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Quantitative investigation into the influence of temperature on carbide and austenite evolution during partitioning of a quenched and partitioned steel

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ABSTRACT

The influence of partitioning temperature on microstructural evolution during quenching and partitioning was investigated in a 0.38C—1.54Mn—1.48Si wt.% steel using Mössbauer spectroscopy and transmission electron microscopy. η-carbide formation occurs in the martensite during the quenching, holding, and partitioning steps. More effective carbon partitioning from martensite to austenite was observed at 450 than 400 °C, resulting in lower martensite carbon contents, less carbide formation, and greater retained austenite amounts for short partitioning times. Conversely, greater austenite decomposition occurs at 450 °C for longer partitioning times. Cementite forms during austenite decomposition and in the martensite for longer partitioning times at 450 °C.

The quenching and partitioning (Q&P) steel heat treatment [1–3] produces microstructures containing primarily martensite (M) and retained austenite (RA) [4,5]. Q&P involves quenching to a quench temperature (QT) between the martensite start (M_s) and finish temperatures, partitioning at a temperature (PT) the same or higher temperature than the QT, followed by a final quench (FQ) to room temperature (RT) [2,6]. The goal is to partition carbon (C) from martensite to austenite, thereby reducing the C supersaturation of the martensite and stabilizing the austenite before the FQ [6,7]. Experimental austenite amounts measured after Q&P [1,3,8] are often lower than values calculated assuming immobile martensite-austenite interfaces and/or all C in the martensite partitions to the austenite [6,9]. The discrepancy may be in large part due to austenite decomposition (e.g., by martensite-austenite interface movement and/or bainite formation) during the partitioning step [6,10–15] and/or incomplete C partitioning. The latter may result from competing tempering mechanisms, such as C trapping at defects [16], C clustering [17] and transition carbide and/or cementite (θ) formation [18,19]. The present authors identified η-carbide by transmission electron microscopy (TEM) and Mössbauer effect spectroscopy (MES) in 0.38C—1.54Mn—1.48Si wt.% steel after partitioning at 400 °C for 10 and 300 s and developed novel MES spectral analysis techniques to enable the measurement of η-carbide amounts near 1 at.% [19]. η-carbide quantities of 1.4 and 2.4 at.% were measured after partitioning at 400 °C for 10 and 300 s, respectively, which consumed 24 to 41% of the total bulk C, respectively [19].

The significant C consumption by carbides after partitioning at 400 °C for 10 or 300 s indicates that carbide formation competes with C partitioning from martensite to austenite. However, additional data are required to further understand the evolution of carbides during Q&P [19]. MES revealed the fractional resonance due to Fe in carbides of a 1.22 wt.% C steel increased with increasing tempering temperature during tempering for times of 1 h at temperatures from 150 to 300 °C [20,21]. In contrast, increasing the PT from 250 to 400 °C during Q&P processing of 0.60C—0.95Mn—1.96Si wt.% steel results in an increase in RA attributed to an apparent decrease in carbide formation, according to qualitative TEM observations [8,22]. Similarly, a lower apparent density of ε-carbides was observed by TEM in a sample of 0.3C—3.5Mn—1.6Si wt.% steel partitioned at 400 °C for 60 s than after partitioning for 5 s [15]. The authors suggested that ε-carbides precipitated during the initial quench (IQ) decompose during isothermal holding at 400 °C, resulting in an enhancement of the extent of C partitioning to austenite. Quantitative studies are required to further clarify how Q&P processing parameters (e.g., PT and partitioning time (Pt)) and alloying (which is beyond the scope of this study), influence the trade-off between carbide formation

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and C partitioning. In the present work, previously developed quantitative MES methodologies [19] are employed to investigate the influence of Pt and PT on carbide formation and C partitioning from martensite to austenite in 0.38C—1.54Mn—1.48Si wt.% (1.71C—1.52Mn—2.86Si at.%) steel.

