Effects of Alloy Elements on Carbon Partitioning in Early Stages of Proeutectoid Ferrite Transformation in Low Carbon Mn–Si Steels

Takako YAMASHITA,1)* Masato ENOMOTO,2) Yuji TANAKA,1) Hiroshi MATSUDA1) and Kaneharu OKUDA1)

1) Steel Research Laboratory JFE Steel Corp., 1, Kawasaki-cho, Chuo-ku, Chiba, 260-0835 Japan.
2) Ibaraki Univ., 4-12-1, Nakanarusawa-cho, Hitachi, 316-8511 Japan.

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Controlling the carbon concentration and distribution among constituent phases is one of the most important issues for achieving high strength and ductility in the design of steel. The carbon distribution near the α/γ interface in the early stage of isothermal holding at 750°C was measured and visualized in Fe–C–Mn–Si alloys containing 2 mass% Si and 1.5 or 2 mass% Mn using a high precision FE-EPMA developed recently by the authors, and the results were compared with the theory of ferrite growth in multi-component low alloy steel. The carbon concentrations at α/γ interfaces in austenite were generally between the NPLE/PLE and paraequilibrium α/(α + γ) boundary concentrations. In alloys with carbon contents smaller than the NPLE/PLE boundary, the α/γ interfaces appeared to migrate under a condition close to paraequilibrium or with partially developed spikes of alloy elements in the early stages. On the other hand, in alloys with a bulk composition on the boundary and its higher carbon concentration side, Mn enrichment was observed at the interfaces, and the carbon concentrations tended to be higher than those in alloys with lower carbon contents, albeit there were variations at individual interfaces.

KEY WORDS: ferrite transformation; local equilibrium; paraequilibrium; computational microstructure prediction; high tensile low alloy steel.

1. Introduction

In recent years, improvement of both strength and ductility has been required in high tensile strength steel sheets (HTSS) used in automotive parts. Realizing high ductility in the hard phases that provide strength, such as martensite and bainite, while utilizing the strain-induced transformation of the retained austenite phase to improve elongation, is essential for realizing this combination of properties.1–3) When martensite, bainite and retained austenite are used to improve material properties, an understanding of the formation mechanisms of these phases is necessary. In particular, analysis of the relationship between these phases and element partitioning behavior, especially during isothermal annealing below the Ac3 point, is important.4–10)

Beginning in the 1950s, pioneering research on the fundamental theory of phase transformation was carried out by Hillert,11) Kikaldy and Aaronson et al.,12–14) who systematized the theory of diffusional growth with the assumption of local equilibrium. Numerous studies have also been reported by the Enomoto15) and Miyamoto et al. groups in Japan.16) Those studies have been a focus of interest as a fundamental metallurgical theory for recent high strength steels utilizing isothermal holding and intercritical annealing in the α + γ region; the local equilibrium theory has also been discussed even in actual steel production field sites. The local equilibrium modes treated here are the Partition Local Equilibrium (PLE) mode accompanied by partition of substitutional elements, the No-Partition Local Equilibrium (NPLE) mode unaccompanied by partitioning and the paraequilibrium (PE) mode, and the rate of phase transformation differs in these three transformation modes. The partition ratio and the morphology and volume fraction of the austenite (γ) phase in these respective transformation modes are extremely important control factors, especially in steels in which high ductility is achieved by enrichment of substitutional elements such as Mn, etc. in the γ phase to increase retained γ.

With conventional techniques, the lower limit of quantification of carbon had been limited to around 0.1 mass%, even in point analysis. However, in previous work, the authors developed the world’s first field emission electron beam probe microanalyzer (FE-EPMA) which can maintain a lower limit of quantification of carbon of 0.01% or lower in 2-dimensional analysis, and succeeded in visualizing the 2-dimensional distribution of carbon corresponding to the microstructures in steel sheets for the first time.17) In this paper, the developed device is called the Carbon analyzer (C-analyzer), and was used to understand the relationship between the carbon distribution behavior and partitioning of alloy elements during phase transformation.

