# Quantitative Analysis of Atomic-scale Alloying Elements Using TEM

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### Abstract

Steel properties can change greatly depending on the steel microstructures. Understanding the transformation mechanisms of respective grains in the microstructures is indispensable. In the investigation of transformation phenomena, it is important to observe the state of the grain boundary/interface. Scanning/Transmission Electron Microscopy (S/TEM) is a powerful tool for clarifying the crystal structures near the grain boundary and the concentration distribution of alloying elements in nanometer or atomic scale. Through the examples of concentration distributions of alloying elements near the interface, it was shown that quantitative analysis of alloying elements in atomic scale using S/TEM was effective for the clarification of transformation mechanisms.

### 1. Introduction

The mechanical properties of steel significantly vary depending on the arrangement of various crystal grains, their sizes, forms, and phase fraction. Therefore, to control steel properties, it is important to understand the formation of crystal grains, i.e., the mechanism of phase transformation and to use the mechanism.

The behavior of phase transformation greatly relies on the conditions at which the phase transformation occurs. Nano-level crystal structures and alloying elements distribution near grain boundaries and interfaces significantly affect the phase transformation behavior. Therefore, observing crystal structures and studying alloying element distribution near grain boundaries and interfaces are important to understand the phase transformation mechanisms. The phase transformation behavior could largely vary with only 1% concentration difference of alloying elements. Therefore, when alloying element distribution is measured to study the mechanism, quantitative evaluation of concentration is important in addition to whether the concentration of alloying elements is just high or low.

Transmission electron microscopes (TEMs) and scanning transmission electron microscopes (STEMs) can acquire crystal structures and alloying element distribution at the same time, and are thus useful to study phase transformation behavior. In recent years, S/TEMs with the aberration correcting function have spread, making it possible to observe crystal structures and measure alloying element distribution with spatial resolution of nanometers and angstroms. Such resolution made it possible to clearly detect the specific enrichment of alloying elements of the segregation of grain boundary and interface in a narrow range less than 1 nm in addition to the concentration of the alloying elements in the matrix.

Regarding phase transformation behavior for which attention is paid to interfacial segregation in steel, its contribution to the growth of allotriomorphic ferrite<sup>1-4)</sup> and bainite transformation stasis phenomenon<sup>5)</sup> has been discussed. Results of the measurement of grain boundary segregation and distribution concentration near grain boundaries contribute to the clarification of the mechanism.

Regarding the growth of allotriomorphic ferrite in Fe-C-X model alloys (X is a substitutional element, for example, Mn, Mo, and Ni), two modes are proposed: A mode in which allotriomorphic ferrite grows when local equilibrium (LE) of C and X is realized on both sides of an interface (on the austenite and ferrite sides); and another mode in which in the stage where an interface moves at a high speed, X cannot spread quickly enough and only local equilibrium of C is realized (para-equilibrium: PE). The LE mode is further classified into two types: Partition local equilibrium (PLE) in which long range diffusion of X (i.e. partition) occurs; and non-partition local equilibrium (NPLE) in which long range diffusion of X does not occur and local equilibrium occurs only at connections to the interface between ferrite and austenite. In addition, it has been pointed out that ferrite grains do not continue growing in the PE or LE mode, but the growth mode transits.<sup>2, 6)</sup>

In addition, if the affinity between X and interfaces cannot be ignored in ferrite growth, it needs to consider interfacial segregation

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and solute drag (SD) or coupled solute drag effects (in this paper, these are collectively referred to as SD effects) caused by such segregation.<sup>3, 4, 7</sup> Therefore, the relationship between these growth modes and SD effects has not been clearly concluded.

For low carbon steel made by adding Mo, Nb, or B, when upper bainite transformation is made by isothermal holding, the bainitic transformation does not progress to the transformation fraction expected from the phase diagram and the transformation doesn't progress in the middle of the course (transformation stasis phenomenon). Various theories have been proposed for this mechanism: (1) Bainite grains stop growing due to the SD effects of combined C and X, (2) transformation stasis is an essential characteristic of bainite and thereby when bainite is formed to its formation, and (3) when the concentration of the carbon in the austenite phase reaches  $T_0'$  composition, the bainitic transformation ends. The first theory is based on the SD effect, i.e., interfacial segregation. The second and third theories are not based on interfacial segregation.

Regarding the two theories not based on interfacial segregation above, the results of studying concentration distribution of added elements near interfaces will possibly contribute to clarifying the phase transformation mechanism.

To analyze alloying elements by an aberration corrected STEM, usually an electron energy loss spectroscopy (EELS) detector or energy-dispersive X-ray spectroscopy (EDS) detector is used for the measurement. Nippon Steel & Sumitomo Metal Corporation has an aberration corrected STEM (Titan 80-300 Cubed made by FEI) with both type detectors, being capable of measuring alloying element concentration.

