Determination of carbon distributions in quenched and partitioned microstructures using nanoscale secondary ion mass spectroscopy

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A multi-modal characterization technique, which combines nanoscale secondary ion mass spectroscopy (Nano-SIMS) with a spatial resolution of ~100 nm and electron back scatter diffraction (EBSD) to determine carbon distributions in austenite and martensite in a quenched and partitioned (Q&P) Fe-0.29C-2.95Mn-1.59Si steel is presented. Significant carbon enrichment of austenite was measured with decreased levels of carbon in martensite, supporting the carbon partitioning mechanism. Fresh untempered martensite could be identified, and different degrees of enrichment were observed for blocky and lath austenite.

Keywords: Nano-SIMS, carbon partitioning kinetics, Quenching and Partitioning.

Carbon is a very effective austenite stabilizer, and carbon partitioning from martensite into austenite has been proposed as a mechanism to enrich austenite with carbon thereby stabilizing retained austenite at room temperature for advanced high strength steels with lean alloy compositions. The quenching and partitioning (Q&P) process was proposed based on this mechanism to generate multi-constituent microstructures containing elevated austenite volume fractions at room temperature [1-3]. The Q&P process consists of three distinct steps: (1)

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reheating to form austenite in the intercritical temperature region or above the A_3 temperature; (2) quenching to a temperature between the martensite start (M_s) and finish (M_f) temperatures to generate a partially martensitic, partially austenitic microstructure; and (3) isothermal holding (i.e., the partitioning step) at the quench temperature or at an elevated temperature, aiming at carbon enrichment of austenite through carbon depletion of martensite. Significantly elevated austenite volume fractions have been observed in Q&P steels in a number of studies [2,3,4-8]. Higher carbon contents in austenite due to carbon partitioning have also been reported using different experimental techniques, including X-ray diffraction (XRD) [4,5,7], neutron diffraction [9], and differential scanning calorimetry [10]. Computational methods have been adopted to understand the carbon redistribution across the phase interfacial region during partitioning [11,12]. Recently, there have been reports based on atom probe tomography (APT) measurements on carbon partitioning in Q&P steels [3,6,7,13,14] and on alloying element distributions in nano-crystalline bainitic steels [15-18]. APT is well known for its high spatial resolution and analytical accuracy, and can be used to investigate the local distributions of various alloying elements within sub-nanometer scale composite structures. However, as a consequence of the small sampling area and time-consuming sample preparation process, applications of APT to assess overall carbon distributions in different phases in a complex microstructure, such as in Q&P steels, have been limited.

Nanoscale secondary ion mass spectroscopy (Nano-SIMS) has been adopted as an alternative experimental technique in various steel studies to assess elemental distributions within a rather large area (i.e., region with several or tens of grains) [19-22]. However, since the Q&P process produces much more complex microstructures than those considered in previous steel studies [19-22], Nano-SIMS alone is not capable of quantifying the carbon distributions among different

phases. In the present study, a multi-modal characterization technique, which combines Nano-SIMS and electron back scatter diffraction (EBSD), was applied to determine the overall carbon distributions in austenite and martensite in a Q&P steel.

Square coupons ($\sim 25 \text{ mm} \times 25 \text{ mm}$) of 1 mm thick cold rolled Fe-0.29C-2.95Mn-1.59Si alloy were reheated to 820 °C for 120 s, quenched to 180 °C and held for 10 s followed by a partitioning step at 400 °C for 100 s in molten heat treating salts. The reheating step has been shown to result in full austenitization, and the quenching temperature of 180 °C is close to the calculated optimum quenching temperature for maximum retained austenite stabilization [5].

The austenite volume fraction and average austenite carbon content were determined using XRD. Sample was prepared by light grinding, followed by chemical thinning using a mixture of 50 parts 30% hydrogen peroxide, 1 part hydrofluoric acid, and 50 parts water. Data were obtained with a Philips X-pert diffractometer operating at 45 kV and 40 mA, using an X'celerator detector, filtered copper radiation, a 1 degree slit, and a two-theta scan from 40 to 105 degrees. The retained austenite volume fraction was calculated according to the SAE method [23] based on the integrated intensities of four austenite peaks: {111}, {200}, {220}, {311}. EBSD were also performed with a field emission scanning electron microscopy (SEM) on a $25 \mu\text{m} \times 25 \mu\text{m}$ area, using a $0.04 \mu\text{m}$ step size and an accelerating voltage of 20 kV, for phase identification and austenite fraction determination.

