Partitioning of Solute Elements and Microstructural Changes during Heat-treatment of Cold-rolled High Strength Steel with Composite Microstructure

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The partitioning of solute elements during intercritical annealing and the effects of partitioning on ferrite transformation during slow cooling after intercritical annealing in a 0.17% C–1.5% Si–1.7% Mn (mass%) steel were investigated by a new FE-EPMA (field emission electron probe microanalysis) technique. This new technique enables highly accurate measurement of the C distribution. During the intercritical annealing, C and Mn concentrated into austenite, while Si concentrated into ferrite. The distribution of Mn in austenite was inhomogeneous, and austenite with small Mn content was transformed into ferrite during slow cooling. This ferrite transformation proceeded in the NPLE (negligible partitioning local equilibrium) mode. Two kinds of ferrite were produced due to slow cooling, one being intercritically-annealed ferrite, and the other transformed ferrite. The transformed ferrite had larger Mn content than the intercritically-annealed ferrite. Furthermore, the transformed ferrite was classified into the ferrite grown epitaxially from the intercritically-annealed ferrite and that nucleated in the austenite with relatively small Mn content. Prior microstructure and distribution of solute elements before cooling are determined by the intercritical annealing conditions, and then control the ferrite transformation. Precise control of the ferrite transformation is effective for stable production of cold-rolled high strength steel with composite microstructure.

KEY WORDS: phase transformation; reverse transformation; ferrite transformation; dual phase; TRIP; intercritical annealing; partitioning; local equilibrium; paraequilibrium; phase diagram; thermodynamics.

1. Introduction

Cold-rolled high strength steels, such as dual-phase steel and low alloyed TRIP (transformation induced plasticity) steel, have been used in the automotive industry in order to improve automobile safety and to solve environmental problems associated with CO₂ emissions. Besides the demand from automobile companies for high strength and high formability of steels, it is important to reduce the scattering of mechanical properties in terms of stable production in steel companies. Cold-rolled high strength steels with composite microstructure are produced by intercritical annealing in which austenite formation by reverse transformation and partitioning of solute elements occur. In the industrial production of high strength steels, the transformation after intercritical annealing can occur from non-equilibrium state, which complicates microstructure control. Therefore, in order to achieve precise control of the microstructure and

the mechanical properties, it is essential to understand the effects of reverse transformation and partitioning of solute elements on the subsequent transformation after intercritical annealing.^{1–5)}

Speich *et al.*¹⁾ investigated the austenite formation behavior of ferrite-pearlite steel during intercritical annealing, and reported that the austenite formation consisted of three steps: (1) nucleation of austenite at the ferrite-pearlite interface and very rapid growth of austenite into pearlite; (2) further growth of austenite into ferrite after dissolution of pearlite; and (3) final equilibration of the Mn contents between austenite and ferrite controlled by Mn diffusion in austenite. On the other hand, Toji *et al.*²⁾ reported that Mn concentrated into austenite during intercritical annealing, and that the chemical stabilization of austenite by enrichment of Mn led to retardation of the ferrite transformation from austenite during air-cooling. However, in previous conventional studies, quantitative investigations on the partitioning of C and substitutional solute elements were not easy due to difficulty of experimental measurement of C contents in ferrite and austenite in a wide area.

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In the present study, a new FE-EPMA (field emission electron probe microanalysis) technique^{6,7)} was used to overcome such difficulty. This technique enables extremely accurate measurement of not only the distribution of substitutional solute elements, such as Mn and Si, but also the distribution of C. On the basis of the measurement using the FE-EPMA technique, the partitioning of solute elements during intercritical annealing and the effects of partitioning on ferrite transformation during slow cooling after intercritical annealing were quantitatively analyzed by numerical calculation techniques.

2. Experimental Procedures

The chemical composition of the steel used in the present study is shown in **Table 1**. In this table, the A_{c1} and A_{c3} temperatures calculated by Thermo-Calc[®] software are also indicated. Here, A_{c1} is the temperature at which cementite dissolves completely. The vacuum-melted steel was cast into a 50 kg ingot, followed by hot-rolling to produce a 27 mm thick slab. The slab was heated at 1 250°C (1 523 K) and then hot-rolled to a thickness of 4.0 mm with a finishing temperature of 900°C (1 173 K), followed by cooling and holding at 600°C (873 K) for 1 h (3.6 ks). The surface of the hot-rolled sheet was removed by grinding to a thickness of 3.2 mm. After cold rolling to a thickness of 1.2 mm, heat treatments were carried out with a salt bath furnace. **Figure 1** shows schematic diagrams of heat treatment for Patterns A and B. In Pattern A, the specimen was water-quenched from temperature T_q during heating or intercritical annealing at $T_a = 800$ or 740°C (1 073 or 1 013 K) for various times of $t = t_a$. Here, T_q is the quenching temperature, T_a is the

intercritical annealing temperature, and t_a is the intercritical annealing time. Reverse transformation behavior and the partitioning of C, Mn and Si during intercritical annealing were investigated with Pattern A. On the other hand, in Pattern B, the specimen was water-quenched from each temperature during gas cooling at a cooling rate of 10°C/s. The effect of the partitioning of solute elements on ferrite formation during slow cooling of 10°C/s after intercritical annealing was investigated with Pattern B. Furthermore, microstructural observation and FE-EPMA analysis were carried out for the specimens prepared by both Patterns A and B.

