Characterization of Transition Carbides in Quench and Partitioned Steel Microstructures by Mössbauer Spectroscopy and Complementary Techniques

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Abstract

Quenching and partitioning (Q&P) produces steel microstructures with martensite and austenite that exhibit promising property combinations for third generation advanced high strength steels. Understanding kinetics of reactions that compete for the available carbon, such as carbide formation, is critical for alloying and processing design and achieving austenite enrichment and retention during Q&P. Mössbauer effect spectroscopy (MES) was used to characterize Q&P microstructures in a 0.38C-1.54Mn-1.48Si wt. pct. steel after quenching to 225 °C and partitioning at 400 °C for 10 or 300 s, with an emphasis on transition carbides. The recoilless fraction for η -carbide was calculated and a correction for saturation of the MES absorption spectrum was applied, making quantitative measurements of small amounts of η -carbide, including non-stoichiometric η -carbide, possible in Q&P microstructures. Complementary transmission electron microscopy confirmed the presence of η -carbides, and MES and x-ray

diffraction were used to characterize the austenite. The amount of η -carbide formed during Q&P ranged from 1.4 to 2.4 at. pct., accounting for a substantial portion (~24 to 41 pct.) of the bulk carbon content of the steel. The amount (5.0 at. pct.) of η -carbide that formed after quenching and tempering (Q&T) at 400 °C for 300 s was significantly greater than after partitioning at 400 °C for 300 s (2.4 at. pct.), suggesting that carbon partitioning from martensite to austenite occurs in conjunction with η -carbide formation during Q&P in these specimens.

1.0 Introduction

Advanced High Strength Steels (AHSS) are becoming increasingly important for automotive applications as a means to affordably reduce weight and improve passive vehicle safety [1]. Third generation AHSS property targets may be achieved by microstructures containing martensite and retained austenite [1,2]. Quenching and Partitioning (Q&P) has been proposed as a novel heat treatment to produce these microstructures [3,4]. The process consists of intercritical annealing or full austenitization, quenching to a quench temperature (QT) between the martensite start (M_s) and finish (M_f) temperatures, holding at a partitioning temperature (PT) the same or greater than the QT, followed by final quenching to room temperature [3,5]. The goal of the heat treatment is to promote carbon (C) partitioning from martensite to austenite, thereby stabilizing the austenite to prevent transformation during the final quench [5,6].

A quench temperature selection methodology was developed by Speer *et al.* [4,7,8] to predict stable austenite volume fractions as a function of QT and assumes that all of the available C in the martensite partitions to the austenite. This methodology has proven effective for calculating QTs corresponding to maximum austenite fractions. Experimental austenite fractions are often observed to be lower than calculated [5,9] values, which may be related to incomplete partitioning and competing tempering mechanisms, such as C trapping at defects [10], C clustering [11], and cementite and/or transition carbide (e.g., ϵ or η) formation. Transition carbide formation is thought to be particularly influential for two reasons: 1) the QTs and PTs (typically in the range of 140 to 400°C [5,12]) and the relatively short partitioning times (typically 10 to 300 s) are within the reported time-temperature domain for transition carbide formation [10,13-15] and 2) alloying additions of silicon (Si) appear to be less effective at

suppressing transition carbide formation [2,8,15,16] than cementite [6,15,17,18]. However, no quantitative studies on the amount of carbide formation during Q&P processing are available in the literature, due to the difficulties associated with measuring them, albeit qualitative observations have been made [8,19].

The small volume fractions and numerous overlapping peaks [20] associated with transition carbides makes quantitative x-ray diffraction (XRD) analysis difficult. The small volume fractions, morphology (e.g., typically thicknesses below 50 nm), and complex electron diffraction patterns also make transmission electron microscopy (TEM) challenging. Atom probe tomography (APT) provides local chemistry, but without complementary structural information, identification of carbide type is uncertain, especially since the role of alloying elements on transition carbides remains unclear [11]. Alternatively, Mössbauer effect spectroscopy (MES) is well suited for the study and identification of carbides. Most MES studies of transition carbides have focused on quench and tempered (Q&T) microstructures and Fe-C steels with C in the range of 5 to 7 at. pct. (1.2 to 1.6 wt. pct. C) [13,21]. In contrast, Q&P compositions typically contain lower C contents, different alloying element additions, and substantial amounts of retained austenite in the microstructures, resulting in more complex MES spectra and lower carbide fractions near the resolution of MES. Furthermore, the recoilless fraction, a fundamental parameter in quantitative MES analysis, is unknown for transition carbides. The recoilless fraction is related to the binding energy between the iron (Fe) atom and neighbor atoms, and theoretical studies based on density functional theory (DFT) indicate that the elastic stiffness of η -carbide is significantly greater than that of austenite or martensite [22-24], suggesting that the recoilless fraction of transition carbides must be determined for quantitative analysis.

The goals of the present study are to: 1) develop a methodology to measure small amounts of carbides (approximately 1 at. pct.) using MES, 2) validate the methodology through qualitative correlation with microstructural characterization by TEM and C content measurements by XRD, 3) quantify the amount and types of carbides that are forming during Q&P processing of an experimental steel and 4) compare the carbide formation in Q&P and Q&T microstructures to further explain the details of the partitioning process in this steel.

2.0 Experimental Procedure

A 0.38C-1.54Mn-1.48Si wt. pct. (1.71C-1.52Mn-2.86Si at. pct.) steel sheet of 1 mm thickness was received in the cold rolled condition. Coupons approximately 3 cm² were heat treated using molten salts. All samples were austenitized at 820 °C for 120 s, followed by five different thermal treatments selected to observe the microstructure evolution. The heat treatments, designated WQ, Q&P1, Q&P2, Q&P3 and Q&T, consisted of a direct water quench, one step Q&P involving a short equilibration at the QT, Q&P with a short partitioning time, Q&P with a long partitioning time, and Q&T, respectively, and are listed in Table 1 and shown schematically in Figure 1. The salt pot used for the QT was set to 205°C to achieve a sample temperature (as measured by a thermocouple spot welded to each sample) of 225°C after 10 s. The QT was selected to achieve the maximum retained austenite fraction from the QT selection methodology [4,7,8], although an experimental exploration of austenitizing, quench, and partition temperature variations to optimize the Q&P processing was not performed in this study. Room temperature (RT) water was used for the final quench.

XRD samples were prepared using conventional metallographic techniques, finishing by chemical polishing with a solution of 10:10:1 de-ionized water: hydrogen peroxide (70 pct. water:30 pct. H₂O₂):hydrofluoric acid (52 pct. water:48 pct. hydrofluoric acid) for 15 minutes. TEM foils were prepared by grinding 3 mm discs to a thickness of approximately 90 µm. Each disc was electropolished to electron transparency at RT with an electrolyte of 5 pct. perchloric and 95 pct. acetic acid using a twin jet electropolisher. Samples for MES were prepared by chemical thinning from 1 mm to ~100 µm with the same solution composition used for the XRD samples. Samples were further thinned to 26-32 µm by gentle grinding using water lubrication to ensure uniform thickness. No significant heating or cooling of the samples above or below RT occurred during sample preparation.

XRD measurements were conducted with Cu-K_α radiation in a conventional $\theta/2\theta$ diffractometer in the symmetric Bragg-Brentano mode. The graphite monochromator was on the detector side of the sample. Data were collected in a step-scan mode with a step size of 0.05° 2 θ and time per step of 10-60 s. Peak fits were performed with a non-linear least-square fitting routine and the Pearson VII function. The carbon content in the austenite of the Q&P samples was calculated from lattice parameter variations, assuming that changes in the lattice parameter

were due to carbon and no partitioning of substitutional elements during the heat treatments (i.e., $(x_{Fe}/x_j)_{bulk} = (x_{Fe}/x_j)_{austenite}$, where x_{Fe} and x_j are the molar fractions of Fe and any substitutional element j , respectively). Two relationships proposed by Cheng *et al.* [25] were employed: 1) a least-squares fitting of the austenite lattice parameter (determined from XRD) as a function of C content in as-quenched martensite was used to determine C content in sample Q&P1. The relationship assumes the austenite is under strain and is valid for C contents up to ~8 at. pct, and given in Equation (1):

$$a_\gamma(\text{\AA}) = 3.553 + 1.05x_c + 0.1x_{Mn} \quad (\text{\AA}) \quad (1)$$

and 2) a relationship for strain free austenite, consistent with previous investigations on samples partitioned at 400 °C [6,26], was used for samples Q&P2 and Q&P3, where the lattice parameter of pure austenitic Fe was determined by extrapolation of the austenite lattice parameter of Fe-Mn specimens to zero Mn content. The dependence of C content was established from elevated temperature data after correction for thermal expansion, as given in Equation (2):

$$a_\gamma(\text{\AA}) = 3.573 + 0.75x_c + 0.1x_{Mn} \quad (\text{\AA}) \quad (2)$$

where x_c , and x_{Mn} are the molar fractions of the elements. The coefficient for Mn was taken from Dyson and Holmes [27], while Si was assumed to have a negligible influence on the lattice parameter [27]. The lattice parameters for the (111), (200), (220) and (311) reflections were plotted against $\cos^2\theta/\sin\theta$, with the precise lattice parameter obtained by extrapolation to $\cos^2\theta/\sin\theta=0$. The fractions of ferrite (e.g., martensite) and austenite in the microstructures were obtained using the integrated intensities of the (110), (200), (211) and (220) ferrite and the (111), (200), (220) and (311) austenite reflections in accordance with SAE SP-453 (or the abbreviated description [28]).