In the early stages of isothermal holding, only carbon can be partitioned. Therefore, understanding the distribution

* Corresponding author: E-mail: ta-yamashita@jfe-steel.co.jp
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behavior of carbon is essential for manufacturing processes based on short-time heat treatment. In our previous study, we reported that the $\gamma \rightarrow \alpha$ transformation of an Fe-0.15/C-2/Si-1.5/Mn (mass%) alloy proceeded in a condition close to the PE mode after holding for about 15 s at 750°C and 800°C, but at around 1,800 s, the transformation transitioned to the NPLE mode. Furthermore, in an Fe-0.15/C-2/Si-2/Mn (mass%) alloy, the transformation proceeded in the NPLE mode from about 15 s at 750°C.

As in the previous report, here, Fe–C–Si–Mn quaternary system model alloys with different carbon contents were used as the sample materials, and were subjected to comparatively short-time isothermal holding at below $\mathrm{Ae}_3$ after austenitization. The distribution of carbon was measured with the C-analyzer, and the relationship between enrichment of carbon at the interface and the bulk carbon content and the relationship with the distribution of alloy elements were investigated in detail.

2. Experimental Procedures

2.1. Samples

The alloys were vacuum-induction melted using high purity electrolytic iron, high purity carbon, manganese and silicon. The chemical compositions of the alloys are shown in Table 1. Alloys A, B and D are the same alloys as those used in the previous report. Figure 1 shows the projected quaternary Fe–Si–Mn–C alloy phase diagram at 750°C for a constant (2 mass%) Si concentration and the NPLE/PLE boundary (dotted line), calculated by Thermo-Calc. The alloys for this study are positioned on the NPLE/PLE boundary or on the higher carbon side from the boundary.

The ingots were hot-rolled at 1,250°C and then cold-rolled to obtain steel sheets with a thickness of 1 mm. Homogenization treatment was not performed in this experiment. However, according to an EPMA analysis, the variation of the Mn concentration in the specimens used in the measurements was 0.1 mass% at maximum. As shown in Figure 2, following cold rolling, the samples were austenitized at 950°C, and were then held at 750°C below $\mathrm{Ae}_3$ for 15 s to 3,000 s, followed by quenching in water. The sample cross-section parallel to the rolling direction (L cross-section) was mirror-polished, and a quantitative analysis of C, Si and Mn was performed with the C-analyzer. In the measurements with the C-analyzer, the annealed specimens were checked for formation of the ferrite ($\alpha$) phase in advance with an optical microscope. In case of fast transformation, specimens with a holding time of 15 s were selected, and in case of delayed transformation, specimens with holding times (60 s, 90 s, 150 s, 3,000 s) that resulted in an $\alpha$ phase fraction of approximately 10% were selected.

2.2. Experimental Method

To obtain the change in the $\alpha$ phase fraction depending on the holding time, the L cross-sections of the samples were mirror-polished and etched with 3% Nital, and microstructural observation was performed with an optical microscope. The area ratios of the $\alpha$ phase were obtained from images with a magnification of ×400.

In the measurements of carbon with the C-analyzer, an accelerating voltage of 7 kV and probe current of 50 nA were used, and the measurements were performed using the Focused condition, which provides the smallest beam diameter. The quantitative line analysis and 2-dimensional quantitative carbon mapping were performed under conditions that minimized the accumulation of contamination, as described in detail in a previous report. Under the measurement conditions used here, the spatial resolution of the carbon analysis with the C-analyzer was 100 nm or less, and carbon was quantified by the calibration curve method using standard samples of Fe–C alloy. In the point analysis, the quantification accuracy of carbon under the measurement conditions described above was a standard deviation of 3 $\sigma$ and concentration of 30 ppm or less.

Next, mapping measurements of Si and Mn were performed in the same field of view as the carbon analysis. Because the K line was used in the analysis of Si and Mn, the measurements were done with the accelerating voltage...
and probe current of 9 kV and 100 nA, respectively, to reduce the signal-to-noise (S/N) ratio.

In order to observe the microstructure of the same field as that measured by the C-analyzer, after the C-analyzer measurement, the specimens were lightly polished and then etched with 3% Nital, and were then observed with a field emission scanning electron microscope (FE-SEM, Supra55VP, Carl Zeiss). The In-lens mode (best for higher magnification) at an accelerating voltage of 1 kV was used in these observations in order to observe the fine details of the microstructure.

