Carbon Atom Re-Distribution during Quenching and Partitioning

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Quenched and Partitioned (Q&P) steels have been shown in previous literature to exhibit attractive mechanical properties due to austenite and martensite present in the microstructure. However, questions have remained regarding the mechanisms at work during the partition step. In this work, x-ray diffraction and atom probe tomography were utilized to gain insights into phenomena that occur (such as carbon partitioning from martensite to austenite, carbon atom clustering/dislocation trapping, and carbide formation). Evidence of all of these mechanisms was observed.

KEY WORDS: quench and partition; carbon diffusion; martensite; austenite; atom probe tomography.

1. Introduction

Quenched and partitioned (Q&P) steels have been shown to exhibit attractive combinations of mechanical properties due to retained austenite present in the microstructure along with their martensitic nature. Q&P steels are processed via the thermal profile shown (schematically) in Fig. 1(a). The steel is heated to the austenitizing temperature above the A3 temperature to create a fully austenitic microstructure or to a temperature between A1 and A3 temperatures to create a microstructure of austenite and intercritical ferrite. Next, the steel is quenched to a temperature between the martensite start and martensite finish temperatures (well above room temperature). This creates a controlled mixture of martensite and austenite (and any intercritical ferrite formed at the austenitizing temperature). The steel is held at the quench temperature (1-step Q&P) or some elevated temperature (2-step Q&P) to allow carbon to partition from the as-quenched martensite into the austenite. The carbon that enriches the austenite has the effect of stabilizing the austenite (for example, the Ms is lowered) such that the austenite is stable at room temperature. Additionally, competing reactions may take place during the partition step. These competing reactions include conventional tempering reactions, carbon atom trapping at defects as well as iron carbide precipitation in the martensite, decomposition of austenite into other transformation products such as bainite (which can also promote carbon enrichment of austenite), and/or interface migration.

The goal of this work was to study the mechanisms that might occur during partitioning treatment of steel, in particular for the work presented here, to understand the extent of carbon partitioning from martensite to austenite and to understand the extent of conventional tempering reactions that might also occur (including carbon atom trapping at defects in the martensite and carbide formation). The alloys used in this work were designed to stabilize a significant fraction of austenite at room temperature. This allowed for the quench temperature in the Q&P process to be equal to room temperature. In previous Q&P research, the quench temperature was required to be much higher than room temperature (at least 100°C) in order to maintain sufficient fractions of retained austenite upon the completion of quenching (Fig. 1(a)). This elevated quench temperature has not allowed for in situ characterization of the steel after quenching and prior to partitioning. Therefore, many previous studies have had difficulties trying to characterize the microstructural changes during the partitioning step. In this work, because significant fractions of austenite were stable at room tem-

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perature after the initial quench, the thermal profile shown in Fig. 1(a) could be modified such that it looks like that shown in Fig. 1(b). The thermal profile shown in Fig. 1(b) allows for room temperature characterizations of the steel to be made prior to partitioning, then again upon the completion of the partitioning step so that comparisons of the microstructure before and after the partitioning step could be made using x-ray diffraction (XRD) and atom probe tomography (APT) techniques. A similar study using a model steel alloy has been recently published by Toji et al.1

2. Experimental Procedure

2.1. Materials and Heat-Treatment

The steel used for this study was laboratory cast and hot-rolled to 2.54 mm thickness. The steel contained 0.31C-13.95Ni-1.91Si-0.24Mo (wt pct) as measured by LECO carbon analysis and optical emission spectroscopy. The martensite start temperature of this steel was measured using Gleeble dilatometry and found to be 258°C. Salt-pot furnaces (containing various mixtures of barium chloride, potassium nitrate, and sodium nitrite) were used to heat-treat the material according to the designed Q&P thermal profile described in Fig. 1(b). The samples were austenitized at 875°C for 300 seconds and the quenched into water to room temperature. Some samples were left in this as-quenched condition for comparison. Further, some samples were reheated to 200, 300, or 400°C for 30, 60, 100 or 1 000 seconds. This is referred to the partitioning step. After the partitioning step, the samples were quenched in water to room temperature. The partitioned sample will be designated with the partitioning temperature, and partitioning time (e.g. 400°C-100 s).

