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

Kyoo Sil Choi,[a,*] Zihua Zhu,[a] Xin Sun,[a] Emmanuel De Moor,[b] Mark D. Taylor,[b] John G. Speer[b] and David K. Matlock[b]

[a]Pacific Northwest National Laboratory (PNNL), P.O. Box 999, Richland, WA 99352, USA
[b]Advanced Steel Processing and Products Research Center (ASPPRC), Colorado School of Mines, Golden, CO 80401, USA

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.

© 2015 Published by Elsevier Ltd. on behalf of Acta Materialia Inc.

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) 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 (~25 mm × 25 mm) of 1 mm thick cold rolled Fe–0.29C–2.95Mn–1.59Si alloy were reheated to

---

* Corresponding author. Tel.: +1 509 372 6967; fax: +1 509 372 4720; e-mail: kyoosil.choi@pnnl.gov

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° slit, and a two-theta scan from 40° to 105°. 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 μm × 25 μm area, using a 0.04 μm step size and an accelerating voltage of 20 kV, for phase identification and austenite fraction determination.

Nano-SIMS with a resolution of ∼100 nm was conducted at different locations within a metallographic mount to determine the carbon content distributions in the Q&P steel. A Cameca NanoSIMS 50 L spectrometer (AMETEK, Inc – CAMECA SAS, Paris, France) was used in this study. A ∼1.0 pA Cs^+ beam (16 keV) was focused onto a ∼100 nm sized spot and rastered over a 10 μm × 10 μm area. Secondary ions of $^{12}C^-$ and $^{28}Si^-$ were simultaneously detected using two separate detectors. 256 × 256 pixels per frame were used for all images. Each measurement consisted of 10 consecutive frames, and each frame took ∼131 s duration. A ∼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 ∼12 μm × 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 ∼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 "un-raised" 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.

Figure 1b and c 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 Figure 1b and d that significant carbon enrichment occurred in austenite whereas carbon depletion occurred in martensitic regions.
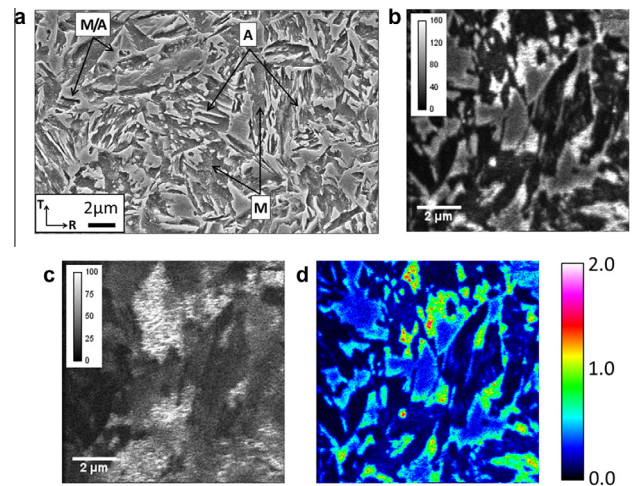
Figure 1. (a) SEM micrograph of a Q&P steel (A, M, M/A represent austenite, tempered/partitioned martensite and mixture of austenite and untempered martensite, respectively). (b) Carbon ($^{12}C^-$) counts, (c) silicon ($^{28}Si^-$) counts per pixel and (d) color coded carbon distribution in wt.% from Nano-SIMS. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)