Enrichment of Mn at the grain boundary was measured with a spherical-aberration corrected scanning transmission microscope (Cs corrected-STEM, JEM-ARM200F, JEOL). Before these measurements, thin-film specimens were prepared by micro-sampling using an integrated focused ion beam milling-scanning electron microscope system (FIB-SEM, Crossbeam 540, Carl Zeiss) to enable vertical cutting of the α/γ interface measured with the C-analyzer, and TEM bright field images were observed at an accelerating voltage of 200 kV. The position in the observed α/γ interface where the interface was perpendicular to the material surface was identified and measured by STEM-EDS.

3. Results

3.1. Ferrite Transformation Curve

Figure 3 shows the change over time in the α fraction at 750°C for the alloys measured using the microstructural photographs taken with the optical microscope. The initial slopes of alloys A, B and D are large, but the α fraction becomes substantially constant at around 100 s. In contrast, the starting slopes of alloys C, E and F are small, and the α fraction continues to increase slowly for an extended time. From the positional relationship of the NPLE/PLE interface, in the former alloys, carbon diffusion appears to be rate-controlling (NPLE or PE mode), whereas in the latter, the transformation is controlled by diffusion of alloy elements from the beginning.

3.2. 2-Dimensional Element Mapping by C-Analyzer

Figures 4(a) and 4(b) show SEM microstructural photographs and carbon mapping for alloys C and D, which have carbon contents of 0.2 mass%. While carbon enrichment occurred near the α/γ interface in alloy D, carbon enrichment to the interface was negligible in alloy C.

Figures 5(a) and 5(b) show SEM microstructural photographs and carbon mapping for alloys E and F, which have carbon contents of 0.3 mass%. In these alloys, carbon is distributed over the entire surface at a high concentration. In alloy E, a long time of $3 \times 10^3$ s is required to achieve the fraction in this data. As reported previously, enrichment of carbon at the interface is observed in alloys A and B, which have carbon contents of 0.15 mass%.

A line analysis of the C, Mn and Si was performed so as to cross the α grains by carbon mapping of alloys C, D and F. The results are shown in Figs. 6(a) to 6(c). To increase sensitivity, the line analysis measurements were performed at an accelerating voltage of 15 kV and current of 200 nA. The results show the X-ray intensity of carbon under the above-mentioned measurement conditions, as the previously-mapped areas were contaminated. In spite of this, clear concentration differences exist between the α
grains and the matrix. Enrichment of Mn occurred at the interface in alloys C and F, but is virtually absent in alloy D. Likewise, the concentration of Si is also substantially the same in the $\alpha$ grains and matrix.

4. Discussion

4.1. Interfacial Concentration of Carbon

Figures 7(a) and 7(b) show the tie-lines for the growth of ferrite under local equilibrium (LE) and paraequilibrium (PE) in the quaternary phase diagram for an Fe–C–Mn–Si alloy. Here, $a$ indicates the point of intersection between a component ray of carbon passing through the bulk composition O and the $\alpha/($ $\alpha + \gamma)$ phase boundary (where the component ray is a straight line from the carbon apex of the tetrahedral phase diagram with a constant composition ratio of Fe, Mn and Si), and c and d are the other ends of equilibrium tie-lines that start at a. In Fig. 7(a), point b, where the carbon component ray and the carbon isoactivity plane pass through c, is the NPLE/PLE boundary at the said temperature of this alloy.

Figures 8 and 9 show the NPLE/PLE, paraequilibrium and orthoequilibrium boundaries and the $T_0$ composition line, as calculated using the interfacial concentration of carbon mapping and the Thermo-Calc database (TCFE7), for alloys with Mn contents of 1.5 mass% and 2.0 mass%, respectively. According to Fig. 8, there is no difference between the interfacial carbon concentrations of alloys B and D, and the interfacial carbon concentration approaches the NPLE/PLE boundary. For alloy F, some data points reach the PE boundary, but large variations exist. In Fig. 9, the interfacial carbon concentration of alloy A is near the NPLE/PLE boundary, but this figure also shows that the interfacial concentration increases as the carbon concentra-

![Fig. 6. Quantitative carbon mapping and line profile of (a) alloy C isothermally held at 750°C for 90 s, (b) alloy D isothermally held at 750°C for 15 s, and (c) alloy F isothermally held at 750°C for 60 s, using C-analyzer.](image)

