Effect of Mn Partitioning during Intercritical Annealing on Following $\gamma \rightarrow \alpha$ Transformation and Resultant Mechanical Properties of Cold-rolled Dual Phase Steels

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(Received on November 9, 2010; accepted on January 31, 2011)

Sequential transformation phenomena of $\alpha \rightarrow \gamma \rightarrow \alpha$ during intercritical annealing and subsequent cooling were investigated to achieve a more advanced control of mechanical properties in a low-carbon cold-rolled DP steel sheet with a chemical composition of 0.13mass%C-1.4mass%Si-2.0mass%Mn. The steel was intercritically annealed at 1 073 K for 0–1 000 s, then air-cooled to 873–1 073 K (quenching start temperature: $T_q$), followed by water-quenching. The tensile strength increased with an extension of the annealing time, especially at the low $T_q$, corresponding to the increase in the volume fraction of martensite. This means the $\gamma \rightarrow \alpha$ transformation during air-cooling was delayed by extending the annealing time.

Microstructural observation and elemental analysis by EPMA indicated that the volume fraction of $\gamma$ during annealing was almost saturated after annealing for 250 s, whereas the Mn content in $\gamma$ was still increasing at that time. These results suggest that the retardation of the $\gamma \rightarrow \alpha$ transformation during air-cooling by extending the annealing time results from the chemical stabilization of $\gamma$ by the enrichment of Mn during intercritical annealing. In order to obtain the less scattering of mechanical properties in cold-rolled DP steel sheets, precise microstructural control considering the partitioning of substitutional alloying elements during intercritical annealing is quite important.

KEY WORDS: $\alpha \rightarrow \gamma$ transformation; $\gamma \rightarrow \alpha$ transformation; intercritical annealing; dual phase steel.

1. Introduction

The automotive industry has a great increasing demand to improve fuel efficiency and passive safety of vehicles. In order to achieve both requirements, down-gauged high strength steel sheets are applied to reduce weight and to improve crashworthiness of car bodies. Low carbon cold-rolled dual phase steels (DP steels) consisting of both ferrite and martensite phases are one of the optimum candidates for the application to car bodies because of having an excellent mechanical properties with both high strength and good formability, and have widely been applied to car bodies.$^{1,2)}$

Recently, from a manufacturing point of view, the less scattering of mechanical properties as well as both strength and formability is regarded as an important property to achieve a high shape-accuracy of press-formed car body parts. Cold-rolled DP steel sheets are generally produced by an intercritical annealing followed by a rapid cooling in Continuous Annealing Liness (CAL). In this process, the annealing time sometimes tends to be varied by processing requirements, and the change in the annealing time is known to affect the microstructural evolution during annealing, causing the change in mechanical properties of the steel sheets. Therefore, it is important to understand the ferrite ($\alpha$) $\rightarrow$ austenite ($\gamma$) transformation kinetics during the intercritical annealing and the influences of the microstructural changes during the annealing on the $\gamma \rightarrow \alpha$ transformation kinetics during the subsequent cooling to achieve a more precise control of mechanical properties in cold-rolled DP steel sheets.

A great number of studies concerning microstructural changes of low carbon steels during intercritical annealing have been reported.$^{3–12)}$ Some studies considered that the partitioning of substitutional alloying elements, such as Mn and Si, was important in the kinetics of the $\alpha \rightarrow \gamma$ transformation.$^{5,6,8,11,12)}$ They had mainly focused on microstructural changes at the annealing conditions with a low range of intercritical temperatures (around 973 K) and long annealing times (more than 1 hour) corresponding to the batch annealing conditions.$^{5)}$ For example, Pussegoda et al.$^{3)}$ investigated the change in the volume fraction of $\gamma$ and the Mn partitioning measured by TEM-EDX during annealing at 968 K, and compared the experimental results with a theoretical one-dimensional model developed by Wycliffe et al.$^{6)}$ The experimental results showed the volume fraction of $\gamma$ saturated after 1 hour but it took approximately 50 hours to reach equilibrium volume fraction according to the calculation results, and the Mn content in $\gamma$ were increasing.
even after 180 hours both in experimental and theoretical results. On the other hand, there is scarce data on microstructural changes considering the partitioning of substitutional elements for the typical annealing conditions in CAL with a higher range of intercritical temperatures (around 1 073 K) and shorter annealing times (less than 500 s). It is uncertain whether thermodynamic equilibrium is established or not during annealing in the typical heat treatment in CAL.