A Philips CM-200 TEM operated at 200 keV and a FEI TF30 TEM operated at 300 keV were used for detailed microstructural characterization. Bright field (BF) and dark field (DF) imaging were performed and selected area diffraction (SAD) patterns were obtained for structural characterization. SAD patterns were simulated using Desktop Microscopist software from Lacuna Laboratories.

MES spectra were acquired at 296 K with a ^{57}Co -Rh source using a spectrometer operating in the triangular constant acceleration mode. Each sample was mounted on a 6.35 mm collimator for all measurements. A Kr-filled proportional counter and a Wissel data acquisition

module (CMCA-550 USB) were used to collect and sort the data into 1024 channels. Both the 1.8 keV Kr escape peak and the 14.4 keV gamma ray were counted using the two-window pulse-height analysis capability of the module. Samples were run until sufficient counting statistics were obtained (an off-resonance baseline of $\sim 1\text{-}3 \times 10^6$ counts per channel). Velocity calibration and the isomer shift zero value were established with a pure bcc (α)-Fe foil (28.5 μm). The counts for each channel (velocity) were normalized (with respect to the total baseline counts) and subspectra were fit to the normalized data using Lorentzian line shapes with WinNormos V3.0 coupled with the IGOR Pro V6.3 software package.

Magnetic six line components (sextets) were used to fit the resonance from martensite and carbide signals [13,21,29,30]. The fit variables for each sextet included: the internal magnetic hyperfine field (B_{hf}), the isomer shift (IS, with respect to pure α -iron) and the quadrupole splitting (QS). The QS for each sextet is related to the individual velocity positions of the outer 4 lines by: $QS = [(V_6 - V_5) - (V_2 - V_1)]/2$, where V_1 and V_6 represent the lowest and highest velocity positions, respectively. Fit variables related to the line shapes of each sextet were: the area of peak 3 (A_3), the area ratios of lines 1 to 3 and 2 to 3 (AR_{13} and AR_{23}), the full width at half maximum (FWHM) of peak 3 (W_3 , mm s^{-1}), and the width ratios of peaks 1 to 3 and 2 to 3 (WR_{13} and WR_{23}). The shapes of lines 1, 2 and 3 are equivalent to lines 6, 5 and 4, respectively.

Single lines and/or doublets were used to fit the austenite resonance. For single lines the fit parameters are the area (A), width (W) and IS. For doublets the parameters are the area of line 1 (lower velocity line, A_1), the area ratio (AR_{21}), width of line 1 (W_1), IS, QS, and width ratio (W_{21}). AR_{21} and W_{21} allow for some asymmetry in the doublet. Further details of the austenite resonance are presented in the results and discussion section.

Sample thickness ranged from 26 to 32 μm and saturation of the absorption spectrum was observed, particularly near velocity positions associated with sites of greatest absorption [31,32]. Thickness effects were corrected using Equations (3) and (4) [33,34], which relate the resonance area to iron concentration:

$$K(T_{ij}) = \frac{2A_{ij}B}{\pi f_s \Gamma} \quad (3)$$

$$K(T_{ij}) = T_{ij} e^{T_{ij}/2} [I_0(T_{ij}/2) + I_1(T_{ij}/2)] \quad (4)$$

where A_{ij} is the resonance area of the i^{th} line of the j^{th} site (calculated from A_3 , AR_{13} and AR_{23} for

sextets and $AR_{2I}=I$ for doublets), f_s is the recoilless fraction of the source (0.78 [35]), Γ_0 is the natural line width of the Mössbauer gamma ray (0.0970 mm s⁻¹) and B is a correction factor to account for unwanted background counts falling in the pulse-height windows (the determination of which is described below). I_0 and I_1 are modified 0 and 1st order Bessel functions, respectively, and T_{ij} is the effective thickness (unitless) of the i^{th} line of the j^{th} site.

The total effective sample thickness is determined from equations (5) and (6):

$$T = \sum_j^k T_j \quad (5)$$

$$T_j = \sum_i^{\alpha_j} T_{ij} \quad (6)$$

where T_j is the effective thickness of the j^{th} site and k and α_j are the total number of sites and the number of hyperfine transitions in a particular site ($\alpha_j=6$ for magnetic components and $\alpha_j=2$ for quadrupole doublets), respectively. For a single phase absorber with a single site, T is related to the actual specimen thickness, t , by Equation (7) [33,34]:

$$T = D f x_{Fe} \rho t \quad (7)$$

where D is a constant equal to 591 cm² g⁻¹, f is the recoilless fraction of the absorber, x_{Fe} is the weight fraction of Fe in the sample and ρ is the density of the absorber. Note that $x_{Fe}\rho t$ is the Fe mass per unit area of absorber. Multiple phase absorbers with multiple Fe sites within each phase are present in the studied system. It is assumed that all Fe sites within a given phase have the same recoilless fraction, but that each phase p can have a different recoilless fraction f_p . The effective thickness of each phase, T_p , is related to the mass per unit area of Fe in phase p and recoilless fraction of phase p , f_p , according to:

$$T_p = D f_p x_{Fe,p} \rho_p t_p \quad (8)$$

where $x_{Fe,p}$ is the weight fraction of Fe in phase p . The background factor B (1.20 ± 0.02) in Equation (3) was determined by adjustment until the experimental value of T calculated using equations (3) through (6) was equivalent to the calculated T value from equation (7) for a pure α -iron calibration standard ($f_{Fe} = 0.805$ [36], $\rho_{Fe} = 7.847$ g cm⁻³ and $t = 28.5$ μ m). Care was taken to apply the thickness corrections appropriately to resolved, partially resolved or unresolved resonance lines. After correcting for absorber thickness, the relative fractions of each Fe site were determined from the relative T values and the recoilless fractions of martensite (f_m),

austenite (f_γ) and η -carbide (f_η). The determination of the recoilless fractions of each phase is detailed in the results and discussion sections below.

3.0 Results and Discussion

3.1 XRD

XRD was performed to obtain the ferrite+martensite and austenite phase fractions, austenite C content, and to aid in interpretation of the MES carbide measurements. The retained austenite fractions in samples Q&P1, Q&P2, and Q&P3 (after correction for carbide fractions obtained from MES) of 3, 15 and 10 vol. pct., respectively, are shown as a function of partitioning time in Figure 2a. The retained austenite determined by MES (after conversion from Fe fraction) is shown for comparison in Figure 2a. Samples Q&P2 and Q&P3, which were partitioned at 400 °C, contain significantly more retained austenite than the other samples. The lattice parameter and C content of the austenite, shown for the Q&P samples in Figure 2b, exhibit sharp initial increases after partitioning for 10 s at 400 °C, consistent with previous experimental observations [6,37] and theoretical calculations [38]. The data suggest that austenite enrichment and transformation are both occurring during the partitioning step. To further investigate, the martensite volume fraction (F_m) of sample WQ was fit to the Koistinen-Marburger relationship [39]:

$$F_m = 1 - e^{-b(M_s - QT)} \quad (9)$$

where the martensite start temperature (M_s) is 320 °C [40], QT is the quench temperature, and the fit yields a rate parameter (b) of 0.014. Quenching to 225 °C yields calculated martensite and austenite volume fractions of 74 and 26 pct., respectively. If the initial C content in the austenite at 225 °C is assumed to be that of the bulk, consistent with the measured austenite C content of sample Q&P1, then the total fraction of the bulk C in the austenite of samples Q&P2 and Q&P3 is 59 and 46 pct. larger, respectively, than that calculated at the initial quench to 225 °C, suggesting significant C partitioning from martensite to austenite. Peaks in the XRD pattern corresponding to η -carbide between 2θ angles of 35 and 50° [20] were only observed in sample Q&T, but quantitative analysis was not possible due to low intensities and peak broadening.

3.2 TEM Observations

TEM characterization, with an emphasis on carbide identification, was performed on samples Q&P2, Q&P3, and Q&T to determine the constituents present in the microstructure and aid in the interpretation of the MES results. Austenite and η -carbide were present in these microstructures, along with highly dislocated ferrite, which likely corresponds to martensite, although the presence of some bainitic ferrite may also be possible in Q&P microstructures [5]. Cementite was not observed in any of the samples. The SAD patterns for the orthorhombic η -carbide and hexagonal ε -carbide are difficult to distinguish [13,41]. The ε -carbide structure, with lattice parameters of c_ε and a_ε may be transformed to an orthorhombic structure with lattice parameters of $a'_\varepsilon = \sqrt{3}a_\varepsilon$, $b'_\varepsilon = c_\varepsilon$ and $c'_\varepsilon = a_\varepsilon$ [41]. Hirotsu and Nagakura [41] showed by TEM that the a, b and c lattice parameters of orthorhombic η -carbide, precipitated in a 1.13C wt. pct. steel after tempering for 1 to 100 days, differed by only -1.3, -0.8, and 2.5 pct, respectively, from the values of a'_ε , b'_ε , and c'_ε reported for ε -carbide.