Nano-SIMS with a resolution of $\sim 100 \text{ nm}$ was conducted at different locations within a metallographic mount to determine the carbon content distributions in the Q&P steel. A Cameca NanoSIMS 50L spectrometer (AMETEK, Inc - CAMECA SAS, Paris, France) was used in this study. A $\sim 1.0 \text{ pA}$ Cs^+ beam (16 keV) was focused onto a $\sim 100 \text{ nm}$ sized spot and rastered over a

10 μm $\times$ 10 μm area. Secondary ions of $^{12}\text{C}^-$ and $^{28}\text{Si}^-$ were simultaneously detected using two separate detectors. 256 $\times$ 256 pixels per frame were used for all images. Each measurement consisted of 10 consecutive frames, and each frame took $\sim$ 131 s duration. A $\sim$ 10 nm Au film was first coated onto the polished sample to reduce any possible charging. Pre-sputtering was required to remove surface contamination including Au-coating, and to prepare a mature crater with adequate Cs implantation. Pre-sputtering was carried out on an area of $\sim$ 12 μm $\times$ 12 μm to avoid crater effects in the analysis area.

For possible identification of fresh untempered martensite, EBSD was then performed on the same surface area previously analyzed by Nano-SIMS. No further surface modification (i.e., additional polishing) was performed, thus preserving the microstructural features analyzed by Nano-SIMS. EBSD was employed on a slightly larger area than the Nano-SIMS scan, using a 0.05 μm step size and an accelerating voltage of 20 kV.

The average austenite carbon content obtained from XRD was 1.13 wt%. The resulting austenite volume fraction was significant and depended on measurement technique, namely 13.8% from XRD and 21.4% from the EBSD analysis. The discrepancy in the two measured austenite volume fractions can be attributed to the accuracy and limitation of the two experimental techniques as well as inhomogeneous microstructural characteristics of the Q&P steels. A calculation of austenite stabilization assuming “idealized” carbon partitioning where full carbon depletion of martensite occurs along with homogeneous carbon distribution in austenite yields $\sim$ 25% volume fraction [5]. This may suggest that less austenite is stabilized and that full carbon depletion was not obtained for the employed partitioning conditions. In addition, a competing phenomenon such as carbide precipitation may have occurred, decreasing the effective carbon content available to enrich and stabilize austenite.

Figure 1a shows a SEM image obtained from the in-plane cross-section after etching with 2% nital. The microstructure contains multiple refined constituents with characteristic lengths less than approximately 3 μm . These constituents include austenite, tempered (or partitioned) martensite, and untempered martensite formed on cooling from the partitioning temperature. In Figure 1a, the “unraised” fine features (identified by arrow **M**) are interpreted to be tempered martensite and, among the “raised” features, the thin-film like grains (arrow **A**) are interpreted to be austenite. The larger constituents (arrow **M/A**) are interpreted to be austenite, untempered martensite, or a mixture of both. Note that the micrograph does not exhibit substantial fractions of bainite, and the 3 wt% Mn contained in the alloy may have delayed bainite formation.

Figures 1b and 1c show the results obtained from Nano-SIMS scans for one scanned location, respectively representing the carbon and silicon counts in gray scale within the region. In general, much sharper distribution contrasts and more detailed features can be observed in Figure 1b than Figure 1c, indicating that carbon exhibits much faster diffusion kinetics than silicon at the partitioning temperature. Local APT measurements on a grain-size region within Q&P microstructures suggest that silicon may have very uniform distributions [7,13]. However, the Nano-SIMS scan in Figure 1c indicates that silicon may also show heterogeneous distributions (i.e., segregation) when a larger area is examined, potentially resulting from earlier processing (i.e., solidification). Figure 1d shows the color coded carbon distribution in wt%, created from the carbon count map in Figure 1b by assuming the average carbon count from the image is consistent with the bulk carbon content (i.e., 0.3 wt%). It appears in Figures 1b and 1d that significant carbon enrichment occurred in austenite whereas carbon depletion occurred in martensitic regions.

