 16 show the trace of the grain boundaries when these started migration. Once the grain boundary reaches to the adjacent fine precipitates distributed in a grain, the coarsening of precipitates is again accelerated on the grain boundary through boundary diffusion of niobium. Although the equilibrium solubility of niobium carbide during annealing at 1 103 to 1 143 K is considerably small, 3 to 8 ppm in carbon content, it is considered that it is possible for the precipitates to solve when a fast path for solution is provided by the grain boundary. Therefore, the solution and the coarsening of niobium precipitates take place accompanied with grain boundary migration, which consequently causes the formation of the unique precipitates-depleted-zone only in one side of grain boundary.

4. Mill Trial

According to the results obtained in the laboratory tests, mill-trial was carried out for the aim of the IF-HSS having...
The tensile strength of 340 MPa. Chemical compositions of steels produced are shown in Table 2. Steel SS is a conventional type of niobium and titanium bearing IF steel under very low carbon in which manganese and phosphorous are added for the solid-solution hardening. Steel SS & PH is a newly developed IF steel which is alloy-designed utilizing both solid-solution hardening and precipitation hardening under higher amount of 0.0066 mass% carbon and 0.093 mass% niobium.

These steels were smelted in the 250 ton LD-converter and subjected to the RH-degassing treatment followed by casting into 220 mm thick slabs. The slabs were soaked at 1523 K and hot-rolled to 2.8 mm thick at the finishing temperature of 1173 K. The hot-rolled coils were pickled and cold-rolled to 0.8 mm thick followed by annealing at 1093 K, hot-dipping with the coating weight of 45 g/m² and galvannealing in the continuous-galvanizing line. Optimum condition of skin-pass elongation was settled by preliminary experiments using cold-rolled sheets.

With respect to the performance of the products, tensile test was carried out using JIS No. 5 specimen and the critical temperature of secondary work embrittlement was evaluated by flanging test using drawn-cup with the cup-height of 35 mm and the drawing ratio of 2.1.

Optical micrographs of the galvannealed sheets are shown in Fig. 20. The mean ferrite grain size of Steel SS & PH is 8 μm and it is smaller than that of Steel SS, 10 μm. Table 3 shows the mechanical properties and anti-secondary work embrittlement of products. The critical temperature of secondary work embrittlement, Tc, was significantly improved from 263 K in Steel SS down to 193 K in Steel SS & PH without bearing special element to improve the grain boundary strength. The yield stress of Steel SS & PH is almost as same as that of Steel SS despite of the fine ferrite grain. Despite of the application of precipitation hardening, the elongation of SS & PH is slightly higher than that of Steel SS in view of the balance between tensile

![Fig. 19. Schematic illustration exhibiting the hypothesis on the mechanism of the PFZ formation in Steel B.](image)

![Fig. 20. Optical micrographs of galvannealed sheets of Steels SS & PH and SS.](image)

### Table 2. Chemical compositions of steels for mill trial. (mass%)

| Type  | C    | Si   | Mn | P   | S   | sol.Al | N   | Nb  | Ti |
|-------|------|------|----|-----|-----|--------|-----|-----|----|
| SS&PH | 0.0066 | 0.01 | 0.35 | 0.020 | 0.0006 | 0.0018 | 0.0093 | -   |
| SS    | 0.0023 | 0.01 | 0.45 | 0.056 | 0.0007 | 0.0052 | 0.0020 | 0.021 | 0.022 |

### Table 3. Mechanical properties and anti-secondary work embrittlement of galvannealed sheets.

| Type  | YS (MPa) | TS (MPa) | EI (%) | n-value | mean r-value | Tc (K) |
|-------|---------|---------|--------|---------|--------------|-------|
| SS&PH | 203     | 344     | 43.0   | 0.219   | 1.77         | 193   |
| SS    | 201     | 368     | 41.0   | 0.220   | 1.60         | 263   |

Tensile specimen: JIS No. 5, transverse direction. Tc: Critical temperature of anti-secondary work embrittlement in the flanging test of drawn-cup with the cup-height of 35 mm and the drawing ratio of cup diameter to blank diameter, 2.1.
strength and elongation. The mean $r$-value of Steel SS & PH is 1.77 which is 0.17 higher than that of Steel SS, 1.60. In Steel SS & PH, the Aging Index evaluated as the increase in stress with 8% tensile strain after aging at 373 K for 3.6 ks is 2 MPa, which indicates essentially the non-aging property. The galvannealed sheet of Steel SS & PH has markedly homogeneous surface appearance and excellent adhesion of coating layer which are suitable for the outer panel of automobiles.

5. Conclusions

New type of IF-HSS with excellent anti-secondary work embrittlement and formability has been successfully developed by combination of the solid-solution hardening with the precipitation hardening and the grain refinement. Developed steel has the following unique properties.

(1) The tensile strength of the 0.0052 mass% carbon and 0.068 mass% niobium bearing developed steel is approximately 30 MPa higher than that of 0.0020 mass% carbon conventional niobium bearing IF steel because of both the precipitation and the grain refinement hardening.

(2) Despite of higher tensile strength, the yield ratio of developed steel is lower than that of the conventional IF steel. This behavior is inferred to be caused by the formation of an unique precipitation-depleted-zone neighboring to the grain boundary accompanied with the resolution and the coarsening of niobium precipitates during annealing.

(3) The mean $r$-value of developed steel is higher than that of the conventional IF steel. It is considered to be caused by the strong development of $\gamma$-fiber texture during annealing, which is attributed to the increase in favorable sites for $\langle 111 \rangle$ grains by the grain refinement of hot-bands accompanied with the retardation of austenite recrystallization during hot-rolling.

(4) The ferrite grain of developed steel is refined to less than 10 $\mu$m, which consequently leads to the significant improvement in the anti-secondary work embrittlement in a galvannealed sheet.

(5) As the result of mill trial to confirm the performance of this developed IF-HSS having the tensile strength of 340 MPa, the anti-secondary work embrittlement and the mean $r$-value were successfully improved preserving the same tensile property as the conventional type of steel.

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