The microstructure was characterized by optical microscopy (OM) and scanning electron microscopy (SEM) for the specimen etched with nital (1% nitric acid + ethanol). The volume fraction f_ϕ of phase ϕ was quantified by the point counting method on the SEM image.

The distributions of C, Mn and Si in the microstructure were measured using the new FE-EPMA technique.^{6,7)} At first, the distribution of C was measured preventing surface from contamination. The accelerating voltage V_e and the probe current I_e were 7 kV and 5 nA, respectively, for the primary electron beam of the C measurement. In order to obtain a larger S/N ratio, V_e and I_e were changed to 9 kV and 10 nA, respectively, for the measurements of Mn and Si. Pure Fe and reference steels with C contents between 0.089 and 0.680 mass% were used as standard specimens to quantify the C content. The Mn and Si contents were quantified by the ZAF correction method⁸⁾ using pure Mn and Si as standard specimens.

3. Results

3.1. Reverse Transformation Behavior and Partitioning of Solute Elements

An OM image of the hot-rolled sheet with a thickness of 4.0 mm is shown in **Fig. 2**. As can be seen, the microstructure of the hot-rolled sheet consists of uniformly-dispersed ferrite and pearlite without severe segregation or layered structure. This implies that microscopic segregation of Mn and Si does not exist in the specimen. Furthermore, the mean grain diameter of the ferrite is approximately 10 μm . Austenite formation behavior during subsequent annealing is affected by such initial microstructure.^{9–12)}

Typical SEM images of the specimens for Pattern A with $T_a = 800^\circ\text{C}$ (1 073 K) and various values of T_q and t_a are shown in **Fig. 3**. Figures 3(a), 3(b) and 3(c) is for $T_q = 650$, 740 and 780°C (923, 1 013 and 1 053 K), respectively, and Figs. 3(d), 3(e) and 3(f) is for $t_a = 1$, 90 and 1 800 s, respectively. Figures 3(a) and 3(b) indicates that the microstructure consisting of a ferrite (α phase) matrix and spheroidal particles of cementite (θ phase), and that recrystallization of the α phase progresses at a certain temperature between 650 and 740°C (923 and 1 013 K). In Fig. 3(c), most of the θ particles disappear and martensite (M phase) is observed along the grain boundary of the recrystallized α phase. The M phase after water-quenching corresponds to the austenite (γ phase) during intercritical annealing. Since attention is focused on the constituent phase in the microstructure generated by intercritical annealing, the M phase is hereafter merely called the γ phase. From Figs. 3(b) and 3(c), we may

Table 1. Chemical composition of steel used in experiment and calculated A_{c1} and A_{c3} temperatures.

Chemical composition (mass%)						A_{c1}	A_{c3}
C	Si	Mn	P	S	Al		
0.17	1.5	1.7	0.010	0.001	0.03	708°C (981 K)	857°C (1 130 K)

Fig. 1. Schematic diagrams of heat treatment patterns.

consider that reverse transformation of the α phase into the γ phase starts at a certain temperature between 740 and 780°C (1 013 and 1 053 K). As can be seen in Figs. 3(d)–3(f), the

Fig. 2. Optical micrograph of hot-rolled sheet.

volume fraction of the γ phase increases with increasing annealing time at 800°C (1 073 K).

SEM images of the specimens for Pattern A with $T_a = 740^\circ\text{C}$ (1 013 K) and various values of t_a are shown in Fig. 4. Figures 4(a), 4(b), 4(c), 4(d), 4(e) and 4(f) is for $t_a = 1, 90, 300, 900, 3\,600$ and $14\,400$ s, respectively. In Fig. 4(a), the microstructure is composed of the recrystallized α matrix and spheroidal particles of the θ phase. The γ phase appears along the grain boundary of the α matrix in Fig. 4(b), and the θ particles completely disappear in Fig. 4(e). As the annealing time increases, the number of the θ particles decreases, but the volume fraction of the γ phase increases.

The corresponding result of the specimen for Pattern A with $T_a = 800^\circ\text{C}$ (1 073 K) and $t_a = 1.8$ ks is shown in Fig. 5. Figure 5(a) indicates the SEM image, and Figs. 5(b), 5(c) and 5(d) represents the elemental mappings of C, Mn and Si, respectively, measured by FE-EPMA. As can be seen,

Fig. 3. SEM images of specimens for Pattern A at $T_a = 800^\circ\text{C}$ (1 073 K) with (a) $T_q = 650^\circ\text{C}$, (b) $T_q = 740^\circ\text{C}$ and (c) $T_q = 780^\circ\text{C}$ or with (d) $t_a = 1$ s, (e) $t_a = 90$ s and (f) $t_a = 1.8$ ks.

Fig. 4. SEM images of specimens for Pattern A at $T_a = 740^\circ\text{C}$ (1 013 K) for (a) $t_a = 1$ s, (b) $t_a = 90$ s, (c) $t_a = 300$ s, (d) $t_a = 900$ s, (e) $t_a = 3.6$ ks and (f) $t_a = 14.4$ ks.

Fig. 5. (a) SEM image and corresponding EPMA elemental mappings of (b) C, (c) Mn and (d) Si of specimen for Pattern A with $T_a = 800^\circ\text{C}$ (1 073 K) and $t_a = 1.8$ ks.