2.2. Transmission Electron Microscopy (TEM)

TEM analyses were performed to characterize the evolution of microstructures during Q&P treatments. In particular, TEM analyses were performed to identify carbides within the microstructure and to further characterize the morphology of martensite and austenite. Transmission electron microscopy was performed with a Philips CM-120 operating at 120 kV accelerating voltage or a Philips CM-200 operating at 200 kV accelerating voltage. Samples were prepared for TEM by electropolishing or focused ion beam (FIB) milling. Electropolished samples were prepared by mechanical grinding to make a foil approximately 100 to 130 microns thick. Discs were punched from the foil with a diameter of 3 mm. The discs were electropolished until perforation at room temperature with a mixture of 95% acetic acid and 5% perchloric acid. The electropolishing was performed with approximately 25 millicamperes and 30 volts.

2.3. X-ray Diffraction (XRD)

X-ray diffraction was used to estimate the retained austenite fraction and average lattice parameters of austenite and martensite. XRD was performed with nickel-filtered copper radiation using a Philips X-pert diffractometer operating at 45 kV and 40 mA and equipped with an X’celerator detector with a 1 degree slit. Samples were ground to remove surface oxides and chemically thinned for approximately 15 minutes in a water-cooled container of 10 parts water: 10 parts 30% hydrogen peroxide: 1 part hydrofluoric acid. Flat samples were scanned through a 2-theta range from 40 degrees to 105 degrees at a rate of 0.052° per second. Four austenite peaks (i{111}, {200}, {220}, and {311}) and four martensite peaks (i{110}, {200}, {211}, {220}) were quantified and the austenite fraction was estimated using the SAE method. Based on measurements made on a standard sample with a known austenite fraction similar to those measured on the samples of interest, it is estimated that austenite volume fraction measurements were accurate within 1% austenite. The austenite lattice parameter for each sample was calculated based on the positions of the {220}γ and {311}γ peaks. The carbon content of the austenite was estimated using the expression given by Santofimia et al.4 which combines data from van Dijk et al.4 and Dyson and Holmes,5 and goes as:

$$a_\gamma = 3.556 + 0.00453x_C + 0.000095x_{\text{Mn}} + 0.00056x_{\text{Al}} + 0.0006x_{\text{Cr}} - 0.0002x_{\text{Ni}}$$

(1)

Here $a_\gamma$ is the lattice parameter of the austenite in nanometers, and $x_C$, $x_{\text{Mn}}$, $x_{\text{Al}}$, $x_{\text{Cr}}$, $x_{\text{Ni}}$ are the concentrations of carbon, manganese, aluminum, chromium, and nickel, respectively, in wt pct. The martensite lattice parameter for each sample was calculated based on the positions of the {211}α' and {220}α peaks. The carbon content of the martensite was estimated using the equation given by Vogel,

$$a_\alpha = 0.2863 + 0.0030x_C$$

(2)

Where $a_\alpha$ is the lattice parameter of the martensite in nanometers, and $x_C$ is the carbon content in percent. Vogel derived this expression from those of Roberts.7 Vogel’s method was used because it allows for the estimation of carbon content of martensite that does not show tetragonality (within the resolution of the XRD system). The carbon concentration for martensite and austenite was assumed to be that of the bulk for samples which were austenitized and quenched. A constant was added to each of the calculated values to account for the effects of substitutional alloying elements on the lattice parameter such that the carbon concentrations of the as-quenched phases were forced to be equal to the bulk.1