Figure 3a presents a representative BF TEM micrograph of the $[100]_\alpha$ zone axis of Q&P2 that shows the presence of η -carbides. The coincident SAD pattern in Figure 3b reveals the $(-210)_\eta$ reflection and $(-110)_\eta$ superlattice reflection that arise from C ordering, consistent with previous interpretations of η -carbide [13,41,42]. The $[3-11]_\alpha$ SAD pattern from the same area as Figure 3a shows the $(210)_\eta$ and $(-101)_\eta$ reflections (Figure 3c). Between the reflections at B and D is a reflection caused by double diffraction between the carbide and the matrix. Simulation of the diffraction patterns indicates that two variants of η -carbide are present. The carbides in Figure 3a have a $(020)_\alpha$ habit plane and, in general, an orientation relationship of the type below with the matrix:

$$[001]_\eta || \langle 100 \rangle_\alpha \quad (10)$$

$$(110)_\eta || \{010\}_\alpha \quad (11)$$

The observed orientation relationship for η -carbides is consistent with that reported by Hirotsu and Nakagura [42] for a martensitic 0.45 wt. pct. C steel.

Using the ferrite (martensite) as a calibration reference, the d-spacings of the (200) and (210) η -carbide planes were measured from $\langle 100 \rangle_\alpha / [001]_\eta$ zone axis SAD patterns, like that in Figure 3b for Q&P2. The average d-spacings are compared with values from the literature for η -

carbide and the analogous (010) and (011) ϵ -carbide spacings in Table 2. The results are in better agreement with the d-spacings for η -carbide. The intensity of the fundamental η -carbide reflections relative to the superlattice reflections often varies [13,41,42], and the intensities of the superlattice reflections are often less than the calculated value, based on Fe_2C stoichiometry [42]. These discrepancies have been attributed to non-stoichiometric η -carbide [21,42], in agreement with other studies that have measured lower than expected C contents in transition carbides using atom probe tomography [6,11]. The absence and variation in the intensity of superlattice reflections have also been observed in the current work, which may indicate the presence of non-stoichiometric η -carbide. This aspect will be further discussed with respect to the MES results. Additional examples of η -carbides in multiple variants (90 degree rotation between their apparent habit planes) within the ferrite are shown in Figure 4 for Q&P2. The thickness of the η -carbides in sample Q&P2 typically did not exceed 30 nm.

η -carbide was also observed in Q&P3. Figure 5a is an off-zone axis BF image of ferrite with high dislocation density (the dislocation density is observed more clearly in other diffracting conditions not shown here). Figures 5b and 5c are $[110]_\alpha$ and $[11-1]_\alpha$ SAD patterns, respectively, generated from the area shown in Figure 5a. The SAD patterns reveal η -carbide reflections and additional reflections indexed as magnetite, consistent with Ohmori and Tamura [44] for tempered martensite. Oxidation of the sample may have occurred during sample preparation. Typical thickness of η -carbides in sample Q&P3 did not exceed 30 nm, similar to Q&P2. Although not shown here, retained austenite was also identified by electron diffraction in the Q&P samples.

The plate-like morphology of the η -carbides is shown in the BF image of the sample quenched and tempered at 400 °C for 300 s (Q&T) in Figure 6a. The DF image using the $(-210)_\eta$ reflection shown in Figure 6b shows contrast variations within the plate-like structures. These contrast variations have been interpreted in some earlier investigations to reflect the possible presence of smaller discrete carbides [13,41,42]. Figure 7a is a $[-31-1]_\alpha$ zone axis BF TEM micrograph of η -carbides from sample Q&T. SAD patterns from the same area are shown in Figures 7b (zone axis = $[-31-1]_\alpha$) and 7c (zone axis = $[-100]_\alpha$). The reflections in both figures are consistent with martensite and η -carbides. The η -carbide superlattice reflections, denoted by B, are shown in Figure 7c. The thickness of the η -carbides in sample Q&T typically ranged up to 50

nm, and these carbides were qualitatively coarser than the carbides observed in the Q&P samples.

3.3 MES Analysis

MES spectra for the five samples are shown in Figure 8. Each spectrum exhibits resonance due to martensite, austenite, and η -carbide. Stick diagrams showing representative peak positions for stoichiometric ($C(\eta_s)$) and nonstoichiometric η -carbide ($C(\eta_{ns})$) are denoted for sample Q&T. Stick diagrams representing A(0,0), A(0,n) and A(C) are shown for sample Q&P2, which correspond to Fe sites in austenite with zero C nearest neighbors (nn) and next nearest neighbors (nnn), with zero C nn but with n ($n=1, 2, 3$ or 4) C nnn [45,46], and Fe with one C nn or two C nn at adjacent sites 90° from one another [47], respectively, for sample Q&P2. For clarity, the stick diagrams of the martensite subspectra are not shown. Resonance due to transition carbides was evident in all samples, but greatest in samples heat treated for longer durations (Q&P3 and Q&T), with the Q&T sample exhibiting significantly larger fractions than the Q&P samples. The two-step Q&P heat treatments, Q&P2 and Q&P3, exhibit significantly more austenite resonance than samples WQ, Q&P1 and Q&T.

The three austenite sites were fit with two quadrupole doublets. The width and area ratios of the doublet corresponding to A(0,0) and A(0,n) were varied. Only the width ratio of the doublet accounting for resonance A(C) was allowed to vary to account for asymmetries, due to the possibility of multiple Fe sites as stated above. As presented later, low velocity scans over the range from -1.5 to 1.5 mm s^{-1} were also performed to analyze the austenite resonance in greater detail, and singlets were used to fit A(0,0) and A(0,n).

3.3.1 Determination of the Recoilless Fraction of Each Phase

The recoilless fractions for the constituent phases are necessary to quantify their relative amounts (see Equation 8). Limited experimental data on the recoilless fractions of martensite (f_m) and austenite (f_γ) for steel with similar compositions to the present alloy exist, and no experimental data is available for η -carbide (f_η). Abe and Schwartz [34] measured a recoilless fraction of 0.705 and 0.684 for martensite and austenite, respectively, for a composition of Fe-27 at. pct. Ni in both phases. Since the recoilless fraction is closely related to the binding energy of the atoms, and additions of Ni up to ~ 36 wt. pct. to Fe result in a drastic reduction in the elastic

stiffness [48,49], the values of the recoilless fractions reported by Abe and Schwartz may be significantly smaller than those for austenite and martensite in the present alloy. As an alternative, the recoilless fractions for this work were estimated from the Debye temperature [50]:

$$f = \exp \left[-\frac{3}{2} \frac{E_R}{k\theta_D} \left(1 + 4 \frac{T^2}{\theta_D^2} \right) \int_0^{\frac{\theta_D}{T}} \frac{x dx}{e^x - 1} \right] \quad (12)$$

where E_R is the recoil energy of ^{57}Fe (0.001956 eV), T is the test temperature (296 K), and k is the Boltzmann constant (8.617×10^{-5} eV K $^{-1}$). Gunkelmann *et al.* [51] calculated the Debye temperature of Fe-C martensites from elastic constants and showed that it remained nearly constant at 466 ± 5 K for C contents ranging from 0 to 2.2 at. pct. In the present work, the contributions of Mn and Si to the Debye temperature are neglected. Assuming the Debye temperature of 466 K is the same for each sample yields $f_m = 0.82$ from Equation (12). The recoilless fraction of martensite calculated here is assumed equal to the other ferritic components in the microstructures and is in close agreement with that of 0.805 ± 0.003 [36] for pure iron.

Neither the recoilless fraction, nor the Debye temperature are available for Fe-C austenite. Instead, Debye temperatures were estimated from their relationship to the mean sound velocity through the material using Equations (13-17) [52]:

$$\theta_D = K v_m \quad (13)$$

$$K = \frac{h}{k} \left(\frac{3}{4\pi V_a} \right)^{1/3} \quad (14)$$

where h is Planck's constant (6.6261×10^{-34} m 2 kg s $^{-1}$), V_a is the atomic volume and v_m is the mean sound velocity:

$$3v_m^{-3} = v_l^{-3} + 2v_t^{-3} \quad (15)$$

The terms v_l and v_t are the longitudinal and transverse sound velocities and are related to the polycrystalline elastic constants according to [48]:

$$E = 3\rho v_t^2 \left(v_l^2 - \frac{4}{3} v_t^2 \right) / (v_l^2 - v_t^2) \quad (16)$$

$$G = \rho v_t^2 \quad (17)$$

where ρ (calculated from the XRD lattice parameter and C content), E , and G are the density,

Young's modulus and shear modulus, respectively. An atomistic simulation of the elastic properties of Fe-C austenite as a function of C shows moderate increases in the Young's and shear moduli with increasing C content up to 8 at. pct. [53]. Empirical equations for the Young's modulus and shear modulus [53], along with density and composition from the XRD measurements, were used in conjunction with Equations (13-17) to determine the Debye temperatures of austenite, listed in Table 3. The calculated recoilless fraction of austenite exhibits a small increase with C content, from 0.80 for WQ to 0.82 for Q&P3, as the austenite is stabilized by C. These austenite recoilless fractions are equal to or only slightly less than that calculated for martensite, which is similar to the results of Abe and Schwartz [34], who reported the recoilless fraction of austenite was only ~3 pct. lower than that of martensite in the Fe-27 at. pct. Ni alloys.