![Fig. 7. (a) Local equilibrium tie-line (ac) and (b) paraequilibrium interfacial tie-line (ad) for growth of ferrite in an Fe–C–Mn–Si alloy (O). O’ is the projection onto a basal plane or Fe–C–Mn phase diagram. Thick arrows in (a) indicate the movement of the carbon concentration at the $\alpha/\gamma$ interface when the PLE mode begins to operate.](image)
The measured results of the transformation fraction are initially near PE, but the increase stopped at around 100 s and thereafter displayed behavior similar to the curve of LE. Similar behaviors are also obtained with alloys A and B. The interface migration speed in alloy D at $t = 15$ s is $1.7 \times 10^{-7}$ m/s. From the volume diffusion coefficient of Mn in $\gamma (D_{Mn} \approx 10^{-18} \text{ m}^2/\text{s})$, the width of the Mn spike is $10^{-11}$ m, which is smaller than the interatomic distance. Thus, the interfacial carbon concentration (Fig. 8) is larger than the NPLE/PLE boundary, and the transformation fraction (Fig. 10(a)) suggests paraequilibrium or a condition near PE. In this connection, Hutchinson et al.\textsuperscript{20} discovered that the growth rate of proeutectoid $\alpha$ in an Fe–C–Ni alloy slowed suddenly several tens of seconds after the start of transformation, and reported the possibility that this rapid growth occurs under a condition close to PE because the diffusion spike of Ni is absent in the stage before growth slows. In light of those results, the wide peak of Mn in Fig. 6(a) suggests the possibility of segregation to the $\alpha/\gamma$ interface.

Figure 10(b) shows the comparison with the simulation results for the transformation fraction of alloy F. In this alloy as well, the measured result in the early stage (15 s) is close to the simulation result for PE, but the fraction immediately increases along the curve of the PLE mode. Alloy C also displays a similar tendency. Even assuming that time is required for Mn enrichment in the transition to the PLE mode, the transformation is considered to proceed under PE during the initial short-time period. The measured value for alloy F is larger than the value calculated for the PLE mode over a long time period. However, this is attributed to acceleration of $\alpha$ growth by grain boundary diffusion of alloy elements.\textsuperscript{21}
4.2. STEM-EDS Measurement of Mn Enrichment in Vicinity of Interface

Figure 6(b) indicated the possibility that the $\alpha$/$\gamma$ interface of alloy D moves under a condition close to PE. Therefore, whether Mn enrichment occurs or not is analyzed in detail by STEM-EDS. Figures 11(a) and 11(c) shows the C-analyzer back-scattered electron (BSE) image and the carbon mapping data. Figure 11(b) shows a STEM image of the FIB-milled thin-film specimen around the $\alpha$ grain indicated in Fig. 11(a) and the EDS analysis position. Figure 11(d), showing the line profile of Si and Mn along Line 1, clearly indicates that virtually no Mn enrichment has occurred.

Next, focusing on alloy F, in which comparatively large Mn enrichment could be seen in the 2-dimensional mapping, an interface parallel to the electron beam was selected by STEM-EDS, and enrichment of Mn and Si was analyzed once again. In Fig. 7(a), the blue arrows show the change of the composition in austenite at the $\alpha$/$\gamma$ interface and the mean composition of the untransformed austenite immediately after the shift from NPLE to PLE. The gray arrow shows the projection on the Fe–C–Mn ternary section. If the composition in austenite at the interface is passed through point b, the condition is the PLE mode, and the composition c on the $\gamma$ side of the interface moves in the direction indicated by the blue arrow. Accompanying this, the concentrations of C and Si increase from the NPLE interface composition, and the concentration of Mn decreases. Figures 12(a) to 12(c) show the BSE image and carbon mapping data and a TEM image of the FIB-milled thin-film specimen, and Figs. 12(d) to 12(f) show the line analysis spectra of Lines 1 to 3. These spectra are taken from the vicinity of the same $\alpha$ grain. Lines 1 and 2 are taken from the same $\gamma$ grain, and Line 3 is taken from a different $\gamma$ grain. Lines 2 and 3 show enrichment of Mn at the interface and a slight decrease of the Mn concentration in the $\alpha$ grain, suggesting that the interfaces of Lines 2 and 3 have transited to the PLE mode. The increased width of the carbon spike and migration of the interfacial tie-lines to the high carbon side in the PLE mode are consistent with a condition relatively close to the PE boundary.

