Quantitative and microscopic analytical technique of trace carbon and its application on microstructural analysis of dual phase steels

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Abstract: A quantitative microanalytical technique for trace carbon in steel materials was proposed. Effects of anti-contamination devices (ACDs) on the formation of hydrocarbon contamination during electron-beam irradiation were investigated. We found that specimen heating during a measurement was the most effective technique for suppressing contamination. Contamination-free carbon mapping in a µm scale was achieved with the proposed technique. This technique was applied to analyses of carbon distribution in dual-phase (DP) steels. Experimentally obtained carbon concentration in martensite phase corresponded well to that of thermodynamic simulation. This implies that the actual dynamics of transformation interface is well described by local equilibrium theory.

1. INTRODUCTION

The element carbon critically affect phase transformation and the microstructural formation of steel materials. However quantitative microanalysis of carbon is difficult when an electron probe is used. This difficulty is caused by contamination which forms under the electron-beam irradiated area on the specimen surface. The origin of this contamination are hydrocarbon molecules in the vacuum chamber of the microscope or that on the specimen surface. The carbon component of the contaminant becomes the dominant source of carbon signals from the specimen. Thus, analysis of trace carbon is difficult, even by qualitative carbon analysis. To overcome the contamination problem, some techniques have been proposed, such as a liquid nitrogen (LN2) trap or a plasma cleaner. A LN2 trap is used for capturing residual gas in the vacuum chamber. A plasma cleaner dissociates contaminant molecules. In spite of these efforts, few reports are found about quantitative microanalysis of carbon in an electron microscope [1]. To date, only quantitative line analysis has been performed. Quantitative map analysis has not been achieved due to unavoidable contamination, even though the map analysis is very important to understand carbon distribution in steel microstructure. To enable quantitative microanalysis of carbon in steel, we developed an original field-emission gun electron probe microanalyzer (FE-EPMA) equipped with various anti-contamination devices (ACDs). The installed ACDs are a LN2 trap, a plasma cleaner, and a specimen heating system for use during measurement. The concept of this microscope is reported elsewhere [2]. The individual effects of the above-mentioned ACDs were investigated in a scanning electron microscope (SEM) or a transmission electron microscope (TEM). However the practical effects of using these in combination for the sake of quantitative analysis of carbon have not been studied yet. In this report, we investigated effects of the ACDs and their combination. A technique for quantitative map analysis of trace carbon will be proposed. It was applied to an analysis of phase transformation in dual-phase (DP) steels. The results were compared with a thermodynamic phase transformation simulation.

2. EXPERIMENTAL PROCEDURE
2.1. Effect of ACDs

The ACDs used in this study were a LN2 trap, a plasma cleaner, and a specimen heating system. The plasma cleaner was installed in the measurement chamber of the FE-EPMA. Its working time was

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set to 5 min to clean both the chamber and specimen surface. The specimen heating system can maintain a constant temperature on the specimen surface with the original heating holder. The target temperature was set to 373 K during measurement. The intensity of the C-K characteristic X-ray from a pure iron sheet was measured to investigate the effects of the above-mentioned ACDs. Since the specimen does not contain the element carbon, the emitted X-ray should be a continuous X-ray as background at the wavelength of the C-K characteristic X-ray. Thus an increment of the detected intensity can be regarded as an increment of contamination on the specimen surface. The specimen was mirror-polished with alumina suspension. The polished specimen was cleaned in an ultrasonic bath with alcohol. It was dried with hot air and then set into the heating holder. The EPMA measurements were performed with an acceleration voltage of 7 kV and a probe current of 50 nA. Three wavelength dispersive spectrometers were simultaneously used for the detection of the C-K characteristic X-ray in order to maximize sensitivity. The increment of X-ray intensity from the same point was measured with a dwell time of 10 s for point analyses. Map analyses were performed for 20 x 20 μm^2 area with a dwell time of 50 ms and a pixel size of 256 x 256.

2.2. DP steels

The chemical compositions of the steel sheet used in this study are shown in Table 1. They were held at an austenitizing temperature of 1223 K for 10 min. Isothermal transformation was promoted at an intercritical temperature of 1073 K or 1023 K for 15 s or 1800 s, and then it was quenched.

Table 1. Chemical composition of studied materials (mass%).

steel	C	Si	Mn
A	0.15	2.0	1.5
B	0.20	2.0	1.5
C	0.15	2.0	2.0

The specimens were cut into small pieces and their cross sections were mirror-polished. They were cleaned in the same manner as the above-mentioned pure iron specimen. EPMA measurements were performed with an acceleration voltage of 7 kV and a probe current of 50 nA. The LN2 trap, plasma cleaner, and specimen heating system were used as ACDs. Carbon concentration was quantified by the calibration curve method. The dynamics of the phase transformation of the materials were calculated by DICTRA software which simulates the diffusion controlled phase transformation [3]. The Ferrite phase of 1 nm width was set as the boundary position of a simulated cell of 10 μm width as the initial condition. The time evolution of the interface position and the local chemical composition were simulated. A TCFE7 database was used for the thermodynamics parameters. An MOB2 database was used for mobility parameters.