Several theoretical studies of the structural properties of η -carbide report Debye temperatures [22-24] or elastic properties from which the Debye temperature was calculated in this work. The results are listed in Table 3. The values of E , G and θ_D for η -carbide (note: the aggregate values of E and G have been obtained by methods that average the single crystal elastic constants) are substantially larger than martensite or austenite, as shown in Table 3. Lv *et al.* [24] attributed these differences to the strong directional bonding between Fe and C that occurs in η -carbide. Consequently, the recoilless fractions f_η calculated in the present work are 0.88 (listed in Table 3), showing excellent agreement between studies, and suggests that for quantitative analysis the recoilless fraction of η -carbide should not be assumed to be equal to that of martensite or austenite. Additionally, greater than expected amounts of carbides, considering the bulk alloy C content, would be obtained using a recoilless fraction closer to that of martensite or austenite.

The thickness (μm) associated with each phase, t_p , is calculated from Equation (8) and provided in Table 4, along with the total thickness, t_{tot} (a summation of the calculated thickness of each phase). For comparison, the average sample thickness was determined while mounted on the 6.35 mm collimator for the Mössbauer measurement: the off-resonance count rate was compared to that from the 28.5 μm pure Fe foil, using the mass absorption coefficients for the 14.4 keV gamma ray of all the significant elements (Fe, Si, Mn, C) in the steel, together with the average density of the steel, ρ_a , based on the fractions of martensite, austenite and carbide from

the MES analysis, a thickness, t_{meas} , was determined [54]. The calculated t_{tot} exhibits good agreement with t_{meas} , differing on average by approximately 4 pct. However, if saturation of the absorption spectrum due to sample thickness is ignored, t_{tot} is approximately 17 pct. less than t_{meas} . Since absorption saturation disproportionately affects the martensite and austenite subspectra, it should be noted that neglecting saturation effects would result in significant overestimation of the amount of transition carbides for samples in the present thickness range (~26 to 32 μm).

3.3.2 Martensite

Numerous authors have interpreted the MES spectrum of martensite [13,46,55-60]. Resonance due to many Fe sites is observed, depending upon the condition of the martensite (fresh, aged or tempered), even in binary Fe-C martensite. For instance, Ino *et al.* [21] observed the presence of three Fe sites in freshly quenched martensite of a Fe-1.26C wt. pct. (5.6C at. pct) alloy, with the help of an externally applied magnetic field: a) Fe with no C nn, b) Fe with either a C atom in the nn tetrahedral interstitial site or the next nn (nnn) octahedral interstitial site and c) Fe with a C nn in the octahedral site along the z axis. During RT aging for 100 days, additional Fe sites appeared in the Mössbauer spectrum, which the authors attributed to the formation of an ordered Fe_4C_x ($x < 1$) phase [21]. In a similar alloy (Fe-1.2C wt. pct.), only after tempering at 250 °C for 5 h did the martensite resonance exhibit only one Fe martensite site (Fe with no C nn) [13]. The addition of substitutional alloying elements makes de-convoluting the Mössbauer spectrum more complex [57-60].

Multiple approaches to fit the martensite resonance were evaluated in the present study. Following previous work, Fe sites (Fe with zero, or various combinations of Mn, Si and C nn or nnn) with significant relative abundance were identified from binomial distributions [55,58]. The value of the B_{hf} for each site may be estimated based on experimental observations of the influence of nn and nnn Mn, Si, and C atoms [55,58]. However, attributing small amounts of resonance to Fe sites with C and/or Si/Mn nn or nnn's is complex, particularly for Fe with C neighbors, which may occur in one of three different sites [21,55] and overlap with the resonance due to other sites. For instance, Fe with both a Si and Mn nn may exhibit a similar hyperfine field as Fe with a C nn along the tetragonal axis, according to empirical relationships [55,58]. Finally, some evidence suggests that the hyperfine field of the Fe atom in the structure may be

significantly influenced by impurity atoms beyond the first and second neighbor shells [57], which further increases complexity and contradicts earlier work [58].

Alternatively, five sextets with varying hyperfine fields and other sextet fitting parameters were used to account for the total resonance of the complex distribution of Fe sites in the martensite and no attempt was made to quantitatively associate the exact configuration of the Fe sites with each resonance. This approach led to excellent fitting of the total martensite resonance, values of χ^2 less than 3.5 for the entire spectrum (an acceptable value considering the complexity of the spectrum and the high baseline levels of $\sim 1\text{-}3 \times 10^6$ counts) and stable fitting parameters, which facilitated fitting subspectra to small areas of carbide resonance. The martensite MES parameters for the WQ sample, which contained the smallest amount of carbides, along with previous MES studies on Fe-C martensite [13,21], were used to help differentiate resonance due to carbides from martensite.

3.3.3 Austenite

The austenite resonance of the Q&P steels overlaps with resonance from lines 3 and 4 of non-stoichiometric and stoichiometric η -carbide (see Figure 8), requiring accurate fitting of the austenite resonance to enable quantitative analysis of small amounts of η -carbide. Many interpretations of Fe-C austenite resonance have been proposed [13,29,45-47,61,62]. Choo and Kaplow [29] fitted the resonance of splat quenched 8.2 at. pct. C austenite with a quadrupole split doublet to account for Fe with one C nn and a central peak due to all other Fe sites. Williamson *et al.* [13] studied a 5.4 at. pct. alloy after tempering, attributed the central resonance of retained austenite to Fe sites with no C nn and further C neighbors, and improved the fitting of this resonance by employing two unresolved lines ($QS \sim 0.1 \text{ mm s}^{-1}$) of equal intensity.

Using conversion electron Mössbauer spectroscopy (CEMS), Bauer *et al.* [45] and Uwakweh *et al.* [46] suggested that the central resonance of Fe-C austenite is comprised of two components of unequal intensity: one arising from Fe atoms with no C nn or nnn, A(0,0), and a second, A(0, n), due to Fe atoms with no nearest neighbor C atoms but with n ($n=1, 2, 3$ or 4) C next nearest neighbors. The same authors [45,46] concluded that repulsion between C atoms is significant, resulting in suppression of Fe components with more than one C nn and that an ordered superstructure occurs (e.g., $\text{Fe}_8\text{C}_{1-x}$) [45,46]. Laneri *et al.* [62] also reported good agreement between the central resonance of the austenite spectra, as fit with A(0,0) and A(0, n)

components, and Monte Carlo simulations. Oda *et al.* [47] showed that additions of Mn, which have a strong affinity for C, result in significant quantities of Fe components with two C nn at 90° ($A(2C,90^\circ)$) with respect to each other, and that resonance due to $A(2C,90^\circ)$ is unresolved from that due to Fe with a single C nn ($A(C)$) [47].

In the present work, retained austenite amounts of 3.2, 12.0 and 9.2 at. pct. were obtained from the high velocity MES spectra (Figure 8) for Q&P1, Q&P2 and Q&P3, respectively. The observed trend is consistent with the XRD results (see Figure 2a), although the retained austenite amounts from MES are slightly lower, possibly due to some austenite transformation that may have occurred during preparation and handling of the foil. Low velocity MES spectra of Q&P1, Q&P2 and Q&P3, shown in Figure 9, were acquired to better interpret the austenite resonance, MES parameters, and ensure the relative fractions of the Fe sites in austenite in the more complex high velocity spectra are consistent. Fitting the central austenite resonance using two singlets: $A(0,0)$ and $A(0,n)$ [45,46,62], resulted in better fitting and lower values of χ^2 compared to fitting this resonance with a doublet of two unresolved lines [13]. A quadrupole split doublet, component $A(C)$, accounts for austenite resonance primarily from Fe with one C nn, but also from 2C nn at 90° [47]. The width ratio of the doublet corresponding to $A(C)$ was allowed to vary to account for the two components of $A(C)$, which could have small differences in the IS and QS [47]. The outer two lines in the low velocity spectra are due to the inner 3 and 4 lines of the complex martensite resonance and were fit well with three quadrupole doublets. The MES parameters (IS, QS and W_1 and W_{12}) from the low velocity spectra are listed in Table 5 and are in good agreement with other studies [13,46,47]. The fraction $r(C)$, the ratio of resonance $A(C)$ to all austenite resonance, increases significantly from Q&P1 to Q&P2, and more modestly from Q&P2 to Q&P3, consistent with the increasing austenite C content observed by XRD (Figure 2b). The fraction of Fe sites with no C nn $r(0)$ ($r(0,0)+r(0,n)$) and $r(C)$ are in general agreement with studies of binary Fe-C and ternary Fe-Mn-C alloys having Mn and C contents similar to the present alloy [46,47,62]. However, the fractions $r(0)$ and $r(C)$ are slightly larger and smaller, respectively, for Q&P2 and Q&P3 than those measured by MES for binary Fe-C steels with similar austenite C content [45,46,62]. These small differences are partially attributed to the strong attraction between Mn and C atoms, which would result in an increase in the sum of resonances due to $A(0,0)$ and $A(0,n)$ and a decrease in $A(C)$ [47].