A lot of investigations had also conducted concerning the diffusional decomposition during cooling after annealing. Limited studies, however, investigated the influences of microstructural changes and the partitioning of substitutionals during the intercritical annealing on the $\gamma \rightarrow \alpha$ transformation during the subsequent cooling. In particular, there are no reports on the influences of the partitioning of substitutionals during the intercritical annealing on mechanical properties after cooling in cold-rolled DP steel sheets produced by CAL.

In this study, in order to achieve a more precise microstructural control to obtain the less scattering of mechanical properties in cold-rolled DP steel sheets produced by CAL, the $\alpha \rightarrow \gamma$ transformation behavior during annealing at a relatively higher range of intercritical temperatures corresponding to the general annealing conditions in CAL was studied. Furthermore, its influences on the $\gamma \rightarrow \alpha$ transformation behavior during the subsequent cooling and mechanical properties after cooling were also investigated, especially focusing on the partitioning of substitutional elements during the intercritical annealing.

2. Experimental Procedure

The material used in this study is a cold-rolled steel sheet with a thickness of 1.4 mm. The chemical composition of the steel is listed in Table 1. The microstructure consists of cold-rolled ferrite and pearlite phases, and the reduction of cold rolling is approximately 50%. The schematic diagram of the heat treatment is shown in Fig. 1. The specimens cut from the steel were intercritically annealed at 1 073 K for 0–1 000 s using a salt bath furnace, then air-cooled to 873–1 073 K (quenching start temperature: Tq), followed by water-quenching. The average air-cooling rate from 1 073 K to 873 K was approximately 10 K/s. The quenched specimens for tensile test were tempered at 573 K for 600 s. The tensile strength of the heat-treated specimens was measured according to the JIS Z 2241. The microstructures were observed by a scanning electron microscope (SEM: ERA-8800FE operated at 15 kV). The volume fractions of martensite were estimated by an image analysis of the SEM micrographs. The distributions of concentrations for each alloying elements were mapped by an electron probe micro analyzer (EPMA: JXA-8200 operated at 10 kV with LaB6 electron gun).

3. Results and Discussion

3.1. Effect of Intercritical Annealing Time on Tensile Strength and Microstructure

Figure 2 shows the influences of the quenching start temperature (Tq) and the intercritical annealing time on the tensile strength (TS) of the specimens tempered after quenching. The TS decreases with a decrease in the Tq for every annealing time. Compared between the specimens quenched from the same Tq, the TS is higher with an increment of the annealing time, and the difference in the TS by changing the annealing time is significant.

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

| C  | Si  | Mn  | P   | S   | Al  | N   | Fe  |
|----|-----|-----|-----|-----|-----|-----|-----|
| 0.125 | 1.40 | 1.98 | 0.016 | 0.001 | 0.032 | 0.0034 | Bal. |