3. RESULTS AND DISCUSSION
3.1. Effect of ACDs

The changes in the intensity of the C-K characteristic X-ray from pure iron are shown in Fig. 1. The lines of the LN2 trap and the plasma cleaner showed increments in the X-ray intensity. They increased with the increase in the number times of analysis. Thus, it can be seen that the LN2 trap or the plasma cleaner – used alone or in combination – cannot suppress contamination completely. The lines of specimen heating showed a constant value even if the analysis was iterated. Specimen heating is the most effective technique in point analysis for supressing contamination. Although the LN2 and plasma cleaner could not prevent contamination during iterative analyses, the first measurement provided a similar intensity among the tested ACDs. Thus, single point analysis gives a reliable value without any contamination artefacts. When iterative analyses are performed, specimen heating is the only technique to suppress contamination.
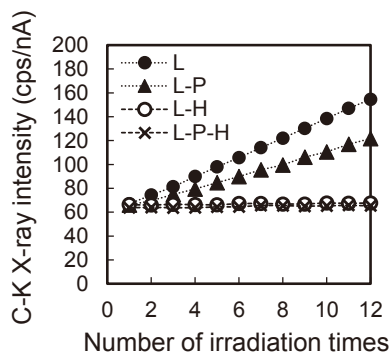
Figure 1. C-K X-ray intensity as a function of number of analysis times. L, P, and H stand for LN2 trap, plasma cleaner, and specimen heating respectively.

Figs. 2 shows the result of map analysis. The intensity increments due to contamination appeared in the horizontal and vertical profiles of the LN2 and plasma cleaner, while a constant intensity was obtained for the case of specimen heating. Specimen heating during map analysis has a significant effect in suppressing contamination as well as during point analysis. On the other hand, the intensity increased after the second map analysis. This indicates that specimen heating suppresses and retards contamination formation. However this technique cannot remove contamination that is formed during the analysis. Thus a strategy for quantitative map analysis of carbon is to use specimen heating and to obtain map data with a single scan. The mechanisms of contamination suppression was discussed elsewhere [4].
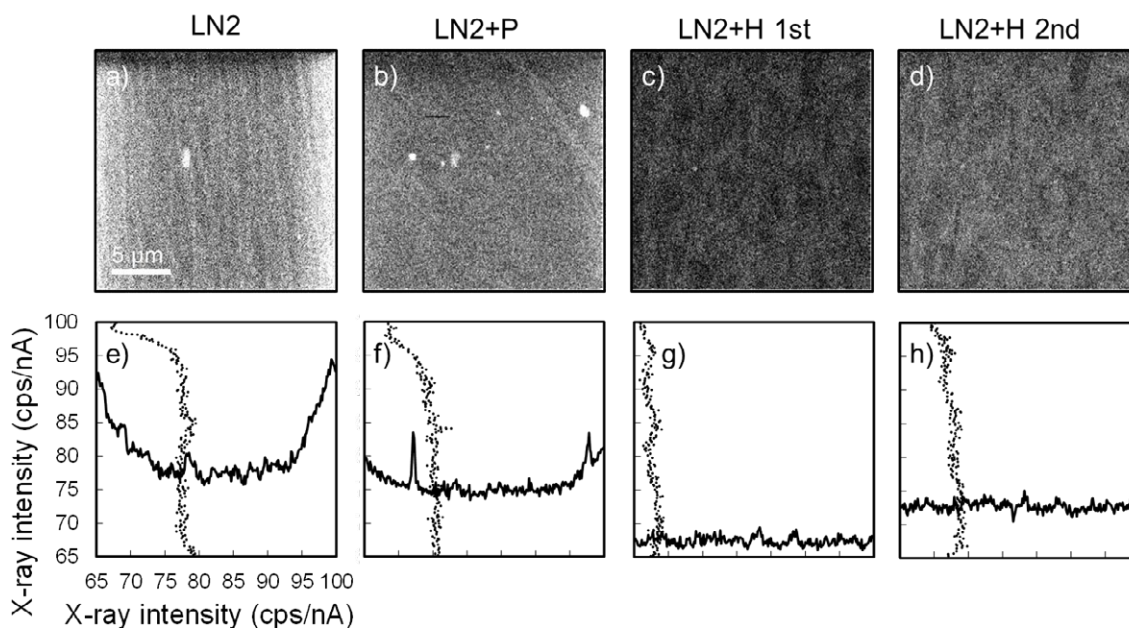

Figure 2. a-d) Carbon elemental map with various ACDs. d) is the map results of the second analysis for the identical area of c). e-h) Horizontal and vertical line profiles of elemental map.