Fig. 6. (a) SEM image and corresponding EPMA elemental mappings of (b) C, (c) Mn and (d) Si of specimen for Pattern A with $T_a = 740^\circ\text{C}$ (1 013 K) and $t_a = 14.4$ ks.

the region with large C and Mn contents is the γ phase, and that with a large Si content is the α phase. Thus, C and Mn concentrate into the γ phase, while Si concentrates into the α phase. Furthermore, the dispersion of the C content in the γ phase and that of the Si content in the α phase are small, but that of the Mn content in the γ phase is as large as about 1.4 mass%. In the γ phase, the Mn content tends to be larger near the grain boundary than at the center of grain. This suggests that the diffusion of C in the γ phase and that of Si in the α phase are much faster than that of Mn in the γ phase.

The corresponding result of the specimen for Pattern A with $T_a = 740^\circ\text{C}$ (1 013 K) and $t_a = 14.4$ ks is shown in **Fig. 6**. Figure 6(a) indicates the SEM image, and Figs. 6(b), 6(c) and 6(d) represents the elemental mappings of C, Mn and Si, respectively. Like the specimen in **Fig. 5**, C and Si homogeneously concentrate into the γ and α phases, respectively, while Mn inhomogeneously concentrates into the γ phase with dispersion of about 1.0 mass%.

Figure 7 shows the dependence of the chemical composition for the γ phase on the annealing time. The results for $T_a = 800$ and 740°C (1 073 and 1 013 K) are indicated in Figs. 7(a) and 7(b), respectively, and the mean C, Mn and Si contents are represented as open squares, solid circles and triangles, respectively, with error bars. Here, the mean content was obtained from a line analysis in a manner such that the content of each solute element was measured in several γ grains at an interval of $0.09\ \mu\text{m}$, and the error bar indicates the standard deviation. The equilibrium contents of Mn and Si in the γ phase calculated by Thermo-Calc[®] are also shown with horizontal dashed lines in **Fig. 7**. As the annealing time increases, the Mn content increases, but the C and Si contents decrease. As can be seen, both the Mn and Si contents reach to the equilibrium ones at each longest annealing time. This is also the case for the Mn and Si contents in the α phase, though the corresponding results are not indicated in **Fig. 7**. The Mn content at the longest annealing time is greater for $T_a = 740^\circ\text{C}$ (1 013 K) than for $T_a = 800^\circ\text{C}$ (1 073 K). The partition ratio of Mn between the γ and α phases at $T_a = 740^\circ\text{C}$ (1 013 K) for $t_a = 14.4$ ks

Fig. 7. Dependence of chemical composition for γ phase on annealing time at (a) $T_a = 800^\circ\text{C}$ (1 073 K) and (b) $T_a = 740^\circ\text{C}$ (1 013 K). Mean C, Mn and Si contents are shown as open squares, solid circles and triangles, respectively, with error bars.

is about 1.9, which is much greater than that of Si between the α and γ phases.

3.2. Ferrite Transformation Behavior after Intercritical Annealing

As mentioned in Section 2, the effect of the partitioning of solute elements on ferrite formation during slow cooling after intercritical annealing was examined for Pattern B at $T_a = 800^\circ\text{C}$ (1 073 K) for $t_a = 1.8$ ks and at $T_a = 740^\circ\text{C}$ (1 013 K) for $t_a = 14.4$ ks. Such intercritical annealing conditions were chosen so as to cause large change in the initial partition of each solute element between the α and γ

Table 2. Volume fractions, f_α and f_γ , of ferrite and austenite, respectively, and mean contents of solute elements in austenite under various annealing conditions.

Annealing conditions		Volume fractions		Mean contents in γ phase		
Temperature, $T_a/^\circ\text{C}$	Time, t_a/ks	α phase, f_α	γ phase, f_γ	C/mass%	Mn/mass%	Si/mass%
800	1.8	0.34	0.66	0.27	2.1	1.3
740	14.4	0.73	0.27	0.42	2.9	1.2

Fig. 8. SEM images of specimens for Pattern B with $T_a = 800^\circ\text{C}$ (1 073 K) and $t_a = 1.8$ ks at (a) $T_q = 800^\circ\text{C}$ (1 073 K), (b) $T_q = 700^\circ\text{C}$ (973 K), (c) $T_q = 600^\circ\text{C}$ (873 K) and (d) $T_q = 400^\circ\text{C}$ (673 K). **Fig. 9.** SEM images of specimens for Pattern B with $T_a = 740^\circ\text{C}$ (1 013 K) and $t_a = 14.4$ ks at (a) $T_q = 740^\circ\text{C}$ (1 013 K), (b) $T_q = 700^\circ\text{C}$ (973 K), (c) $T_q = 600^\circ\text{C}$ (873 K) and (d) $T_q = 400^\circ\text{C}$ (673 K).

phases before the subsequent ferrite transformation. **Table 2** summarizes the volume fractions f_α and f_γ of the α and γ phases, respectively, and the mean content of each solute element in the γ phase under the intercritical annealing conditions mentioned above.