Fig. 2. Influences of quenching start temperature (Tq) and annealing time on tensile strength (TS).
annealing time is larger at the lower $T_q$. Figure 3 shows the influences of the $T_q$ and the annealing time on the volume fraction of martensite ($V_M$) in the same specimens shown in Fig. 2. The $V_M$ decreases with decreasing the $T_q$, and with decreasing the annealing time especially at the lower $T_q$. This change in the $V_M$ shows a good correlation with the influence of the annealing time on the TS shown in Fig. 2. Figure 4 shows the relationship between the TS and the $V_M$. The TS increases practically linearly with the increment of the $V_M$. Concentration of the alloying elements in martensite may have influences on the TS of the specimens through the hardness of martensite. However, the difference of carbon content in $\gamma$ during annealing is small between the specimens with different annealing times (100–1 000 s) because the difference of the volume fraction of $\gamma$ just before cooling in these specimens is small (52–55%), and the partitioning of carbon during air-cooling is considered to occur only at the vicinity of the interface under the cooling condition in this study (as shown later). Therefore, the influence of carbon partitioning during annealing and cooling on the hardness of martensite is considered to be small. Concerning Mn, the partitioning during annealing at 1 073 K is relatively big; Mn in $\gamma$ is 2.51 mass% in the equilibrium state according to the Thermo-Calc software. However, the effect of Mn content on the hardness of tempered martensite is known to be small in the case of the low temperature tempering\textsuperscript{22,23} such as 573 K in this study. Furthermore, the partitioning of Si during annealing at 1 073 K is small (Si in $\gamma$ is 1.35 mass% even in the equilibrium state according to the Thermo-Calc. software) and the contributions of the other minor alloying elements such as P on the strength are considered to be negligible.

Therefore, the increase in the TS with an increment of the annealing time is mainly attributed to the corresponding increment of the $V_M$.

3.2. $\alpha \rightarrow \gamma$ Transformation during Intercritical Annealing

In order to clarify the reason why the $V_M$ increases with increasing the intercritical annealing time, the change in the microstructure and the distribution of Mn and Si concentrations during annealing were investigated.

Figure 5 shows SEM micrographs of the specimens before and after annealing at 1 073 K for several times, followed by water-quenching directly. The microstructure before annealing consists of cold-rolled ferrite ($\alpha$) and pearlite phases. At the onset of annealing, just after raising a temperature to 1 073 K, the cold-rolled $\alpha$ has already recrystallized; a considerable amount of martensite, which is austenite ($\gamma$) phase before quenching, has already existed. Figure 6 shows the change in the volume fraction of $\gamma$ (mar-
tensile in the quenched specimens) during annealing. The volume fraction of $\gamma$ increases with increasing the annealing time and is almost saturated at 250 s. However, as shown in Fig. 3, the volume fractions of martensite with a $T_q$ of 873 K are different between the specimens annealed for 250 s and 1 000 s. Hence the difference in the volume fraction of martensite after cooling can not be explained only by the volume fractions of $\gamma$ during annealing. Figure 7 shows the SEM microstructure and the EPMA elemental mappings of Mn and Si concentrations of the steel before annealing (as cold-rolled). The EPMA mappings show Mn and Si are distributed almost uniformly. It is known that Mn concentrates in cementite but Si is not soluble in cementite. Therefore, it is considered that pearlite formed during the hot rolling process is not in an equilibrium state due to a rapid cooling after hot rolling.

Figure 8 shows the change in the distribution of Mn and Si concentrations of the specimens annealed at 1 073 K for 30–1 000 s, followed by water-quenching directly. Although a considerable amount of martensite ($\gamma$ at the annealing temperature) has already generated at an annealing time of 30 s in the SEM backscattered electron images, the partitioning of Mn and Si between $\alpha$ and $\gamma$ is not occurred. As the annealing time increases, it seems to reach into the equilibrium condition; the volume fraction of $\gamma$ increases, Mn concentrates into $\gamma$, and Si concentrates into $\alpha$. The change in the volume fraction of $\gamma$ (martensite in the quenched microstructure) and the Mn content in $\gamma$ during annealing at 1 073 K are shown together in Fig. 9. The volume fraction of $\gamma$ is almost saturated at 250 s as mentioned above, whereas the Mn content in $\gamma$ is still increasing at that time. Therefore, at the early stage of the $\alpha \rightarrow \gamma$ transformation during annealing.