3.3.4 η -Carbide

In previous work [13], η -carbide was identified in the early stages of tempering in an Fe-1.22C wt. pct. alloy by TEM and MES. The authors proposed two sets of MES parameters attributed to η -carbide with hyperfine fields, namely 17.8 ± 0.4 or 25.0 ± 0.5 T. Resonance corresponding to both magnetic fields increased with tempering time at 150 and 200°C at the expense of resonance attributed to Fe atoms in martensite with a C nn, consistent with the proposed 1st stage of tempering in high-carbon martensite [63]. Ino *et al.* [21] obtained the Mössbauer spectra of a martensitic Fe-1.26C wt. pct. (5.6C at. pct) alloy, finding evidence of three potential sites that could be attributed to η - or ε -carbide after aging at 140 °C (a distinction between η - or ε -carbide was not made). The magnetic hyperfine fields of the three sites are 16.7, 25.3 and 25.6 T, with the first site attributed to stoichiometric Fe₂C η - or ε -carbide and the latter two sites attributed to non-stoichiometric η - or ε -carbide. The latter sites, with similar hyperfine fields, were distinguished by significant differences in the quadrupole splitting. Le Caër *et al.* [64] noted that Fe in the stoichiometric Fe₂C η -carbide has three C nn at distances of 1.904 and 1.945 Å (two neighbors) and that, assuming no further distortion from the Fe₂C to the Fe_{2+x}C η -carbide structure, two different Fe sites with two C nn may be present in the carbon deficient η -carbide structure (one site with C nns at 1.904 and 1.945 Å and another with neighbors at 1.945 Å). Although Ino *et al.* made no distinction between the ε - or η -carbide structure, the likelihood of two different Fe sites in the C deficient η -carbide structure, and the confirmation of η -carbide by TEM in an alloy with nearly identical C content and after similar tempering treatments [13], suggests that the carbide resonance observed by Ino *et al.* was that of η -carbide.

In the present work, two magnetic components are observed and attributed to stoichiometric and non-stoichiometric η -carbide, respectively. The non-stoichiometric η -carbide, with two C nns, has Fe₃C stoichiometry [64] and non-stoichiometric η -carbide components with one or zero C nns, if present, cannot be distinguished from the martensite resonance. The non-stoichiometric Fe₃C η -carbide component is not to be confused with cementite, which was not observed by TEM and exhibits significantly different MES parameters [13]. MES parameters are reported in Table 6 and correspond to the average of the parameters measured for samples Q&P3 and Q&T and are in general agreement with those reported in the literature [13,21] (also listed in Table 6). The small differences in the MES parameter likely stem from different steel

compositions (e.g., Mn additions are known to influence the MES parameters of cementite [65]). The small resonance corresponding to non-stoichiometric η -carbide could not be resolved into two distinct resonances, as was reported in other work [21]. Certain Fe sites in the martensite of a Fe-1.64C wt. pct. (7.2C at. pct) steel aged between RT and 90 °C, which have one C nn, are reported to have magnetic hyperfine fields of 26.4 and 27.0 T [21], only slightly larger than the values of B_{hf} reported here for non-stoichiometric η -carbide. The martensite of a Fe-1.2C wt. pct. steel after tempering at 250 °C for 5 h exhibited only one Fe martensite site (Fe with no C nn) [13]. The tempering parameters associated with the heat treatments of samples Q&P3 and Q&T are slightly greater than the aforementioned heat treatment. Therefore, the MES parameters of η -carbide in the present study are only reported for Q&P3 and Q&T, since they are unlikely to be influenced by resonance from non- η -carbide components. Similarly, in the quantitative analysis of η -carbide in samples WQ, Q&P1 and Q&P2, the MES parameters of η -carbide have been fixed at the average values of Q&P3 and Q&T to more accurately distinguish η -carbide from other martensite components.

The influence of both η -carbide components on the MES spectrum is best illustrated on an expanded scale near the predominantly resolved 2 and 5 lines of each resonance. Figure 10a and b show the experimental counts, stoichiometric and non-stoichiometric η -carbide subspectra, and the fit when the η -carbide components are included and subtracted for Q&P3 and Q&T, respectively. Figure 10 reveals that the η -carbide resonance accounts for a significant portion of the total resonance near the 2 and 5 lines of both sample Q&P3 and Q&T, and is substantially larger for sample Q&T. A noticeably poorer fit and increase in the χ^2 value results from removing the carbide subspectra from the total fit.

The amount of stoichiometric, non-stoichiometric and total η -carbide for each sample are listed in Table 7 (note: Fe fractions have been converted to at. pct.). The reliability of the carbide amounts measured by MES were assessed using atomic balance considerations (total C = 1.75 at. pct.). The amount of each phase, along with the C content in the austenite and stoichiometric and non-stoichiometric η -carbide, were employed to estimate the C content remaining in solution in the martensite and any non-martensitic ferrite that may be present. The average calculated C contents of the martensite+ferrite decrease with partitioning time and are within the range bounded by the base alloy C content and the solubility limit of C in ferrite. Furthermore, the

calculated C content in the martensite of sample Q&T is 0.2 ± 1 at. pct. and is similar to that of approximately 0.3 at. pct. (determined by electrical resistivity measurements) in a Fe-0.39C wt. pct. alloy [10] after a tempering treatment (234°C for 17 h) with similar value of the tempering parameter, giving additional support to the methodologies used in the present work to measure carbide fractions.

The presence of carbides in as-quenched martensite depends upon factors such as M_s temperature, C content and cooling rate [11,66]. η -carbide was observed by TEM in 4340 steel oil quenched martensite with a C content of 0.42 wt pct., and APT qualitatively revealed further developed carbon clustering after oil quenching compared to ice-water quenching [11]. Hennessy *et al.* [66] studied carbide or carbon cluster size (no differentiation was made) in 0.56C-1.90W and 0.50C-2.05Ni wt pct. steels using small angle x-ray scattering as a function of quench rate, and reported that the size was significantly greater at a quench rate of $8,333 \text{ }^\circ\text{C s}^{-1}$, compared to quench rates ranging from 21,500 to $87,000 \text{ }^\circ\text{C s}^{-1}$. In contrast, Speich [10] found no evidence of carbide formation in TEM observations of Fe-xC ($0.026 < x < 0.57$ wt. pct) 0.254 mm thick steel sheet when quenched in iced brine (quench rate $\sim 10,000 \text{ }^\circ\text{C s}^{-1}$). In a Mössbauer study [21], 5.0 at. pct. C sheet steel of 30 μm thickness was quenched in ice water and no evidence of carbide formation was detected in the MES spectrum in the as-quenched specimens or those aged for 100 days at RT. However, ϵ - or η -carbide formed after tempering at 140 $^\circ\text{C}$ for one hour. In the present work, a cooling rate of approximately $340 \text{ }^\circ\text{C s}^{-1}$ was measured for the WQ sample in the temperature range of martensite formation. Non-stoichiometric and stoichiometric η -carbide amounts of 0.7 and 0.3 at. pct., respectively, are present in sample WQ. The slower cooling rate (relative to the aforementioned studies) likely facilitated carbide formation during the initial quench between the M_s and $\sim 140 \text{ }^\circ\text{C}$ [13,21]. In Q&P1, which was quenched to 225°C and held for 10 s, 0.5 and 1.0 at. pct. of non-stoichiometric and stoichiometric η -carbide were measured, respectively, representing a significant increase in both the amount and normalized C content (27.5 to 30.5 at. pct) of the η -carbides relative to sample WQ. The C consumed by η -carbide corresponds to approximately 27 pct. of the total C in the alloy in Q&P1, likely resulting in less C available for partitioning from martensite to austenite during the second (partitioning) step of the Q&P process. In contrast, the short characteristic diffusion distances of C in both ferrite and austenite [67], relative to the length scales of the martensite laths and interlath austenite, limit C

partitioning from martensite to austenite during the initial quench and hold at 225 °C.