2.4. Atom Probe Tomography (APT)

Atom probe tomography was used to observe the location of alloying elements in 3-dimensions and to measure local carbon concentrations in martensite and austenite. Samples were prepared for APT analysis by electropolishing or focused ion beam (FIB) lift out. The samples that were electropolished were first sectioned into wires with a square cross-section of approximately 300×300 microns. The samples were then electropolished using the standard two stage method in which the first electrolyte used was a mixture of 75% acetic acid and 25% perchloric acid, and the second electrolyte used was a mixture of 98% 2-Butoxyethanol and 2% perchloric acid. The samples that were prepared by FIB lift out were first observed by electron-backscatter diffraction (EBSD) using a Nordlys high sensitivity camera in a

1 If any carbon re-distribution takes place during quenching or aging at room temperature, this assumption would not be strictly valid.
Zeiss Nvision 40 SEM workstation equipped with a field emission gun to identify regions of interest (ROI) that contained austenite in the form of a film-like morphology). Selected ROI’s were lifted out as 20×2 μm² walls about 2 μm thick, using a Kleindick micromanipulator. EBSD was used again to precisely locate austenite regions, which were ion-milled to 2×2×5 μm³ blanks. These blanks were attached to a pre-sharpened support tip. Finally, annular milling was performed to create APT needles from these blanks using a Orsay Physics column installed in a Leo 1530 SEM. Care was taken to keep the austenite regions at the apex of prepared APT specimens.

APT samples were analyzed with an energy compensated wide angle tomographic atom probe (ECoWATAP) in the electric mode. Voltage pulses corresponding to 20% of the standing voltage were applied to the specimen at a frequency of 30 kHz at a temperature of 80 K. The instrument is equipped with an advanced delay line detector (ADLD). The data were analyzed and displayed using software developed at the University of Rouen, France. Natural isotopic ratios were used to ascertain the peak assignments. At 6 and 12 Da, only atomic carbon was detected (peaks at 6.5 and 13 Da representing 1% of the 6 and 12 Da ones). The peak at 18 Da is assigned to carbon trimers (C3) doubly charged. The presence of a minor peak at 18.5 Da representing 2.8% of the peak at 18 Da confirms this classical assignment. A minor peak at 36 Da was assigned to singly charged carbon trimers. This could not be confirmed by the 37 Da peak which is at the background noise level. The peak at 24 Da was assigned to singly charged dimers because of the absence of any peak at 24.5 Da (that should be 4% of the peak at 24 Da if only doubly charged quadrimers would be detected). As a consequence, impacts at 6, 6.5, 12 and 13 Da were counted as one single C ion, impacts at 18, 18.5 and 36 Da to three carbon ions, and impacts at 24 and 25 Da to two carbon ions. It should be noted that this specific assignment is only valid for austenite, and would be different in other phases, such as carbides or ferrite.

3. Results and Discussion

Figure 2 shows a bright field TEM image of the steel after austenitization and water quenching. The figure shows lath martensite and an absence of carbides which was representative of all regions of interest observed. Figure 3 shows a bright field image after partitioning for 100 s at 400°C. The image shows laths and packets of martensite within prior austenite. The features identified as “A” in Fig. 3 are likely transition carbides (ε or η carbides). Figure 4 shows a high magnification bright field and dark field image of the interior of a lath of martensite that exhibits features that might be transition carbides. Similarities of the diffraction patterns between the various transition carbides, and the fine size of the features present make unambiguous identification of the transition carbide difficult; however, it is thought that the features are most likely ε-carbide or η-carbide.

Fig. 2. Bright field TEM image after water quenching. The image shows the primarily lath-like morphology of martensite and an absence of carbide formation quenching to room temperature.

Fig. 3. Bright field TEM image after partitioning at 400°C for 100 seconds. Image shows laths and packets of martensite along with clear evidence of prior austenite grains. The regions marked with “A” show evidence of carbide formation.