![Fig. 7. SEM microstructure (a) and EPMA elemental mappings of Mn (b), Si (c) of the steel before annealing, F: Ferrite, P: Pearlite.](image1)

![Fig. 8. SEM backscattered electron images (a) and corresponding EPMA elemental mappings of Mn (b), Si (c) of the specimens annealed at 1 073 K for 30–1 000 s followed by water quenching directly, F: Ferrite, M: Martensite.](image2)
at 1 073 K, substitutional alloying elements such as Mn and Si are hardly partitioned; the formation of γ occurs mainly only with the partitioning of carbon, same as the previous studies with lower intercritical annealing temperatures.\(^9\) As increasing the annealing time, substitutional alloying elements are partitioned between α and γ in order to decrease the total free energy toward the equilibrium states. From these results, it is clarified that the annealed steel under the typical annealing conditions in CAL (annealing temperature: 1 073 K, annealing time: less than 500 s) before cooling is in a metastable state where substitutional alloying elements are not fully partitioned even though the formation of γ during annealing is saturated.

### 3.3. γ → α Transformation during Cooling after Inter-

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**Critical Annealing**

In this section, the mechanism of the increment of \(V_M\) caused by the increase of the annealing time (shown in Fig. 3) is discussed, especially focusing on the difference in the partitioning of substitutional alloying elements just before cooling, as described above, on the γ → α transformation during air-cooling after intercritical annealing.

**Figure 10** shows the change in the volume fraction of γ during air-cooling of the specimens intercritically annealed for 100 s and 1 000 s. The data in this figure are the same data in Fig. 3, but the x-axis is reversed in order to make it easier to understand the change in the volume fraction of γ with the cooling rate before quenching. Mn contents in γare different between these two specimens as mentioned in Fig. 9. The volume fraction of γ decreases on the course of cooling in the both specimens. However, the γ → α transformation rate in the specimens with an annealing time of 100 s is a little faster than that with the annealing time of 1 000 s, which has higher amount of Mn in γ. Hence Mn content in γ just before cooling is considered to control the γ → α transformation kinetics during subsequent cooling. In order to understand this phenomenon, the γ → α transformation and the partitioning of Mn during cooling was investigated in detail. **Figures 11 and 12** show the change in the EPMA elemental mappings of Mn concentrations and the corresponding SEM backscattered electron images of the specimens during air-cooling after annealing at 1 073 K for 100 s and 1 000 s respectively. The martensite phases, which are γ phases before quenching, decrease with decreasing quenching start temperature, being independent of the annealing time. The EPMA images, however, do not change almost by air-cooling. This suggests that the partitioning of Mn can hardly occur during air-cooling. **Figure 13** shows the detailed comparison between the SEM backscattered electron image and the EPMA elemental mapping of Mn concentration of the specimen annealed for 1 000 s, then air-cooled to 873 K, followed by water-quenching. The EPMA mapping shows Mn concentration is high in the center region of red circles, whereas a part of martensite disappeared in the same area in the SEM image. This means the γ transforms to the α during air-cooling without accompanying the diffusion of Mn. From these results, it is found that the partitioning of Mn hardly occurs during air-cooling under the conditions in this study, independent of the Mn content before cooling.

In order to understand these experimental results more deeply, simulation of γ → α transformation during cooling was carried out by DICTRA software.**25,26** **Figure 14** shows schematic diagrams of the initial conditions of the simulation; the volume fractions and the Mn contents of α and γ in the specimens annealed for 100 s and 1 000 s just before cooling are set to be the values of the experimental data. The volume fraction of γ is almost same in the both specimens, whereas the Mn content in γ is higher in the specimen annealed for 1 000 s. As discussed above, the difference in the Mn content in γ is considered to affect the γ → α transformation kinetics during air-cooling. The calculation was performed based on the assumption that thermodynamic equilibrium is established locally at the front of α - γ transformation. The diffusion data was taken from a multicomponent diffusion database, MOB1.**26** The cooling rate is set to be 10 K/s, which is about the same as the average experimental air-cooling rate before water-quenching. The calculation results are shown in **Fig. 15**. The experimental data are also plotted in the figure. The calculated γ → α transformation rate of the specimen annealed for 100 s is faster than that of the specimen annealed for 1 000 s. **Figure 16** shows profiles of carbon and Mn concentration at the vicinity of the transformation front calculated by DICTRA. The carbon is clearly partitioned into γ phase as the γ → α transformation proceeds. On the other hand, Mn is hardly partitioned during cooling. These calculation results show
similar tendency with the experimental data. Hence it is suggested that the assumptions in this calculation are qualitatively correct; the given initial conditions are roughly reasonable and thermodynamic equilibrium is established locally at the front of $\alpha$ - $\gamma$ transformation. Therefore, the retardation of the $\gamma \rightarrow \alpha$ transformation during cooling by increasing the annealing time is considered to be caused by the thermodynamic stabilization of $\gamma$ by the enrichment of Mn during the intercritical annealing. However, in this study, the distribution of alloying elements in each phase at the stage just before air-cooling was not taken into consideration. Furthermore, solute drag like effect may also affect the kinetics of the $\gamma \rightarrow \alpha$ transformation. 27) More precise experimental and theoretical analysis considering the distri-