No significant changes in the carbide fraction between samples partitioned at 225 °C/10 s (Q&P1) and at 225 °C/10 s and then 400 °C/10 s (Q&P2) could be inferred, within the measurement uncertainty. However, substantial C depletion in the martensite occurs during this interval primarily due to partitioning of C to austenite, suggesting the dominant mechanism for reducing the supersaturation of martensite is η -carbide formation during the initial quench and hold at 225 °C but changes to C partitioning to austenite for the first 10 s at 400 °C. An increase in the amount (1.4 to 2.4 at. pct) and normalized C content (30.3 to 30.9 at. pct.) of η -carbide occurs with partitioning time from 10 to 300 s at 400 °C. The total amount of C contained in η -carbides in samples Q&P2 and Q&P3 represents 24 and 41 pct. of the bulk carbon content, respectively, which may help explain the lower-than-calculated retained austenite fractions in the present alloy (see Table 7).

The Q&T sample tempered at 400 °C for 300 s contained 5.0 at. pct. of η -carbides which were qualitatively coarser and more C enriched (31.6 at. pct C) than the η -carbides in the Q&P samples. The η -carbide fraction in Q&P3 is substantially smaller than in the Q&T condition. Assuming similar carbide nucleation and growth in Q&P3 and Q&T, the expected range of η -carbide fraction in Q&P3 would be approximately 3.7 (i.e., 5.0×0.74) to 4.4 (i.e., 5.0×0.87) at. pct., where 0.74 and 0.87 are the initial calculated martensite fraction at the QT and final measured fraction of martensite+ferrite in Q&P3, respectively. Carbide formation in austenite is typically thermodynamically unfavorable [7] and was not observed by TEM. The measured carbide fraction in Q&P3 of 2.4 at. pct. is 35 pct. less than the lower end of the calculated range, indicating significantly less carbide precipitation following a Q&P vs. Q&T heat treatment, which may relate to disparate driving force and/or kinetics of carbide formation. Foremost, C partitioning from martensite to austenite in sample Q&P3 reduces the martensite C content, along with the driving force and rates of η -carbide nucleation and growth [68,69], and is primarily responsible for the lower carbide fractions in sample Q&P3. This understanding is consistent with the XRD results that show significant increases in the total mass of C in the austenite after the partitioning treatments. C partitioning from martensite to austenite during the 400 °C 300 s partitioning step is facilitated by, amongst other factors: 1) diffusion distances for C in ferrite and austenite that are large compared to the thicknesses of the martensite laths and

interlath austenite [38,67] and 2) a lower activation energy for C diffusion in martensite (approximately 92 kJ mol^{-1} [70]) compared to nucleation and growth of η -carbide ($102\text{-}142 \text{ kJ mol}^{-1}$ [70-72]). Additional factors, such as a slower cooling rate and smaller amounts of martensite formation during the initial quench of Q&P3 compared to Q&T may influence the dislocation density of the martensite and thereby potentially, carbide nucleation and C partitioning. For instance, dislocations are known to trap carbon and act as nucleation sites for carbides [73]. The martensite dislocation density in sample Q&P3 is expected to be lower than that of Q&T, due to the smaller differential between the M_s and initial quench temperature [74], which could conceivably reduce carbide formation kinetics.

4.0 Summary and Conclusions

Mössbauer effect spectroscopy (MES) with complementary TEM and XRD analyses have been performed to identify and quantify the carbides present in a 0.38C-1.54Mn-1.48Si wt pct. (1.71C-1.52Mn-2.86Si at. pct) steel after Q&P and Q&T. Q&P affords the creation of microstructures that contain martensite and retained austenite mixtures of interest for achieving 3rd generation AHSS property targets. This study constitutes the first MES measurements in complex Q&P steel microstructures with martensite, retained austenite, and alloying additions of Mn and Si. From this work, the following insights and conclusions were obtained:

1. MES revealed η -transition carbides, including non-stoichiometric carbides. The presence of η -carbides was confirmed by complementary TEM. The quantity ranged from 1.4 to 2.4 at. pct. after Q&P, consuming a substantial portion (~24 to 41 pct.) of the bulk carbon content in this alloy. The percentage of total C contained within the transition carbides is likely an important factor in the lower austenite fractions measured by XRD and MES compared to the fractions predicted assuming full partitioning.
2. A Q&T heat treatment involving tempering at 400 °C for 300 s resulted in 5.0 at. pct. of transition carbides versus 2.4 at. pct. after a Q&P treatment with a partitioning temperature of 400 °C and a partitioning time of 300 s. The reduced carbide fraction measured after Q&P is consistent with C partitioning from martensite to austenite and competition between partitioning and transition carbide formation.

3. The recoilless fraction of η -carbide was calculated to be 0.88 which is significantly greater than that for martensite or austenite, making the use of this parameter important for quantitative MES investigations of η -carbides.
4. A correction for saturation of the MES absorption spectrum was applied, which significantly improved the accuracy of the measured carbide fractions.

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References

- [1] D. K. Matlock, J. G. Speer, Design Considerations for the Next Generation of Advanced High Strength Steels, in: proc. of The 3rd International Conference on Advanced Structural Steels, Korean Institute of Metals and Materials, Seoul, South Korea, 2006, pp. 774-781.
- [2] J. G. Speer, E. De Moor, K. O. Findley, D. K. Matlock, B. C. De Cooman, D. V. Edmonds,

- Metall. Mater. Trans. A. 42 (2011) 3591-3601.
- [3] J. Speer, D. K. Matlock, B. De Cooman, J. G. Schroth, *Acta Mat.* 51 (2003) 2611-2622.
 - [4] J. G. Speer, D. V. Edmonds, F. C. Rizzo, D. K. Matlock, *Curr Opin Solid St M*, 8 (2004) 219-237.
 - [5] A. J. Clarke, J. G. Speer, M. K. Miller, R. E. Hackenberg, D. V. Edmonds, D. K. Matlock, F. C. Rizzo, K. D. Clarke, E. De Moor, *Acta Mat*, 56 (2008) 16-22.
 - [6] Y. Toji, H. Matsuda, M. Herbig, P-P. Choi, D. Raabe, *Acta Mat.* 65 (2014) 215-228.
 - [7] J. G. Speer, A. M. Streicher, D. K. Matlock, F. Rizzo, G. Krauss, Quenching and Partitioning: A Fundamental New Process to Create High Strength Trip Sheet Microstructures, in: E. B. Damm, M. Merwin (Eds.), *Austenite Formation and Decomposition*, TMS/ISS, Warrendale, 2003, pp. 505-522.
 - [8] D. V. Edmonds, K. He, F. C. Rizzo, B. C. De Cooman, D. K. Matlock, J. G. Speer, *Mater Sci Eng A*. 438-440 (2006) 25-34.
 - [9] T. D. Bigg, D. K. Matlock, J. G. Speer, D. V. Edmonds, *Sol St Phen.* 172-174 (2011) 827-832.
 - [10] G. R. Speich, *Trans. Metall. Soc. AIME*. 245 (1969) 2553-2564.
 - [11] A. J. Clarke, M. K. Miller, R. D. Field, D. R. Coughlin, P. J. Gibbs, K. D. Clarke, D. J. Alexander, K. A. Powers, P. A. Papin, G. Krauss, *Acta Mat.* 77 (2014) 17-27.
 - [12] E. De Moor, J. G. Speer, D. K. Matlock, J-H. Kwak, S-B. Lee., *Stl Res Int.* 83 (2012) 322-327.
 - [13] D. L. Williamson, K. Nakazawa, G. Krauss, *Metall Trans A*. 10 (1979) 1351-1363.
 - [14] G. R. Speich, W. C. Leslie, *Metall Trans.* 3 (1972) 1043-1054.
 - [15] G. M. Michal, J. A. Slane, *Metall. Mater. Trans. A*. 17 (1986) 1287-1294.
 - [16] J. H. Jang, I. G. Kim, H. K. D. H. Bhadeshia, *Scripta Mat.* 63 (2010) 121-123.
 - [17] E. Kozeschnik, H. K. D. H. Bhadeshia, *Mater. Sci. Tech.* 24;3 (2008) 343-347.
 - [18] G. Miyamoto, J. C. Oh, K. Hono, T. Furuhashi, T. Maki, *Acta Mat.* 55 (2007) 5027-5038.