SEM images of the specimens with $T_a = 800^\circ\text{C}$ (1 073 K) and $t_a = 1.8$ ks are shown in **Fig. 8**. Figures 8(a), 8(b), 8(c) and 8(d) indicates the results for $T_q = 800, 700, 600$ and 400°C (1 073, 973, 873 and 673 K), respectively. In all the SEM images in Fig. 8, the microstructure consists of the α and γ phases. As can be seen, the volume fraction f_α of the α phase increases with decreasing quenching temperature T_q . This means that the ferrite transformation of the γ phase into the α phase occurs during slow cooling. The corresponding results for $T_a = 740^\circ\text{C}$ (1 013 K) and $t_a = 14.4$ ks are shown in **Fig. 9**. Figures 9(a), 9(b), 9(c) and 9(d) indicates the SEM images for $T_q = 740, 700, 600$ and 400°C (1 013, 973, 873 and 673 K), respectively. Also in this case, the microstructure is composed of the α and γ phases. As the quenching temperature decreases, however, the microstructure hardly changes in Fig. 9.

Figure 10 shows the dependence of the volume fraction f_α of the α phase on the quenching temperature T_q . In this figure, the result for $T_a = 800^\circ\text{C}$ (1 073 K) and $t_a = 1.8$ ks is indicate as solid circles, and that for $T_a = 740^\circ\text{C}$ (1 013 K) and $t_a = 14.4$ ks is represented as open squares. For the solid circles, the value of f_α is 0.35 at $T_q = 800^\circ\text{C}$ (1 073 K), and monotonically increases with decreasing quenching temperature. Between $T_q = 700$ and 600°C (973 and 873 K), f_α is considerably sensitive to T_q . At $T_q = 400^\circ\text{C}$ (673 K), f_α finally reaches to 0.67. On the other hand, for the open

Fig. 10. Dependence of volume fraction f_α of α phase on quenching temperature T_q . Result for $T_a = 800^\circ\text{C}$ (1 073 K) and $t_a = 1.8$ ks is indicate as solid circles, and that for $T_a = 740^\circ\text{C}$ (1 013 K) and $t_a = 14.4$ ks is represented as open squares.

squares, f_α is close to 0.67 independently of T_q . Thus, there is a difference in the dependence of f_α on T_q between the solid circles and the open squares.

Figure 11 shows SEM images and elemental mappings of the solute elements for the specimens with $T_a = 800^\circ\text{C}$ (1 073 K) and $t_a = 1.8$ ks. Figures 11(ai), 11(bi), 11(ci) and (di) indicates the results for $T_q = 800, 700, 600$ and 400°C (1 073, 973, 873 and 673 K), respectively. Furthermore, $i = 1$ for the SEM image, and $i = 2, 3$ and 4 for the elemental mappings of C, Mn and Si, respectively. At $T_q = 800$ and 700°C (1 073 and 973 K), the distribution of C in the γ

Fig. 11. (a1, b1, c1, d1) SEM images and (a*i*, b*i*, c*i*, d*i*) elemental mappings of C, Mn and Si for $i = 2, 3$ and 4 , respectively, of specimens for Pattern B with $T_a = 800^\circ\text{C}$ (1 073 K) and $t_a = 1.8$ ks at (a) $T_q = 800^\circ\text{C}$ (1 073 K), (b) $T_q = 700^\circ\text{C}$ (973 K), (c) $T_q = 600^\circ\text{C}$ (873 K) and (d) $T_q = 400^\circ\text{C}$ (673 K).

Fig. 12. (a1, b1) SEM images and (a*i*, b*i*) elemental mappings of C, Mn and Si for $i = 2, 3$ and 4 , respectively, of specimens for Pattern B with $T_a = 740^\circ\text{C}$ (1 013 K) and $t_a = 14.4$ ks at (a) $T_q = 740^\circ\text{C}$ (1 013 K) and (b) $T_q = 400^\circ\text{C}$ (673 K).

phase and that of Si in the α phase are rather homogeneous, but that of Mn in the γ phase is slightly inhomogeneous. As the quenching temperature T_q decreases, the volume fraction of the α phase increases, and thus that of the γ phase decreases. At $T_q = 600$ and 400°C (873 and 673 K), the homogeneity for C deteriorates, and the distributions of Mn and Si hardly change. The C content in the γ phase is greater for Figs. 11(c2) and 11(d2) than for Figs. 11(a2) and 11(b2). The dispersion is about 0.30 mass% for the C content in the γ phase at $T_q = 400^\circ\text{C}$ (673 K). Comparing Figs. 11(c2) and 11(d2) with Figs. 11(c3) and 11(d3), respectively, we may find that the region of large Mn content does not necessarily coincide with that of large C content. The former one is broader than the latter one. The corresponding results for $T_a = 740^\circ\text{C}$ (1 013 K) and $t_a = 14.4$ ks are shown in Fig. 12. Figures 12(ai) and 12(bi) indicates the results for $T_q = 740$ and 400°C (1 013 and 673 K), respectively. Like Fig. 11, $i = 1$ for the SEM image, and $i = 2, 3$ and 4 for the elemental mappings of C, Mn and Si, respectively. Unlike Fig. 11, however, distinct dependencies of the volume fraction of each phase and the content of each solute element on the quenching temperature are not recognized in Fig. 12. This means that the ferrite transformation is suppressed for the specimens in Fig. 12. Such differences between the results in Figs. 11 and 12 will be discussed in detail later on.