Samples were austenitized for 120 s at 850 °C, followed by quenching to approximately 250 °C and holding for 10 s, then partitioning at 400 or 450 °C for 10, 30, 60 and 300 s. Quenching to 250 °C results in a calculated RA amount of 32 vol.% [23,24]. Samples are designated QPXXX-YYY, where XXX and YYY refer to PT (°C) and Pt (s), respectively. A water quenched sample (WQ) and sample quenched to 250 °C and held for 10 s, followed by water quenching to RT (QP250-10), were also analyzed. Sample preparation, TEM, and MES procedures employed in this study are similar to those used previously [18,19], except where noted.

All MES spectra exhibited resonance due to martensite, austenite, and η-carbide. θ was detected in relatively small amounts in QP450-60 and in larger amounts in QP450-300. MES spectra for QP450-300 are shown in Fig. 1a and on an expanded scale in Fig. 1b. In Fig. 1a, stick diagrams representing the A(0,0), A(0,n) and A(C) resonances are shown that 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 [19,25,26], and Fe with one C nn or two C nn at adjacent sites 90° from one another [27]. Stick diagrams showing representative line positions for stoichiometric (η_s) and non-stoichiometric η-carbide (η_{ns}), as well as θ, are also denoted in Fig. 1a. Resonances corresponding to η_s, $(Fe,Mn,Si)_2C$, and η_{ns}, $(Fe,Mn,Si)_3C$, are attributed to Fe atoms in η-carbide with three and two C nn, respectively [19,28]. The θ in QP450-60 and QP450-300 is assumed to be stoichiometric $(Fe,Mn,Si)_3C$ [17,29]. Despite the same stoichiometry, $(Fe,Si,Mn)_3C$, the MES parameters of θ and η_{ns} are significantly different due to different lattice parameters and atom locations within their respective orthorhombic unit cells [28]. The levels of Si and Mn in the present steel result in significant fractions of Fe sites in carbides with 1 and 2 nn Mn and or Si atoms [30]. The nn Si and or Mn atoms are known to significantly reduce the magnetic hyperfine field (B_{hf}) of Fe in θ [30,31] and might also influence the B_{hf} of Fe in η_s. In the present work, single sextets with broadened lines are employed to account for the total resonance, due to multiple different Fe sites in each of the η_s, η_{ns}, and θ resonances.

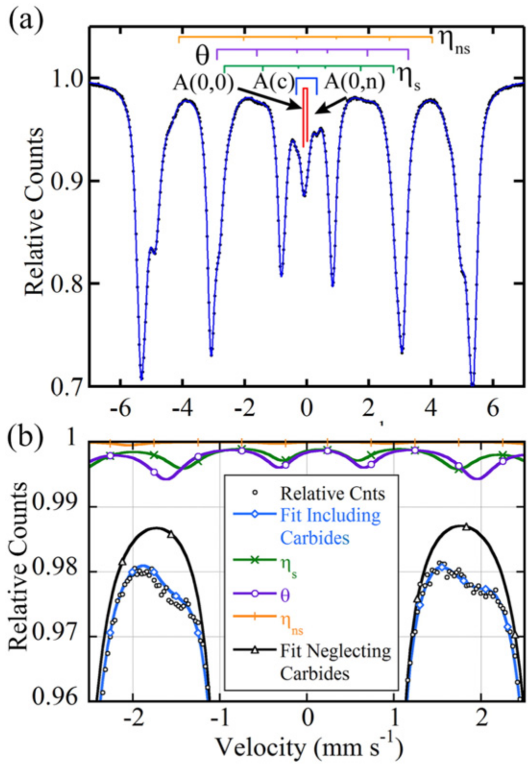

Fig. 1. MES spectra for QP450-300 shown on (a) full velocity range and (b) expanded scale. In (a), the stick diagrams representing the carbide and austenite resonances are not to scale. The solid line through the experimental data points is fitted by summation of all subspectra. In (b), the relative counts, carbide subspectra, and fit including and neglecting carbides are shown. Other subspectra removed for clarity. Zero velocity represents the center of the pure α-iron calibration spectrum.