Generally, the contamination rate varies according to specimen treatment, instrumental conditions, and other unknown factors. Thus, linearity between carbon concentration and the measured intensity of carbon is poor due to different contamination levels. The proposed analytical technique here, specimen heating and single analysis, provides highly accurate and precise results for trace carbon measurement. Figure 3 shows an example of the calibration curve for carbon quantification with this technique. It showed good linearity. We also find that the variance is very small for each measurement. Quantified values of carbon concentration have reproducibility and can be compared with those of different specimens.
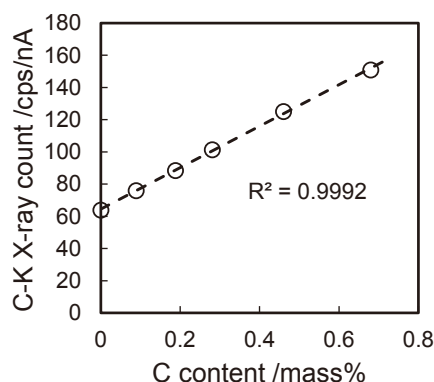
Figure 3. Calibration curve of carbon concentration and intensity of C-K characteristic X-ray. The LN2, plasma cleaner, and specimen heating were used as ACDs.

3.2. Application to DP steels

Figure 4 shows a quantitative carbon map and the result of a DICTRA simulation for steel A with a holding temperature of 1023 K for 15 s. The carbon concentration in the ferrite was small. In addition, it was highest at ferrite-martensite interface. It gradually decreased across the martensite grain. These features appear clearly on the map. These carbon profiles are caused by the ejection of carbon from ferrite into austenite through the interface and the diffusion in austenite. Quantified carbon profiles was correspond approximately to the DICTRA results. However the map showed that local carbon concentration depend on grains or grain boundaries. They cannot be represented by the unique profile given in the DICTRA results. This indicates that the actual mobility of the interface is variable. Quantitative carbon measurement in 2 dimensions and mesoscopic scale is important to understand phase transformation.
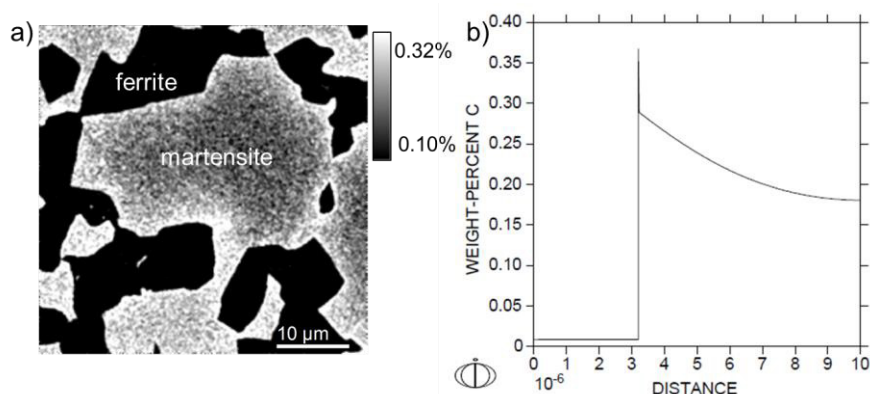

Figure 4. a) Quantitative carbon map of steel A for holding temperature of 1023 K for 15 s. b) Simulated carbon profile of steel A at holding time of 15 s.

While carbon profiles were variable at the initial stage of transformation, they became more constant at the stage of holding time of 1800 s. Carbon concentration in martensite grains were almost the same except for fine grains. This being the case, the carbon concentration in martensite of steel A, B, and C were evaluated and compared to that of the simulated values given by DICTRA. The results are shown in Fig. 5. They corresponded well. Here, the DICTRA simulation assumes local equilibrium at the interface. The consistency of experimental and simulation values shown in Fig. 5 implies this local equilibrium assumption is reasonable. Since carbon is an interstitial element and its microanalysis had been difficult, a detailed experimental validation for the theory had not been carried out. The proposed technique will introduce new insights in this field [5].
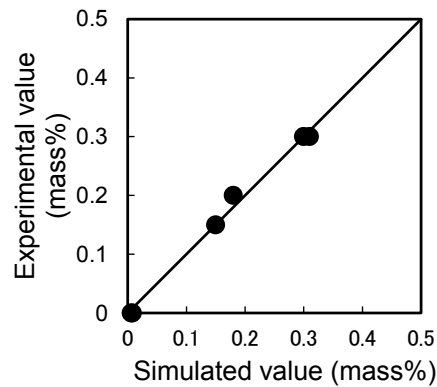
Figure 5. Comparison of carbon concentration in austenite (martensite) between DICTRA simulation and experimental values for steel A, B, and C.

4. CONCLUSION

Effect of ACDs were investigated for the sake of microanalysis of carbon in steel materials. The specimen heating technique has a significant effect on contamination suppression. Single analysis with specimen heating as an ACD will give reliable quantitative values of local carbon concentration. This technique was applied to the study of the transformation of DP steels. The quantified carbon concentration agrees with local equilibrium theory.

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