4. Discussion

4.1. Simulation of Reverse Transformation and Partitioning of Solute Elements

Reverse transformation and the partitioning of solute elements between the α and γ phases during intercritical annealing were simulated by DICTRA[®] with the TCFE7 and MOBFE2 databases. The size of the simulation cell was set to $5\text{ }\mu\text{m}$ as half of the mean distance between the centers of adjacent α grains. The initial microstructure was set as the $\alpha + \gamma$ two-phase microstructure. For the simulation of $T_a = 800^\circ\text{C}$ (1 073 K), the thickness of the γ phase was set to $2\text{ }\mu\text{m}$, which is half of the mean grain size of the γ phase when annealing at 800°C (1 073 K) started, and C was partitioned between the α and γ phases while Mn and Si were not partitioned in the cell. For the simulation of $T_a = 740^\circ\text{C}$ (1 013 K), the thickness of the γ phase was set as extremely

thin ($1 \times 10^{-3}\text{ }\mu\text{m}$) because the γ phase was not observed when annealing at 740°C (1 013 K) started, and C, Mn and Si were not partitioned in the cell.

Under such conditions, the dependence of the volume fraction f_γ of the γ phase on the annealing time was calculated by DICTRA[®]. The calculations for $T_a = 800$ and 740°C (1 073 and 1 013 K) are shown as solid curves in Figs. 13(a) and 13(b), respectively, in comparison with the experimental results indicated as solid circles. At $T_a = 800^\circ\text{C}$ (1 073 K), the calculation shows good agreement with the experiment. However, at $T_a = 740^\circ\text{C}$ (1 013 K), the calculation provides much faster growth of the γ phase than the experiment. The profiles of the C and Mn contents in the cell are shown in Fig. 14. Figures 14(a) and 14(b) indicates the C and Mn profiles, respectively, for $T_a = 800^\circ\text{C}$ (1 073 K), and Figs. 14(c) and 14(d) represents the C and Mn profiles, respectively, for $T_a = 740^\circ\text{C}$ (1 013 K). In Fig. 14, the γ phase is initially located at the left-hand side of the cell and grows into the α phase at the right-hand side. Under the annealing conditions in Fig. 14, both C and Mn are partitioned between the α and γ phases. For the α and γ phases, the distribution of Mn is inhomogeneous in Figs. 14(b) and 14(d), but that of C is rather homogeneous in Figs. 14(a) and 14(c). The Mn content c_{Mn}^γ in the γ phase is typically greater at the γ/α interface than at the other region. Since the value of c_{Mn}^γ at each location is insensitive to the annealing time, the Mn content $c_{\text{Mn}}^{\gamma\alpha}$ at the γ/α interface increases with increasing thickness of the γ phase and thus with increasing annealing time. According to the measurement by FE-EPMA, $c_{\text{Mn}}^{\gamma\alpha}$ is about 2.5 mass% at $T_a = 800^\circ\text{C}$ (1 073 K) for $t_a = 1.8$ ks, and c_{Mn}^γ is about 1.7 mass% far from the γ/α interface. The value $c_{\text{Mn}}^\gamma \approx 1.7$ mass% is close to the overall Mn content of the steel. The calculation for $T_a = 800^\circ\text{C}$ (1 073 K) in Figs. 14(a) and 14(b) indicates good agreement with the experiment in Fig. 7(a). On the other hand, according to the FE-EPMA measurement for $T_a = 740^\circ\text{C}$ (1 013 K) and $t_a = 14.4$ ks, c_{Mn}^γ is greater than 2 mass% even in the center of the γ grain. In Fig. 14(d), however, c_{Mn}^γ is about 1.7 mass% far from the γ/α interface. Thus, like the relationship in Fig. 13(b), the calculation of the Mn content for $T_a = 740^\circ\text{C}$ (1 013 K) deviates from the experiment.

Sun and Pugh¹³⁾ reported that Mn diffused from the α

Fig. 13. Calculations by DICTRA[®] for dependence of volume fraction f_γ of γ phase on annealing time shown as solid curves: (a) $T_a = 800^\circ\text{C}$ (1 073 K) and (b) $T_a = 740^\circ\text{C}$ (1 013 K). Experimental results are indicated as solid circles.

Fig. 14. Calculations by DICTRA[®] for profiles of C and Mn contents at various annealing times: (a) C at $T_a = 800^\circ\text{C}$ (1 073 K), (b) Mn at $T_a = 800^\circ\text{C}$ (1 073 K), (c) C at $T_a = 740^\circ\text{C}$ (1 013 K) and (d) Mn at $T_a = 740^\circ\text{C}$ (1 013 K). (Online version in color.)

phase to the α/γ interface and formed a Mn-rich rim during intercritical annealing, and that the Mn gradient in the γ phase was finally eliminated by diffusion of Mn in the γ phase. Pussegoda *et al.*¹⁴⁾ indicated that Mn could diffuse to the center of γ grain in a few hours at 695°C (968 K) after development of Mn-enriched rim. They suggested the increase in the diffusion coefficient of Mn in the γ phase by increase of the Mn content and the presence of defect structure.