The B_{hf} determined by MES for the η_s resonance of samples ranged from 16.9 to 17.4 T, consistent with that of 17.4 ± 0.5 T reported previously for this same alloy [19], and within the range of 16.2 [32] to 17.9 T [20] reported for η_s. In [32] a distinction between ε or η was not made, but previous research suggests the resonance was due to η_s [19]. The small fractions of the η_s resonance necessitated the isomer shift (IS) and quadrupole splitting (QS) be fixed at 0.16 and -0.09 mm s^{-1}, respectively [19]. The B_{hf} of the η_{ns} resonance ranged from 25.1 to 25.6 T, falling within the range of 23.7 to 25.7 T and reported previously [19,28,32]. Similarly, the small η_{ns} resonance necessitated that the IS and QS be fixed at 0.13 and -0.36 mm s^{-1} [19], respectively. In samples QP450-60 and to a greater extent, QP450-300, carbide resonance distinct from η_s and η_{ns} is detected with a B_{hf} that is ~1–2 T higher than that measured for η_s. This additional resonance, attributed to θ, could not be detected by MES in other samples and θ was not observed by TEM in samples of this alloy partitioned at 400 °C in previous work [19]. Since additions of Mn and Si do not significantly influence the IS and QS of θ [30,33], these values are fixed at those for pure Fe_3C θ, 0.18 and 0.02 mm s^{-1} [33], respectively. Conversely, Mn and Si additions significantly reduce the B_{hf} of Fe in θ [30,31] below the value for that of pure Fe_3C θ (20.7 T, [33]). As such, the θ and η_s resonances overlap significantly, making a precise quantification of the relative amounts complex. Consequently, a series of fits were conducted with possible ranges of $B_{hf,}$ from 18.5 T to 19.6 T for θ and 16.9 to 17.4 T for $\eta_{s,}$ in order to estimate the average amounts and probable ranges of the fractions of each component. The fit that produced values of the relative amounts of θ and η_s resonance nearest to the average values was selected for the quantitative analysis and standard deviations in the relative amounts were assessed from all fits for QP450-60 and QP450-300, respectively. The overlap of the η_s and θ resonances is illustrated in Fig. 1b, which shows the area of the MES spectrum where the 2 and 5 lines of each carbide resonance are predominantly resolved. The recoilless fraction of 0.86 for θ used in the quantitative analysis was calculated using previous methodologies [19] and a Debye temperature of 538 K [34]. Recoilless fractions for martensite, austenite and η-carbide are 0.82, 0.81, and 0.89, respectively [19].

TEM confirmed the presence of both η and θ in QP450-300, along with highly dislocated ferrite, which likely corresponds to martensite, although the presence of some bainitic ferrite may also be possible. χ-carbide was not observed. The η-carbides were predominantly present as plate-like precipitates in the martensite [19]. The bright-field (BF) image in Fig. 2a, recorded a few degrees from the $[-13\text{-}1]_\alpha$ zone axis (ZA), shows two different "tempered" martensite laths with a small degree of misorientation. Plate-like η-carbides are present in both laths with their habit-plane-normals approximately parallel to $(-3\text{-}10)_\alpha$, consistent with a $(00\text{-}2)_\alpha$ habit plane for η-carbide as reported elsewhere [19,35]. Separating the two martensite laths is a region of predominately θ and ferrite. The dark-field (DF) image in Fig. 2b, generated using the $(2\text{-}1\text{-}1)_\theta$, $(2\text{-}2\text{-}1)_\theta$, and $(2\text{-}3\text{-}1)_\theta$ reflections at the same foil orientation as Fig. 2a, shows a series of irregular, discrete, nano-scale cementite precipitates formed along the inter-lath region. The morphology of this inter-lath region suggests that an austenite film, separating the two martensite laths, may have been present upon the IQ but decomposed to θ and ferrite during the partitioning step, as no remaining austenite was observed in this area. In addition, discrete precipitates near or bordering the plate-like η precipitates are visible in the DF image, suggesting the beginning of intra-lath θ precipitation that grew from η, consistent with similar observations in a Q&T 1.5 wt.% C alloy [36]. The presence of θ was also observed by TEM after tempering