Fig. 4. TEM images after partitioning at 400°C for 100 seconds. (a) Bright field image. (b) Dark field image using carbide reflection.
carbide based on morphology. A large number of interplanar spacings are associated with cementite; therefore, it can be difficult to exclude cementite using diffraction data.\textsuperscript{9) However, cementite is not expected to form due to the high level of silicon.\textsuperscript{10,11) Cementite in tempered martensite typically exhibits a distinctive plate-like morphology with three variants; not observed in the present microstructures.}

3.1. X-Ray Diffraction (XRD)

The austenite fractions as a function of partitioning time are shown in Fig. 5. The austenite fractions were essentially constant with partitioning times up to 1 000 seconds for partitioning temperatures of 200, 300, or 400°C. Figure 6 shows the lattice parameters of martensite and austenite. Recall that the austenite fraction was not substantially influenced by partitioning in this alloy. The samples partitioned at 200°C do not seem to show much variation with partitioning time. However, there seems to be an expansion of the austenite lattice parameter with partitioning time for the samples partitioned at 300 and 400°C (the samples partitioned at 400°C show the most pronounced and faster effect). Barring any significant partitioning of substitutional elements (see APT results presented later), the change in lattice parameters can be related to changes in carbon concentrations through Eqs. (1) and (2). The estimated carbon concentrations are shown in Fig. 7. As seen in the figure, austenite is enriched with significant amounts of carbon in the first 30 seconds of the partitioning step at a temperature of 400°C. Austenite is enriched with significant carbon for partitioning times up to 1 000 seconds for the sample that was partitioned at 300°C. The carbon content of the martensite seems to decrease slightly during partitioning at these temperatures. The carbon enrichment of the austenite might be considered as a direct proof of carbon partitioning. Further evidence that the change in lattice parameter is the result of carbon partitioning is supported by literature reports that nickel decreases the austenite lattice parameter.\textsuperscript{2–4) Nickel is an austenite stabilizer, thus it would tend to partition into austenite (not out of it). Therefore, nickel partitioning into austenite cannot be used to explain the increase in the lattice parameter of austenite. Therefore it is very likely that the effect observed is a direct result of carbon enrichment of austenite via partitioning from martensite. APT techniques were used to verify this conclusion and are discussed below.

Figure 8 shows the result of carbon mass balance calculations performed after partitioning for various times at various temperatures. The calculations account for carbon in the samples contained in martensite and austenite and are based on the martensite and austenite fractions shown in Fig. 5 and carbon concentrations of austenite and martensite shown in Fig. 7. The calculations were performed by multiplying the fraction of a phase by its carbon content and then adding them together giving the total carbon concentration. Recall, that the carbon content of “as-quenched” martensite and austenite were assumed to be that of the bulk and all of the results were adjusted to force this condition. Further, the carbon mass balance only considers austenite and martensite. Thus, any carbon that is “lost” during the partitioning step might be the result of the formation of
another carbon containing phase such as carbides. However, the phase fraction of such carbides is expected to be so low, that direct observation was not possible via XRD methods. Nonetheless, the analyses shown in Fig. 8 suggest that carbide formation likely occurred during the partitioning treatment. The analysis suggests that the most carbides were formed at 200°C and the least carbides were formed at 400°C. This might be due to the relative stability of carbide as a function of partitioning temperature. Thus, at 400°C more carbon partitioned into austenite as compared to at 200°C more carbon was trapped as carbide.

### 3.2. Atom Probe Tomography (APT)

Atom probe tomography (APT) techniques were used to confirm that the carbon content of both phases in the as-quenched state was that of the bulk alloy, that austenite was enriched with carbon after partitioning and that martensite was depleted of carbon after partitioning. Additionally, APT was used to gain some insight into some tempering reactions that might occur (such as carbon atom clustering, carbon trapping at dislocations, and iron carbide precipitation) and could account for the loss of carbon previously observed.