SEM images and elemental mappings for the specimens with various heat treatments are shown in Fig. 15. Figure 15(a*i*) indicates the results for $T_a = 800^\circ\text{C}$ (1 073 K) and $t_a = 1$ s, 15(b*i*) represents those for $T_a = 740^\circ\text{C}$ (1 013 K) and $t_a = 1$ s, and 15(c*i*) shows those for $T_a = 740^\circ\text{C}$ (1 013 K) and $t_a = 900$ s. Here, $i = 1$ for the SEM image, and $i = 2, 3$ and 4 for the elemental mappings of C, Mn and Si, respectively. In Figs. 15(a1)–15(a4), C concentrates into the γ phase, while Mn and Si are hardly partitioned between the γ and α phases. In Figs. 15(b1)–15(b4), the microstructure consists of the α phase and spheroidal particles of the θ phase without the γ phase, and the C content is greater in the region of θ -particle aggregate than in the α phase, while the dispersion of Mn content is small except for topical concentration of Mn in the θ phase. In Figs. 15(c1)–15(c4), the γ phase forms and both C and Mn concentrate into the γ phase. As shown in Fig. 13, $f_\gamma = 0.42$ at $T_a = 800^\circ\text{C}$ (1 073 K) for $t_a = 1$ s, $f_\gamma = 0$ at $T_a = 740^\circ\text{C}$ (1 013 K) for $t_a = 1$ s, and $f_\gamma = 0.25$ at $T_a = 740^\circ\text{C}$ (1 013 K) for $t_a = 900$ s. Thus, in the early stages of the reverse transformation, the γ phase forms with partitioning of Mn at $T_a = 740^\circ\text{C}$ (1 013 K) but without partitioning of

Mn at $T_a = 800^\circ\text{C}$ (1 073 K). The Mn concentration in the γ phase at $T_a = 800^\circ\text{C}$ (1 073 K) can be understood by the diffusion of Mn after the γ formation as reported by many researchers.^{3,13–16)} However, it is not so easy to understand the Mn concentration in the γ phase at $T_a = 740^\circ\text{C}$ in the early stages of the reverse transformation.

Figure 16 shows the Fe-rich corner of the isothermal section at 740°C (1 013 K) of the phase diagram in the quasi-ternary Fe–1.5 mass% Si–C–Mn system. The $\alpha + \gamma$ two-phase region is divided into the negligible partitioning local equilibrium (NPLE) and partitioning local equilibrium (PLE) regions for the reverse transformation according to a theoretical model of local equilibrium.^{17–21)} The chemical composition of the α phase in the specimen with $T_a = 740^\circ\text{C}$ (1 013 K) and $t_a = 1$ s measured by FE-EPMA is shown as an open circle in Fig. 16. In this figure, a solid circle indicates the initial chemical composition of the α phase used for the kinetic calculation in Fig. 14. As can be seen in Fig. 16, the open circle is located in the PLE region. As a result, the α phase should be transformed into the γ phase with partitioning of Mn. Zhang *et al.*²²⁾ investigated the kinetics and the partitioning of solute elements during the γ formation from the lath M phase. They²²⁾ reported that the presence of the θ phase and the partitioning of Mn and Si between the θ phase and the α matrix prior to the reverse transformation retarded the kinetics of the reverse transformation and induced a transition from the partitionless growth to the partitioning growth. According to the experiment in the present study, it took times longer than 900 s in order for the θ phase to dissolve completely, and both the reverse transformation and the dissolution of the θ

Fig. 15. (a1, b1, c1) SEM images and (a2, b2, c2) elemental mappings of C, Mn and Si for $i = 2, 3$ and 4 , respectively, of specimens with various annealing temperatures and times: (a) $T_a = 800^\circ\text{C}$ ($1\,073\text{ K}$) and $t_a = 1\text{ s}$, (b) $T_a = 740^\circ\text{C}$ ($1\,013\text{ K}$) and $t_a = 1\text{ s}$ and (c) $T_a = 740^\circ\text{C}$ ($1\,013\text{ K}$) and $t_a = 900\text{ s}$.

Fig. 16. Isothermal section at 740°C ($1\,013\text{ K}$) of phase diagram in quasi-ternary Fe-1.5Si-C-Mn system. The $\alpha + \gamma$ two-phase region is divided into the PLE and NPLE regions for the reverse transformation. Chemical composition of α phase in specimen with $T_a = 740^\circ\text{C}$ ($1\,013\text{ K}$) and $t_a = 1\text{ s}$ measured by FE-EPMA is shown as an open circle, and initial chemical composition of α phase used for kinetic calculation in Fig. 14 is indicated as a solid circle.

phase occurred simultaneously. The existence of the θ phase caused decreasing of the C content in the α phase, and the reverse transformation proceeded in the PLE mode. As a result, Mn concentrated into the γ phase in the early stages of the reverse transformation, and the Mn content in the γ phase became large even in the center of the γ grain.

However, due to the difficulty for the calculation of the

reverse transformation with the simultaneous dissolution of the θ phase by DICTRA[®], the calculation deviated from the experiment. On the other hand, because the θ phase completely dissolved before the reverse transformation started at $T_a = 800^\circ\text{C}$ ($1\,073\text{ K}$), the reverse transformation behavior could be simulated by DICTRA[®]. As described above, the reverse transformation proceeds in the PLE mode, when both the reverse transformation and the dissolution of the θ phase occur simultaneously.