This paper presents, using EELS and EDS, the measurement results of the concentration distribution near interfaces where ferrite allotriomorph grows in Fe-C-Mn model steel and where bainitic transformation reaches stasis in Fe-C-Mn-Mo model steel and considers the phase transformation mechanism. This paper also introduces techniques for measuring the segregation of grain boundary/interface and concentration profiles near grain boundaries and interfaces.

### 2. Measurement of Mn Concentration Distribution Near Allotriomorph Growing Ends

To study the relationship between the growth behavior of allotriomorphic ferrite and alloying element distribution near interfaces, some samples were provided. The samples were made by austenitizing Fe-0.12C-2.0Mn (mass%) by keeping it at 1373 K for 60 s, by isothermal holding at 973 K (isothermal holding time was 30, 300, 3000, and 10000 s), and then by quickly cooling it. The Mn concentration distribution near the growth ends of ferrite grains was measured by STEM-EELS. The results are shown below.<sup>8)</sup>

In EELS measurement, because electron beams spread in samples due to scattering or samples slightly move during measurement, influence by such movement needs to be reduced as much as possible. Samples need to be made thinner to reduce the spread of electron beams. However, if they are too thin, quantitative evaluation of them takes more time and thereby the samples may move more during measurement. In this measurement, therefore the thickness of samples was 20 to 30 nm. This measurement was accurate such that the Mn concentration was approximately 0.2 mass% for accumulation of 16 s. Regarding the movement of the samples in the measurement, as the drift speed gradually decreases from when the samples were set in the measuring position, the measurement was started after a drift speed of less than 0.3 nm/16 s. Figure 1 shows measured EELS spectra from 580 to 740 eV. An aberration corrected STEM (Titan 80-300 Cubed made by FEI) was used for the EELS. In these experiment results, the Mn concentration was assessed at an accuracy of  $\pm 0.2$  at%.

Figure 2 shows STEM images near interfaces of the four samples described above and the sections at which alloying element concentration distribution was measured. The measurement direction was from the ferrite side to the austenite side perpendicular to







Fig. 2 STEM images near ferrite/martensite interfaces and positions of EELS measurement

the ferrite/austenite interfaces. Letters "a" to "d" in the images indicate the samples held for 30, 300, 3000, and 100000 s, respectively. Number "1" in the images indicates that the STEM images are in the wide view. Number "2" indicates that the images are enlarged ones of the measured sections. The letter "a" indicates ferrite, "M" indicates martensite, and "RA" indicates residual austenite.

As mentioned above, the areas for which signals were obtained were wider than the size of the incident electron beams because the incident electron beams spread and the samples moved. Other factors to expand the measurement range are the convergent angle of the incident electron beams, EELS acceptance angle, and the fact that the interfaces and electron beams were not completely parallel at the interfaces. In this paper, all the factors mentioned above are referred to as broadening factors.

The formula (Doig, et al.)<sup>9)</sup> below was used for the scattering of the electron beams in the samples.

 $I(r, t) = I_e \{\pi(2\sigma^2 + \beta t^3)\}^{-1} \exp(-r^2/(2\sigma^2 + \beta t^3))$  (1) Where, "*T*" is the intensity of the electron beams to the distance from the center of the electron beams (*r*) and the depth of the sample (*t*), "*I*<sub>e</sub>" is the total intensity of the electron beams, " $\sigma$ " is the diameter of the incident electron beams. " $\beta$ " can be calculated using the formula below.

 $\beta = 500 (4Z/E_0)^2 (\rho/A)$  (2) Where, "Z" is the mean atomic number, " $E_0$ " is the acceleration voltage, " $\rho$ " is the atomic density, and "A" is the atomic weight. In addition, the electron beams' convergent angle was 24 mrad and the EELS acceptance angle was 15 mrad. The sample drift was 0.3 nm for a single measurement point.

Figure 3 shows the distribution of the electron beam intensity to the depth of the samples in consideration of the broadening factors described above. This figure shows that the electron beams widely spread in the samples and thereby the broadening factors have a greater effect as the samples are thicker. Therefore, the obtained experimental results show blunted profiles compared to the true concentration profile, so the results need to be corrected to obtain true concentration distribution.

In order to obtain the true concentration profile, a model profile was created first and then the broadening factors were convoluted with the model profile to obtain blunted distribution. If the blunted distribution matches the experimental results, the model is possibly the true distribution.

**Figure 4** shows the results of EELS measurement at the sections shown with the straight lines in Fig. 2 (a-2) to (d-2) and the model profile with the broken lines along with the blunted profile with the



Fig. 3 Electron beam expansion in the specimens

solid lines. Letters "a" to "d" indicate the samples held at 973 K for 30, 300, 3000, and 10000 s, respectively. The experimental results and the solid lines almost match, so the model profile is possibly the true concentration distribution.



Fig. 4 Concentration profiles measured by EELS and corrected profiles

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Figure 4(a) shows that no interface segregation nor partition occurred on the sample held for 30 s. This means that the moving rate of the interface was fast enough, so the scattering of Mn could not maintain pace with the moving of the interface. Therefore, on the sample held for 30 s, the ferrite grains possibly grew in the PE mode.