- [19] K. He, D. V. Edmonds, J. G. Speer, D. K. Matlock, F. C. Rizzo, Martensite Tempering Behaviour Relevant to the Quenching and Partitioning Process, in: S. Richter, A. Schwedt (Eds.), European Microscopy Conference, Aachen, 2008, pp 431-432.
- [20] A. Königer, C. Hammerl, M. Zeitler, B. Rauschenbach, Phys Rev B. 55 (1997) 8143-8147.
- [21] H. Ino, T. Ito, S. Nasu, U. Gonser, Acta Metall. 30 (1982) 9-20.
- [22] C. K. Ande, First-Principles Calculations on the Stabilization of Iron Carbides (Fe_3C , Fe_5C_2 and $\eta\text{-Fe}_2\text{C}$) in Steels, Technische Universiteit Delft, Delft, 2013.
- [23] A. Oila, C. Lung, S. Bull, J Mater Sci. 49 (2014) 2383-2390.
- [24] Z. Q. Lv, S. H. Sun, P. Jiang, B. Z. Wang, W. T. Fu, Comp Mater Sci. 42 (2008) 692-697.
- [25] L. Cheng, A. Böttger, T. de Keijser, E. J. Mittemeijer, Scripta Metall Mater. 24 (1990) 509-514.
- [26] G. A. Thomas, J. G. Speer, Mater Sci Tech Ser. 30;9 (2014) 998-1007.
- [27] D. J. Dyson, B. Holmes, JISI. 208 (1970) 469-474.
- [28] C. F. Jaczak, SAE Technical Paper 900426, 1980.
- [29] W. K. Choo, R. Kaplow, Acta Metall. 21 (1973) 725-732.
- [30] M. Lesoille, P. M. Gielen, Metall Trans. 3 (1972) 2681-2689.
- [31] D. W. Hafemeister, Nuclear Properties Determined from Mössbauer Measurements, in: L. May (Ed.), An Introduction to Mössbauer Spectroscopy, Plenum Press, New York, 1971, pp. 45-74.
- [32] P. Jernberg, Nucl Instrum Meth B. 4 (1984) 412-420.
- [33] D. L. Williamson, T. W. Guettinger, D. W. Dickerhoof, Quantitative Investigations of Pyrite and Coal, in: J. G. Stevens, G. K. Shenoy (Eds.), Mössbauer Spectroscopy and Its Chemical Applications, American Chemical Society, Washington, D.C., 1981, pp. 177-208.
- [34] N. Abe, L. H. Schwartz, Mater Sci Eng. 14 (1974) 239-251.
- [35] Z. M. Stadnik, Mössbauer Spectroscopy Source Materials and Their Properties, in: J. W. Robinson (Ed.), Handbook of Spectroscopy III, CRC Press, Boca Raton, 1981, pp. 415-

421.

- [36] W. Sturhahn, T. S. Toellner, E. E. Alp, X. Zhang, M. Ando, Y. Yoda, S. Kikuta, M. Seto, C. W. Kimball, B. Dabrowski, *Phys Rev Lett.* 74 (1995) 3832-3835.
- [37] T. D. Bigg, D. V. Edmonds, *Mater Sci Forum.* 654-656 (2010) 33-36.
- [38] M. J. Santofimia, J. G. Speer, A. J. Clarke, L. Zhao, J. Sietsma, *Acta Mat.* 57 (2009) 4548-4557.
- [39] D. P. Koistinen, R. E. Marburger, *Acta Metall.* 7 (1959) 59-60.
- [40] J. Mahieu, J. Maki, B. C. De Cooman, S. Claessens, *Metal Trans A.* 33 (2002) 2573-2580.
- [41] Y. Hirotsu, S. Nagakura, *Acta Metall.* 20 (1972) 645-655.
- [42] Y. Hirotsu, S. Nagakura, *Trans JIM.* 15 (1974) 129-134.
- [43] S. Nagakura, *J. Phys. Soc. Jpn.* 14 (1959) 186-195.
- [44] Y. Ohmori, I. Tamura, *Metall. Trans. A.* 23 (1992) 2737-2751.
- [45] P. Bauer, O. N. C. Uwakweh, J. M. R. Génin, *Hyperfine Interact.* 41 (1998) 555-558.
- [46] O. N. C. Uwakweh, J. P. Bauer, J. M. R. Génin, *Metall Trans A.* 21 (1990) 589-602.
- [47] K. Oda, H. Fujimura, H. Ino, *J. Phys.: Condens. Matter.* 6 (1994) 679-692.
- [48] H. M. Ledbetter, R. P. Reed, *J Phys Chem Ref Data.* 2 (1973) 531-617.
- [49] G. R. Speich, W. C. Leslie, *Metall Trans.* 4 (1973) 1873-1875.
- [50] U. Gosner, From a Strange Effect to Mössbauer Spectroscopy, in: U. Gosner (Ed.), *Topics in Applied Physics*, vol. 5: Mössbauer Spectroscopy, Springer-Verlag, New York, 1975, pp. 1-48.
- [51] N. Gunkelmann, H. Ledbetter, H. M. Urbassek, *Acta Mat.* 60 (2012) 4901-4907.
- [52] H. M. Ledbetter, *J. Appl. Phys.* 44 (1973) 1451-1454.
- [53] A. Oila, S. J. Bull, *Comp Mater Sci.* 45 (2009) 235-239.
- [54] P. Gülich, E. Bill, A. X. Trautwein, *Mössbauer Spectroscopy and Transition Metal*

- Chemistry: Fundamentals and Applications, Springer, New York, 2011.
- [55] C. Djega-Mariadassou, B. Decaudin, L. Bessais, G. Cizeron, J. Phys: Condens. Matter. 9 (1997) 4931-4942.
 - [56] M. Ron, Iron-Carbon and Iron-Nitrogen-Systems, in: R. L. Cohen (Ed.), Applications of Mössbauer Spectroscopy, vol. 2, Academic Press, New York, 1980, pp. 329-392.
 - [57] T. E. Cranshaw, J. Phys. F: Metal Phys. 2 (1972) 615-624.
 - [58] G. K. Wertheim, V. Jaccarino, J. H. Wernick, D. N. E. Buchanan, Phys Rev Lett. 12 (1964) 24-27.
 - [59] D. L. Williamson, F. M. Kustas, D. F. Fobare, M. S. Misra, J. Appl. Phys. 60 (1986) 1493-1500.
 - [60] D. H. Sherman, S. M. Cross, S. Kim, F. Grandjean, G. J. Long, M. K. Miller, Metall Trans A. 38 (2007) 1698-1711.
 - [61] A. L. Sozinov, A. G. Balanyuk, V. G. Gavriljuk, Acta Mater. 45 (1997) 225-232.
 - [62] K. F. Laneri, J. Desimoni, G. J. Zarragoicoechea, A. Fernández-Guillermé, Phys Rev B. 66;134201 (2002) 1-7.
 - [63] D. H. Jack, K. H. Jack, Mater Sci Eng. 11 (1973) 1-27.
 - [64] G. Le Caër, J. M. Dubois, M. Pijolat, V. Perrichon, P. Bussière, J. Phys. Chem. 86 (1982) 4799-4808.
 - [65] P. Schaaf, S. Wiesen, U. Gonser, Acta Metall Mater. 40 (1992) 373-379.
 - [66] D. G. Hennessy, V. Sharma, G. S. Ansell, Metall Trans A. 14 (1983) 1013-1019.
 - [67] G. A. Thomas, A Study of Partitioning Mechanisms Operating During Q&P Heat Treatment of Steel, Colorado School of Mines, Golden, 2012.
 - [68] D. Turnbull, J. C. Fisher, J Phys Chem. 17 (1949) 71-73.
 - [69] N. Fujita, H. K. D. H. Bhadeshia, Mater. Sci. Technol. 17 (2001) 403-408.
 - [70] E. De Moor, C. Föjer, J. Penning, A. J. Clarke, J. G. Speer, Phys Rev B. 82;104210 (2010) 1-5.

- [71] P. V. Morra, A. J. Böttger, E. J. Mittemeijer, *J Therm Anal Calorim.* 64 (2001) 905-914.
- [72] E. De Moor, S. Lacroix, L. Samek, J. Penning, J. G. Speer, Dilatometric Study of the Quench and Partitioning Process, in: *proc. of The 3rd International Conference on Advanced Structural Steels*, Korean Institute of Metals and Materials, Seoul, South Korea, 2006.
- [73] R. H. Doremus, *Acta Metall.* 6 (1958) 674-679.
- [74] A. Shibata, S. Morito, T. Furuhashi, T. Maki, *Acta Mat.* 57 (2009) 483-492.

Figure Captions

- Figure 1 Schematic representation of heat treatments corresponding to samples WQ, Q&P1, Q&P2, Q&P3 and Q&T.
- Figure 2 (a) Volume pct. of austenite determined by XRD and MES for all samples and (b) austenite lattice parameter and C content determined by XRD for Q&P1, Q&P2, and Q&P3 as a function of tempering and or partitioning time.
- Figure 3 (a) $[100]_{\alpha}$ zone axis BF TEM micrograph showing η -carbides within the ferrite matrix in Q&P2, (b) $[100]_{\alpha}$ SAD pattern corresponding to the image in (a) (filled circles = matrix reflections, open circles = η reflections, open circle with x = η superlattice reflections), where $A=(00-2)_{\alpha}$, $B=(-210)_{\eta}$, and $C=(-110)_{\eta}$, and (c) $[3-11]_{\alpha}$ SAD pattern (filled circles = matrix reflections, open circles = η reflections) where $A = (011)_{\alpha}$, $B = (210)_{\eta}$, $C=(-1-12)_{\alpha}$, and $D=(-101)_{\eta}$.
- Figure 4 Off-zone axis BF TEM micrograph of η -carbide within the ferrite matrix in Q&P2.
- Figure 5 (a) Off-zone axis BF TEM micrograph showing η -carbides within the ferrite matrix of Q&P3, (b) $[110]_{\alpha}$ SAD pattern from the same area as (a) (A are $\{440\}_o$ type reflections from magnetite, B is a $(0-1-1)_{\eta}$ reflection, C is a $(-110)_{\alpha}$ reflection, D is a $(020)_{\eta}$ reflection, $d_{\alpha,o}$ = double diffraction between matrix, and arrows point toward double diffraction reflections between the matrix and carbide), and (c) $[11-1]_{\alpha}$ SAD pattern from same area as (a) (A is a $(-110)_{\alpha}$ reflection, B is a $(020)_{\eta}$ reflection, C is a $(-10-1)_{\alpha}$ reflection, and D is a $(-10-1)_{\eta}$ reflection).
- Figure 6 (a) Off-zone axis BF TEM micrograph of sample quenched and tempered at 400°C for 300 s (Q&T) with η -carbides in the martensite matrix and (b) near $[100]_{\alpha}$ zone axis DF TEM micrograph using the $(-210)_{\eta}$ reflection in the SAD pattern (inset in (b)) denoted by the arrow.
- Figure 7 (a) $[-31-1]_{\alpha}$ zone axis BF TEM micrograph of η -carbides in the sample quenched

and tempered at 400°C for 300 s (Q&T), (b) $[-31-1]_{\alpha}$ SAD pattern from (a) showing reflections from η -carbides, and (c) $[-100]_{\alpha}$ SAD pattern with η -carbide reflections, position A corresponds to $(-210)_{\eta}$ and position B corresponds to $(-110)_{\eta}$ superlattice reflections.