Fig. 11. SEM backscattered electron images (a) and corresponding EPMA elemental mappings of Mn (b) of the specimens annealed at 1 073 K for 100 s followed by water quenching from each quenching start temperature (Tq), F: Ferrite, M: Martensite.

Fig. 12. SEM backscattered electron images (a) and corresponding EPMA elemental mappings of Mn (b) of the specimens annealed at 1 073 K for 1 000 s followed by water quenching from each quenching start temperature (Tq), F: Ferrite, M: Martensite.

Fig. 13. SEM backscattered electron image (a) and corresponding EPMA elemental mapping of Mn (b) of the specimens annealed at 1 073 K for 1 000 s followed by water quenching from 873 K, F: Ferrite, M: Martensite.
bution of alloying elements in each phase and $\alpha$ - $\gamma$ interface should be required for profound understanding. For example, by combining the information of the elemental distribution with the curvature of the interface and the crystallographic characterization across the interface, more advanced analysis of $\alpha \rightarrow \gamma$ and $\gamma \rightarrow \alpha$ transformation could be possible. In that case, two-dimensional observations of the elemental distribution using EPMA\textsuperscript{28} shown above would be quite useful when comparing with the two-dimensional simulation of microstructural changes such as phase field method.

In this way, it is cleared that the microstructural evolution including the partitioning of Mn during intercritical annealing affects the $\gamma \rightarrow \alpha$ transformation during subsequent cooling, and the mechanical properties of the steel after cooling. Therefore, precise microstructural control considering the partitioning of substitutional alloying elements during intercritical annealing in CAL is quite important to obtain the less scattering of mechanical properties in cold-rolled DP steels. In order to obtain the stable mechanical properties, the minimum annealing time in CAL should be regulated depending on the chemical compositions and annealing temperatures.

4. Conclusions

Sequential transformation phenomena of $\alpha \rightarrow \gamma \rightarrow \alpha$ during the intercritical annealing at 1 073 K and the subsequent cooling were investigated to achieve a more advanced control of mechanical properties in the low-carbon cold-rolled DP steel sheet, and the influence of the intercritical annealing time on the tensile strength was discussed. The results obtained in this study are summarized as follows:

(1) At the early stage of the $\alpha \rightarrow \gamma$ transformation during annealing at 1 073 K, substitutional alloying elements such as Mn and Si are hardly partitioned; it is considered that the formation of $\gamma$ occurs mainly only with the partitioning of carbon.

(2) The annealed steel under the typical annealing conditions in CAL (annealing temperature: 1 073 K, annealing time: less than 500 s) just before cooling is in a metastable state where substitutional alloying elements are not fully partitioned even though the formation of $\gamma$ during annealing is saturated.

(3) Although the volume fraction of $\gamma$ is almost same just before cooling, the $\gamma \rightarrow \alpha$ transformation kinetics differs depending on the Mn content in $\gamma$.

(4) The tensile strength and the volume fraction of martensite increase with an extension of the annealing time, especially at the low quenching start temperature. This retardation of the $\gamma \rightarrow \alpha$ transformation during subsequent cooling with an extension of the annealing time could be attributed to the chemical stabilization of $\gamma$ by the enrichment of Mn during intercritical annealing.

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