### 3.3. APT Analysis of the As-quenched Condition

Figures 9 and 10 show carbon distribution maps of as-quenched martensite. The distribution of carbon was inhomogeneous and the figures show significant evidence of carbon atom clustering. As these samples were not tempered, this carbon ‘clustering’ must have occurred sometime after the martensitic transformation, by carbon atom diffusion during quenching (i.e. autotempering) or by carbon diffusion at room temperature. Table 1 shows the compositions of the analyzed volumes shown in Figs. 9 and 10. As seen in the table, the concentrations of substitutional elements are approximately those of the bulk alloy, as expected for low Ms alloys. The carbon concentrations were found to be slightly lower than those of the bulk. This might indicate some carbon has left martensite (for austenite or carbide) during autotempering or holding at room temperature. It should be noted that these values are obtained on small volumes (2.5×10⁻⁴ μm³), and that they could be due to macro-segregation effects. Significantly more analyses would be necessary to study this issue in more detail.

### 3.4. APT Analysis of Partitioned Condition

Figures 11 and 12 show carbon distribution maps of volumes of materials that were collected in martensitic regions after partitioning for 100 seconds at 400°C. The figures show that carbon is not homogeneously distributed and show regions of very high concentration of carbon atoms. The carbon contents of the features observed were measured between 6 and 9 atomic percent. These carbon concentrations are considerably lower than the ideal compositions of ε, η carbides or cementite (~33, ~29, or ~25 at pct C, respectively). Thus, further investigation of measured carbon concentrations is warranted. Nonetheless, these observations indicate the occurrence of carbon atom clustering or early carbide formation; this is further supported by TEM analysis.
discussed above.

Figure 13 shows the results of APT performed on a sample that was prepared using EBSD and FIB techniques to ensure that austenite was present within the analyzed volume. It is evident that austenite is carbon enriched relative to martensite. Figure 13 shows the location of a volume along which the concentration profiles were measured. Figure 15 quantifies the concentration profiles along the volume that starts in austenite and ends in martensite as shown in Fig. 13. The concentrations shown in Fig. 15 were calculated over slices 0.1 nm in thickness with no overlapping. The concentration profiles of substitutional elements clearly indicate that no partitioning of Ni and Si between austenite and martensite occurred. Carbon is significantly enriched in austenite and significantly depleted in martensite relative to the bulk carbon composition. This is strong evidence of carbon partitioning from martensite to austenite during the partitioning step.

XRD analysis presented above also showed significant enrichment of austenite after partitioning treatments relative to martensite. Figure 13 shows the location of a volume along which the concentration profiles were measured. Figure 15 quantifies the concentration profiles along the volume that starts in austenite and ends in martensite as shown in Fig. 13. The concentrations shown in Fig. 15 were calculated over slices 0.1 nm in thickness with no overlapping. The concentration profiles of substitutional elements clearly indicate that no partitioning of Ni and Si between austenite and martensite occurred. Carbon is significantly enriched in austenite and significantly depleted in martensite relative to the bulk carbon composition. This is strong evidence of carbon partitioning from martensite to austenite during the partitioning step.

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to the as-quenched state. The absolute magnitude of carbon enrichment estimated by XRD was much less than that measured by APT, however, the same trend was observed. The reasons for measured differences are unclear, however, may be related to assumptions made to convert austenite lattice parameters to carbon contents. Nonetheless, both methods, XRD and APT, have shown compelling trends to support the theory that carbon partitions from martensite to austenite.

4. Conclusions

XRD analyses have shown direct evidence of carbon partitioning from martensite to austenite when treated at 300 and 400°C. This result is in agreement with that shown by Toji et al.\textsuperscript{1)} Further, mass balance calculations using phase fractions and carbon concentrations estimated from XRD data indicate that carbides in these steels likely form in the martensite for all partitioning treatments at 200, 300, or 400°C for times up to 1 000 seconds. APT analyses have confirmed the XRD analysis that demonstrated the carbon partitioning mechanism. Additionally, APT analyses have shown evidence of carbon atom ‘clustering’ in martensite and tempering phenomena (i.e. carbide formation) during the partitioning step. Thus, carbon partitioning from martensite to austenite and tempering phenomena are not mutually exclusive and occur simultaneously in these steels.

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