- Figure 8 Mössbauer spectra for samples WQ, Q&P1, Q&P2, Q&P3, and Q&T. The stick diagrams represent the A(0,0), A(0,n), A(C), C(η_s) and C(η_{ns}) resonance (stick diagrams are not to scale and components attributed to martensite have been removed for clarity). The zero velocity point represents the center of the pure α -iron calibration spectrum. The solid line through the experimental data points is the sum of all subspectra.
- Figure 9 Low velocity MES spectra of Q&P1 (top), Q&P2 (middle), and Q&P3 (bottom). Subspectra due to resonance from austenite components A(0,0), A(0,n) and A(C) are shown, along with the experimental counts and computer generated spectra. The martensite subspectra are not shown for clarity.
- Figure 10 Relative counts, η_s - and η_{ns} -carbide subspectra, and fit including and neglecting η -carbide for (a) Q&P3 and (b) Q&T samples as a function of source velocity. Other subspectra removed for clarity.

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Tables

Table 1 - Heat treatment parameters

Heat treatment designation	Austenitization temperature/ Hold time	Quench temperature/ hold time	Partitioning/ annealing temperature/hold time
WQ	820 °C/120 s	RT	N/A
Q&P1	820 °C/120 s	225 °C/10 s	N/A
Q&P2	820 °C/120 s	225 °C/10 s	400 °C/10 s
Q&P3	820 °C/120 s	225 °C/10 s	400 °C/300 s
Q&T	820 °C/120 s	RT	400 °C/300 s

Table 2 – Comparison of η - and ε -carbide d-spacings.

η -carbide	$d_{(200)}$ (Å)	$d_{(210)}$ (Å)
Present work	2.33	2.05
Fe-1.22C wt. pct, tempered at 120 °C [13]	2.33	2.07
Fe-0.45C wt. pct, tempered at 200 °C [42]	2.341	2.058
ε -carbide	$d_{(010)}$ (Å)	$d_{(011)}$ (Å)
Fe films carburized at <200 °C [43]	2.383	2.091

Table 3 –Young's (E) and shear moduli (G), Debye Temperatures (θ_D) and recoilless fractions (f) for martensite, austenite and η -carbide.

	E (GPa)	G (GPa)	θ_D (K)	f
martensite	211 [51]	82 [51]	466 [51]	0.82
austenite	145-166 [53]	77-83 [53]	446-472	0.80-0.82
η -carbide	263 [22]	101 [22]	647 ^a [22]	0.88
	362 [23]	147 [23]	637 ^b	0.88
	350 ^c [24]	137 [24]	619	0.88

^aThe Debye temperature and elastic properties were provided in [22].

^bThe Debye temperature was calculated from elastic properties [23] using Equations (13) through (17).

^cThe Values of E and G were calculated from single crystal elastic constants [24] according to the Voigt averaging method [23].

Table 4 – Calculated effective (T_p), calculated actual (t_p), calculated total (t_{tot}) and measured (t_{meas}) thicknesses, along with the density, ρ , and absorption coefficient, μ , used in the measurement of t_{meas} . The subscript p is replaced by the symbol of the individual phase(s) in the table (m+f corresponds to martensite+ferrite).

Sample	T_{m+f}	T_γ	T_η	t_{m+f} (μm)	t_γ (μm)	t_η (μm)	t_{tot} (μm)	t_{meas} (μm)	ρ (g cm^{-3})	μ (cm^{-1})
WQ	9.7	0.15	0.08	26.7	0.42	0.24	27.4	26.5	7.73	483
Q&P1	9.2	0.30	0.11	25.5	0.82	0.34	26.7	26.9	7.74	484
Q&P2	10.6	1.40	0.13	29.2	3.88	0.39	33.5	31.9	7.76	485
Q&P3	8.8	0.86	0.17	24.3	2.38	0.53	27.2	26.8	7.75	484
Q&T	11.8	0.03	0.46	32.6	0.07	1.41	34.1	31.9	7.68	481

Table 5 – MES parameters (IS and QS), Full Width at Half Maximum (W), Width Ratio (W_{21}) and fractional resonances $r(0,0)$, $r(0,n)$ and $r(C)$ for components A(0,0), A(0,n) and A(C), respectively. The number in parentheses is the uncertainty of the last significant digit(s).

Component	Parameter	Q&P1	Q&P2	Q&P3
A(0,0)	IS (mm s^{-1})	-0.111(2)	-0.109(2)	-0.108(2)
	W (mm s^{-1})	0.307(6)	0.280(4)	0.260(7)
	$r(0,0)$	0.75	0.42	0.30
A(0,n)	IS (mm s^{-1})	0.011(8)	0.014(5)	0.012(5)
	W (mm s^{-1})	0.290(12)	0.312(10)	0.322(11)
	$r(0,n)$	0.15	0.29	0.34
A(C)	IS (mm s^{-1})	-0.027(7)	-0.011(1)	-0.001(1)
	QS (mm s^{-1})	0.664(16)	0.665(2)	0.663(2)
	W_1	0.260	0.285(5)	0.271(4)
	W_{21}	1	0.95(1)	0.99(1)
	$r(C)$	0.10	0.29	0.36

Table 6 – MES parameters for the η -carbide components from the present work and the literature [13,21]: Isomer Shift (IS), Quadrupole Splitting (QS) and Magnetic Hyperfine Field (B_{hf}).

Parameter		Value		
		Present Work Fe-0.38C-1.54Mn- 1.48Si (wt. pct)	Williamson <i>et al.</i> [13] Fe-1.22C (wt. pct)	Ino <i>et al.</i> [21] Fe-1.26C (wt. pct)
Stoichiometric η -carbide	IS (mm s^{-1})	0.16 ± 0.05	0.28 ± 0.08	0.24
	QS (mm s^{-1})	-0.09 ± 0.05	-0.13 ± 0.10	0.03
	B_{hf} (T)	17.4 ± 0.5	17.8 ± 0.4	16.7
Non- stoichiometric η -carbide	IS (mm s^{-1})	0.13 ± 0.05	0.11 ± 0.05	0.05/0.09
	QS (mm s^{-1})	-0.36 ± 0.10	0.20 ± 0.10	-0.38/0.41
	B_{hf} (T)	25.2 ± 0.5	25.0 ± 0.5	25.3/25.6

Table 7 – Atomic phase pct. and atomic pct. C in each phase for each condition. The numbers in parentheses represent the uncertainty of the last significant digit(s). η_{s} and η_{ns} refer to stoichiometric and non-stoichiometric η -carbide, respectively.

Phase	Parameter	WQ	Q&P1	Q&P2	Q&P3	Q&T
Martensite + ferrite	At. Phase Pct	97.3(10)	95.6(10)	83.0(10)	87.0(10)	95.0(10)
	At. Pct. C	1.5(1)	1.3(1)	0.7(1)	0.4(1)	0.2(1)
Austenite	At. Phase Pct	1.7(5)	2.8(5)	15.6(5)	10.6(5)	0
	At. Pct. C	1.7(5) ^a	1.5(5)	4.6(5)	6.2(5)	N/A
η_{s} -Carbide	At. Phase Pct	0.3(2)	1.0(3)	0.9(3)	1.7(3)	4.0(5)
	At. Pct. C	33.3	33.3	33.3	33.3	33.3
η_{ns} -Carbide	At. Phase Pct	0.7(3)	0.5(3)	0.5(3)	0.7(3)	1.0(3)
	At. Pct. C	25	25	25	25	25
Total Measured η -Carbide	At. Phase Pct	1.0(4)	1.5(4)	1.4(4)	2.4(4)	5.0(6)
	Normalized At. Pct. C	27.5	30.5	30.3	30.9	31.6

^aThe austenite C content of sample WQ is assumed to be the same as the base alloy C content.