Figures 4(b) to (d) show that on the samples held for 300 s and longer, Mn segregated at the interfaces and the segregation volume increases as the retention time increases. On the sample held for 300 s, no Mn partition occurred, so the grains possibly grew in a growth mode like paraequilibrium while being influenced by the SD effect using the grain boundary segregation.

In addition, on the samples held for 3 000 s or longer, Mn thickening is seen on the martensite or austenite (MA) structure side. This shows the Mn partition to austenite occurred. Therefore, on the samples held for 3 000 s or more, the ferrite grains possibly grew in the LE mode.

The results above show that, in the growth processes of ferrite grains, not only the mode transits from PE to LE, but also there is probably an RE mode with SD effect between those two modes.

## 3. Measurement of the Concentration Distribution of Mn and Mo Near Bainite Interfaces

When Fe-0.1C-2.0Mn-0.5Mo (mass%) is retained from the austenite range at 823 K, bainite (B) transformation begins in a few seconds after the retention. Approximately 60% transforms in approximately 60 s. After that, the transformation does not progress and even when the sample is held for 1 800 s, the transformation rate remains at 60%.<sup>10</sup> Meanwhile, when a sample similar to the composition above but without Mo is used for a similar experiment, the bainitic transformation progresses to almost 100% without stasis. Therefore, this transformation stasis is probably due to the influence of Mo.

If bainitic transformation stasis is due to the SD effect by grain boundary segregation of Mo, Mo must have been segregated to grain boundaries (interfaces) between bainite and austenite in a sample immediately after stasis so that SD can significantly hinder the interfaces from moving. Accordingly, the concentration profile of Mn and Mo was measured near interfaces to bainite grains and austenite grains using STEM-EDS before transformation stasis, immediately after the stasis, and during the stasis. The results are shown below.

First, we explain how a TEM sample of bainite grains was created. **Figure 5** shows how a TEM sample of a bainite grain was created. A bainite grain is a hexahedron enclosed with parallelograms and it grows such that the direction <111> becomes the major axis. Therefore, when the surface of a bainite grain faces the direction <111>, the bainite grain will be enclosed with interfaces that grow slower than the growth of the major axis. Interfacial segregation tends to occur when the travel speed of interfaces is slower. If interfacial segregation of Mo is not detected on the slowest interface, that means no such segregation could be detected on the faster interfaces.

Figure 5 (b) is a crystal orientation map obtained by the electron backscatter diffraction (EBSD) method. As shown in Fig. 5 (b), a bainite grain for which the surface almost faces the direction <111> was selected and a TEM sample was created in parallel to the surface. Figure 5 (c) is a STEM image of the white-circled area of the TEM sample in Fig. 5 (b). The interface in the longitudinal direction of the obtained TEM sample was the slowest to grow. This interface was measured by the STEM-EDS.

The amount of Mo added to the sample used in this experiment was only 0.5 mass% (0.3 at%), so accumulation was required until sufficient Mo signals were detected. Figure 6 shows the spectra ob-



Fig. 5 Making method of TEM specimen of bainite grains



Fig. 6 EDS spectrums with different Mo concentration (a)–(c) show EDS spectrum with 0.5, 1.0, and 1.5 mass% Mo concentrations, respectively.





tained by the EDS. The aberration corrected STEM (Titan 80-300 Cubed made by FEI) of Nippon Steel & Sumitomo Metal was used for the EDS measurement at an acceleration voltage of 80 kV.

Figure 6 shows EDS spectra of samples for which the concentration of Mo is 0.5, 1.0, and 1.5 mass%, accumulated for 20 s at an acceleration voltage of 300 kV. The figure shows that a slight Mo peak was detected on the 0.5 mass% Mo sample. Therefore, to detect whether Mo thickened, accumulation for 20 s is required for each point.

Figure 7 shows STEM images near bainite interfaces and EDS measurement results. Figure 7(a) shows the results for a sample held for 10 s. Figure 7(b) shows those for one held for 60 s. Figure

7(c) shows those for one held for 1800 s. The sub-numbers "-1" to "-3" in the figures indicate that the results are from the measurement of the lines numbered 1 to 3 in the figures.

Figure 7 shows that no segregation of Mn and Mo is seen at the interface on the sample held for 10 s. For the sample held for 60 s, it seems that a small amount of Mn enriched near the grain boundary, but Mo did not enrich. On the other hand, on the sample held for 1800 s, Mn and Mo thickened at the interface. Because Mo did not thicken on the sample held for 60 s, the transformation stasis of samples with Mo added cannot be explained by the SD effect of interfacial segregation of Mo.

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### 4. Conclusion

This paper showed the measurement results of the concentration profile of alloying elements added to steel samples using the aberration corrected STEM-EELS and EDS in nanometers and at the atomic scale to show that quantitative analysis of alloying elements at the atomic scale using TEM is useful to clarify the phase transformation mechanism.

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