Figure 2a shows the SEM image for the area analyzed by the Nano-SIMS, designated by a red dashed box and the subsequent EBSD scan region designated by a black dashed box. Figure 2a also contains the phase map and the grain orientation map, generated from EBSD analysis, with the Nano-SIMS area designated by the dashed red box in each map. In the phase map, red color dots indicate the austenite phase and green represents the martensite phase. The austenite volume fraction estimated from this phase map (i.e., 15.4%) is lower than the previous EBSD measurement. The difference between the two EBSD measurements may reflect the effects of the adopted step sizes, scanned locations and the sample surface conditions.

Figure 2b overlays the Nano-SIMS gray scale carbon count image on the EBSD phase map, and the comparison helps to identify the high carbon content phases shown in Figures 1b and 1d. In Figure 2b, the relatively high carbon content regions are observed to mostly correspond to the austenite phase in the phase map whereas the regions with reduced carbon levels correlate primarily with martensite. The austenite phase has a wide range of carbon contents (e.g., 0.4~1.8 wt%) since the red-dotted grains in Figure 2b are covered in various colors in the corresponding carbon content map as shown in Figure 1d. Note from Figure 2b that some portions of high carbon content regions, for example, denoted by the black arrows in the figure, appear to be martensite. This indicates that two different martensite types exist in the Q&P microstructure: high carbon content martensite (e.g., 0.3~0.4 wt%) and low carbon content martensite (e.g., ~0.1 wt%). The high carbon content martensite is the fresh untempered martensite formed during the final cooling process, and the lower carbon content martensite is the initially formed and carbon depleted martensite (i.e., tempered martensite). Although the untempered martensite may result in lower indexing quality in EBSD due to its high dislocation density, it will not be indexed as

austenite because martensite and austenite have different crystal structures. However, the two martensites are not readily distinguished from each other by EBSD alone.

Line scans were produced to examine in detail the carbon distributions in different regions of the Q&P microstructure. The specific locations are identified in Figure 3a, and Figures 3b, 3c and 3d show the carbon distribution profiles for the three selected scan locations. For reference, the horizontal black line indicates the bulk carbon content. The carbon content in austenite is quite inhomogeneous within a grain as well as among different grains, and varies widely in the range between 0.4 wt% and 1.8 wt% as indicated in Figures 3b, 3c and 3d. Inhomogeneous carbon distribution within an austenite grain is possibly due to limited carbon diffusivity in austenite. The slight difference in the austenite carbon contents measured from XRD and Nano-SIMS can be attributed to differences in local carbon content of the material, the adopted resolution of the Nano-SIMS as discussed below and the semi-quantitative nature of the technique.

Note that microstructural features which can be analyzed by Nano-SIMS are limited due to the specific spatial resolution of the Nano-SIMS selected for use. Here, the adopted resolution was ~100 nm, thus composition variations within features less than this size cannot be resolved and would only be reflected in the average composition within the specific regions containing smaller features. For example, the presence of very thin austenite films or an array of fine carbides would contribute to carbon signals that are reflected in the overall average martensite carbon content. This limitation may partially contribute to the lower carbon content measured in the thin austenite and the higher carbon content measured in the tempered martensite. Also, high carbon-concentration interfacial-segregated regions between austenite and martensite (~10 nm or less), which have been shown by APT [6] and associated calculations [12] in Q&P steels, would

be below the limit of detection by Nano-SIMS. Thus high interfacial carbon concentration peaks are absent from the line scans shown in Figure 3. As a consequence, the center of some austenite regions exhibits a higher carbon content than the interface, which appears inconsistent with finer resolution APT observations.