4.2. Ferrite Transformation Mode during Cooling

The kinetics of the diffusional transformation relevant to the α and γ phases is classified by the partitioning behavior of substitutional solute element E between the α and γ phases as follows: paraequilibrium (PE), PLE and NPLE modes. In the PE mode, diffusion of C controls the migration of the α/γ interface without diffusion of E, where E corresponds to Mn, Si, etc. On the other hand, in the PLE and NPLE modes, diffusion of E controls the interface migration, maintaining the local equilibrium at the α/γ interface. In the PLE mode, both C and E are partitioned between the α and γ phases. In contrast, in the NPLE mode, the composition of E varies only locally at the α/γ interface, but it remains constant over the α and γ phases. For the ferrite transformation, the growth of the α phase is extremely sluggish in the PLE mode due to the slow partitioning rate of E compared with the NPLE or PE mode.

The chemical compositions of the α and γ phases for the specimens in Figs. 8 and 11 are plotted as open triangles and solid circles, respectively, in Fig. 17. Figures 17(a), 17(b),

17(c) and 17(d) indicates the results for $T_q = 800, 700, 600$ and 400°C (1 073, 973, 873 and 673 K), respectively. In this figure, the horizontal and vertical axes represent the C and Mn contents, respectively. Here, the C and Mn contents were determined from a line analysis in a manner such that the content of each solute element was measured in several α and γ grains at an interval of $0.09\ \mu\text{m}$. Silicon is a ferrite stabilizing element and promotes the ferrite transformation during slow cooling after intercritical annealing. However, the partitioning ratio of Si between the α and γ phases during intercritical annealing is much smaller than that of C or Mn between the γ and α phases as mentioned in Section 3.1. Therefore, hereafter, attention will be focused on the partitioning of C and Mn. At $T_q = 800^\circ\text{C}$ (1 073 K) in Fig. 17(a), the C and Mn contents are smaller for the α phase than for the γ phase. As the quenching temperature decreases to $T_q = 700^\circ\text{C}$ (973 K) in Fig. 17(b), the α phase with larger Mn content forms and the mean C content in the γ phase increases without change of the Mn content. The formation of the α phase with larger Mn content may occur during slow cooling after intercritical annealing. Hereafter, the α phase produced during intercritical annealing is denoted by the α_a phase, and that generated during slow cooling is called the α_c phase. As can be seen in Figs. 17(a) and 17(b), the Mn content is greater for the α_c phase than the α_a phase. As the quenching temperature decreases from $T_q = 800^\circ\text{C}$ (1 073 K) to $T_q = 400^\circ\text{C}$ (673 K), the mean C content of the γ phase increases from 0.27 mass% to 0.5 mass% without change of the Mn content. This indicates that C concentrates into the γ phase during slow cooling without partitioning of Mn.

Isothermal sections at various temperatures of the phase diagram in the quasi-ternary Fe–1.5 mass% Si–Mn–C system are shown in Fig. 18. Figures 18(a), 18(b), 18(c) and 18(d) indicates the isothermal sections at 800, 740, 700 and 600°C (1 073, 1 013, 973 and 873 K), respectively. Fur-

thermore, the chemical composition of the γ phase in each specimen measured by FE-EPMA is represented as various symbols in Fig. 18. The result for $T_a = 800^\circ\text{C}$ (1 073 K) and $t_a = 1.8\ \text{ks}$ is shown as solid circles in Fig. 18(a), that for $T_a = 740^\circ\text{C}$ (1 013 K) and $t_a = 14.4\ \text{ks}$ is indicated as open squares in Fig. 18(b), that for $T_a = 800^\circ\text{C}$ (1 073 K), $t_a = 1.8\ \text{ks}$ and $T_q = 700^\circ\text{C}$ (973 K) is represented as solid circles in Fig. 18(c), that for $T_a = 740^\circ\text{C}$ (1 013 K), $t_a = 14.4\ \text{ks}$ and $T_q = 700^\circ\text{C}$ (973 K) is shown as open squares in Fig. 18(c), that for $T_a = 800^\circ\text{C}$ (1 073 K), $t_a = 1.8\ \text{ks}$ and $T_q = 600^\circ\text{C}$ (873 K) is indicated as solid circles in Fig. 18(d), and that for $T_a = 740^\circ\text{C}$ (1 013 K), $t_a = 14.4\ \text{ks}$ and $T_q = 600^\circ\text{C}$ (873 K) is represented as open squares in Fig. 18(d). In Fig. 18, the $\alpha + \gamma$ two-phase region is divided into the PLE and NPLe regions for the ferrite transformation. The PLE/NPLE boundary lies in larger C content area for the ferrite transformation in Fig. 18 than for the reverse transformation in Fig. 16. At 800 and 740°C (1 073 and 1 013 K) in Figs. 18(a) and 18(b), the solid circles and the open squares are located in the PLE region. However, at 700°C (973 K) in Fig. 18(c), the open squares lie in the PLE region, but the solid circles are rather located on the PLE/NPLE boundary. At 600°C (873 K) in Fig. 18(d), both the open squares and the solid circles almost lie on the PLE/NPLE boundary. This yields that the ferrite transformation for the γ phase with certain chemical composition may occur in the PLE mode at higher temperatures but in the NPLe mode at lower temperatures. The critical temperature T_c between the PLE and NPLe modes is about 700°C (973 K) for the γ phase of the solid circles and about 600°C (873 K) for that of the open squares.