From the STEM measurement results in Fig. 12, the width of the Mn-enriched region is up to 2 nm. According to Hillert11) and Coates,22) a width of approximately 10 d, where d is the interatomic spacing, is necessary in the Mn spike in order to achieve LE. Accordingly, these Mn-enriched regions are thought to be Mn spikes in the NPLE mode or Mn spikes immediately after the transition to PLE. Moreover, Guo et al.14) reported that grain boundary segregation occurred in an Fe–C–Mn–Si alloy having a composition near the NPLE/PLE boundary before the start of Mn partitioning.

The measured and calculated values of the interfacial concentrations of these alloys are compared in Figs. 13(a) and 13(b). The ortho boundary, etc. is a projection of the 2% Si section, and the red line shows the interfacial tie-line according to DICTRA. Since this interfacial tie-line does not coincide with the 2% Si section, both ends deviate from the ortho boundary. The measured values of C and Mn are obtained with the C-analyzer and STEM, respectively. The Mn concentrations of Lines 1 of alloys D and F increase from the bulk concentration. However, as the baseline of the STEM profile changes, the differences of the Mn concentrations are within the error range. Partitioning of Si is small, and changes in the Si concentration are not significant. With
all of these interfaces, the C concentration is larger than the NPLE/PLE boundary but smaller than the ortho and paraequilibrium boundaries. From the results of the simulation of the transformation fraction for alloy D, this is thought to be close to PE. However, under-measurement of the carbon concentration due to inclination of the interface relative to the sample surface or some other factor cannot be ruled out. For alloy F, the PLE mode is estimated from the simulation. In this case, enrichment of Mn as in Lines 2 and 3 would be expected, but is not observed at the Line 1 interface. The
reason for this is unclear. Enrichment due to the Mn spike and segregation to the $\alpha'/\gamma$ interface are thought to contribute to Mn enrichment exceeding the ortho boundary of Line 3. The carbon concentration of the interface in alloy F in Fig. 8 reaches PE. As the width of the carbon profile of this interface is on the order of several $\mu$m and is close to the width of the carbon spike $w \approx D_c/v = 3 \times 10^{-5}$ m obtained from the interfacial velocity $v (= 3.5 \times 10^{-9}$ m/s) calculated by DICTRA, there is a high possibility that the observed result is the carbon profile in the PLE mode, and not the PE mode.

5. Conclusions

The carbon partitioning behavior at the $\alpha'/\gamma$ interface in the early stages of transformation was analyzed with an FE-EPMA (C-analyzer) which eliminates contamination during measurement as far as possible, enabling micro-region carbon analysis with measurement accuracy of 0.01 mass%. The alloys used in this study were six Fe–C–Mn-2mass%Si alloys with different C and Mn contents, which were subjected to isothermal holding at below Ae3. Although significant variations in the interfacial concentration existed due to the interface shape and angle with the specimen surface, soft impingement with adjacent $\alpha$ particles and other factors, the following conclusions were obtained.

(1) In the alloys on the low carbon side from the NPLE/PLE boundary, the initial transformation rate was rapid, and the rate of increase of the $\alpha$ fraction decreased remarkably at around 100 s. In the alloys on the NPLE/PLE boundary or on its higher carbon side, transformation was slow from the beginning, and the $\alpha$ fraction continued to increase after an extended time.

(2) According to carbon mapping, excluding a small number of exceptional cases, the interfacial concentration was in the intermediate area between the NPLE/PLE boundary and the PE boundary.

(3) In alloys with a bulk composition on the low carbon side from the NPLE/PLE boundary, enrichment of Mn was not observed. However, there was an interface where the carbon enrichment exceeded the NPLE/PLE boundary, suggesting that transformation occurred under a condition close to PE.

(4) In alloys on the NPLE/PLE boundary or on its high carbon side, a Mn-enriched layer having a width of up to 2 nm was observed at the interface, and the beginning of interfacial movement dominated by the PLE mode could be observed.

(5) Variations existed in the elemental distribution caused by transformation. This research demonstrated that carbon mapping is a powerful tool for visualizing the tendencies and characteristics of that distribution.

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