For carbon depletion, the Nano-SIMS results indicate that carbon depletion in martensite under the employed partitioning condition is slower than predicted by diffusion calculations for supersaturated ferrite. Note that the calculations for the idealized carbon partitioning [1], precluding other competing phenomena (e.g., bainite formation, carbide precipitation), predict almost full carbon depletion in martensite within relatively short time periods (i.e., < tens of seconds) even with consideration of the mobile austenite/martensite interface [12,24]. Bigg et al. [9] suggested that much of the carbon does not partition to the austenite, using in-situ neutron diffraction experiments in evaluating the microstructural evolution during partitioning. The high dislocation content of the martensite may slow down diffusion kinetics by carbon trapping thereby affecting carbon depletion [15]. It may be suspected that the presence of fine carbides may contribute to the carbon content measured in the martensite due to the adopted Nano-SIMS resolution. It can be noted that carbon is measured to be present in the martensite of Q&P steels with APT [3,6,7,13,14]. Inhomogeneous carbon distribution in martensite can be possibly attributed to inhomogeneous carbide distribution within martensite grains.

The line plots and carbon maps also show an apparent morphology (or size) dependence of measured carbon concentration, namely carbon content in thin austenite film-like structures appears to be lower than the amounts observed in the relatively large-sized blocky austenite grains. For instance, line scan 2 in Figure 3 shows that, between scan positions 1.0 to 2.0 μm and between 6.5 to 8.5 μm on the x-axis (arrow A), the measured carbon contents are much

higher than the bulk carbon content. In contrast, a number of the thin austenite regions with scan widths of 0.5 to 1 μm in line scans 1 and 3 (arrow B) have much lower peak carbon contents. Based on comparison with Figure 3a, the regions at 8.5 μm and 10.5 μm in line scan 3 (arrow B) may indicate the carbon content for thin austenite films, which is about 0.4 wt%. This is a significantly lower level compared to those in other blocky austenite regions as observed in other regions of the line scans, indicating that carbon diffusion kinetics in different phases during partitioning is not only dependent on the local composition, but also on local morphology. A similar morphology-dependence of carbon content was also reported for a Q&P microstructure in Xiong et al. [8].

Compared with APT, the Nano-SIMS technique provides several distinct advantages to assess alloy redistribution during partitioning in Q&P steels. First, a much larger surface area is analyzed. Second, sample preparation follows the same procedures required for preparing metallographic mounts for EBSD analysis, and thus the sample preparation procedure is easier. Also, the ability to utilize SEM and EBSD to analyze the same area evaluated by the Nano-SIMS provides a direct correlation of the microstructural constituents with the measured composition maps. Although the Nano-SIMS has a rather coarse spatial resolution for examining some fine features in Q&P microstructures, it is a very useful tool to examine the overall carbon content distributions within complex Q&P and other multi-phase steel microstructures.

In summary, the present contribution utilized Nano-SIMS with a spatial resolution of ~ 100 nm to determine the carbon distribution in a Q&P microstructure. Significant carbon enrichment of the austenite was measured whereas carbon levels below the nominal bulk carbon concentration were measured in martensitic regions. The presence of carbon in the martensite

may suggest trapping and slower carbon transport than predicted for supersaturated ferrite. The present study showed that Nano-SIMS is a highly capable technique to evaluate solute distribution including carbon and silicon within fine-grained multi-phase steels. Direct microstructure-level carbon distribution characterization may provide information that can assist in optimizing the heat treatment parameters to achieve the desired level of austenite stability through carbon partitioning and enrichment.

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Figure 1. (a) SEM micrograph of a Q&P steel (A, M, M/A represent austenite, tempered/partitioned martensite and mixture of austenite and untempered martensite, respectively). (b) Carbon ($^{12}\text{C}^-$) counts, (c) silicon ($^{28}\text{Si}^-$) counts per pixel and (d) color coded carbon distribution in wt% from Nano-SIMS.

Figure 2. (a) EBSD results for location investigated using Nano-SIMS and (b) overlay of carbon count image from Nano-SIMS on EBSD phase map.

Figure 3. Line scans of carbon distributions.

Figure 1
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Figure 2
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Figure 3
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