The SEM image and the elemental mappings in Figs. 11(d1), 11(d2) and 11(d3) for $T_a = 800^\circ\text{C}$ (1 073 K), $t_a = 1.8\ \text{ks}$ and $T_q = 400^\circ\text{C}$ (673 K) are shown again in Figs. 19(a), 19(b) and 19(c), respectively. If we carefully look at the grains of the α phase indicated by arrows in Fig. 19(a),

Fig. 17. Chemical compositions of α and γ phases for specimens in Figs. 8 and 11 are plotted as open triangles and solid circles, respectively: (a) $T_q = 800^\circ\text{C}$ (1 073 K), (b) $T_q = 700^\circ\text{C}$ (973 K), (c) $T_q = 600^\circ\text{C}$ (873 K) and (d) $T_q = 400^\circ\text{C}$ (673 K).

Fig. 18. Isothermal sections at various temperatures of phase diagram in quasi-ternary Fe–1.5Si–C–Mn system: (a) 800°C (1 073 K), (b) 740°C (1 013 K), (c) 700°C (973 K) and (d) 600°C (873 K). Chemical compositions of γ phase measured by FE-EPMA for different annealing and quenching temperatures are shown as solid circles and open squares for $T_a = 800$ and 740°C (1 073 and 1 013 K), respectively. The $\alpha + \gamma$ two-phase region is divided into the PLE and NPLE regions for the ferrite transformation.

Fig. 19. SEM image and elemental mappings in Figs. 11(d1), 11(d2) and 11(d3) for $T_a = 800^\circ\text{C}$ (1 073 K), $t_a = 1.8$ ks and $T_q = 400^\circ\text{C}$ (673 K) are shown again in (a), (b) and (c), respectively. Solid and dashed arrows indicate α_c grains with and without grain boundaries, respectively, against α_a grain.

we may find that the C content is almost equivalent to each other between these α grains and the other α grains but the Mn content is rather close to each other between these α grains and the γ grains. For the specimen in Fig. 19, the quenching temperature $T_q = 400^\circ\text{C}$ (673 K) is much lower than the critical temperature $T_c = 700^\circ\text{C}$ (973 K). Consequently, it may be concluded that the α phase with large Mn content was produced from the γ phase by the ferrite transformation in the NPLE mode during slow cooling. The α phase produced by the ferrite transformation is the α_c phase, and the other α phase is the α_a phase. In Fig. 19, the α_c grains indicated by solid arrows have grain boundaries with α_a grains, while those indicated by dashed arrows do not have such grain boundaries. It was reported that an α_c grain grew from an α_a grain epitaxially during slow cooling after intercritical annealing.^{23–25)} The epitaxial α_c grain

does not have grain boundary with the adjacent α_a grain. However, according to the experiment in the present study, not only the epitaxial α_c grain but also the α_c grain which have grain boundary with the α_a grain was observed. As can be seen in Fig. 19, the α_c phase tends to form in the γ phase with relatively small Mn content. If the area with small Mn content in the γ phase is near the γ/α_a interface, the α_c phase may grow from α_a toward the γ phase epitaxially. On the other hand, when the small Mn content area is far from the γ/α_a interface, the α_c phase will nucleate in this area. In such a case, a grain boundary may be produced between the α_c and α_a phases. To summarize the above discussion, there are mainly two types of the α phase in the cold-rolled high strength steel with composite microstructure produced by intercritical annealing, one being the α_a phase (intercritically-annealed ferrite) and the other the α_c phase

(transformed ferrite). Furthermore, the α_c phase is classified into that generated by growth from the α_a phase epitaxially and that produced by nucleation and growth in the γ phase.

5. Conclusions

The partitioning of solute elements during intercritical annealing and the effects of the partitioning on the ferrite transformation after intercritical annealing in the 0.17% C–1.5% Si–1.7% Mn (mass%) steel were experimentally examined by a new FE-EPMA technique. The main conclusions are summarized as follows.

(1) In the reverse transformation at 800°C (1 073 K), austenite forms rapidly without partitioning of Mn and Si in the early stages, and the partitioning progresses with increasing annealing time. On the other hand, at 740°C (1 013 K), austenite is produced with partitioning of Mn and Si. The partitioning at 740°C (1 013 K) is caused by austenite formation in the PLE mode due to small C content in ferrite with undissolved cementite.

(2) Manganese inhomogeneously concentrates into austenite with dispersion of about 1.4 and 1.0 mass% during intercritical annealing at 800 and 740°C (1 073 and 1 013 K), respectively, while C and Si homogeneously concentrate into austenite and ferrite, respectively.

(3) The ferrite transformation during slow cooling at a cooling rate of 10°C/s after intercritical annealing at 800°C (1 073 K) for 1.8 ks progresses at temperatures between 700 and 600°C (973 and 873 K). In contrast, the ferrite transformation hardly occurs after intercritical annealing at 740°C (1 013 K) for 14.4 ks. Such a difference in the kinetics may be attributed to the NPLe and PLe modes for the former and latter ones, respectively.

(4) Two types of ferrite mainly exist in cold-rolled high strength steel produced by intercritical annealing, one being intercritically-annealed ferrite, which forms during heating and intercritical annealing, and the other transformed ferrite, which is produced during cooling after intercritical annealing. The Mn content is greater for the transformed ferrite

than for the intercritically-annealed ferrite. Furthermore, the transformed ferrite is classified into that generated by growth from the intercritically-annealed ferrite epitaxially and that produced by nucleation and growth in austenite.

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