Mössbauer Spectroscopy and Transmission Electron Microscopy Analysis of Transition Carbides in Quenched and Partitioned Steel

D. T. Pierce[1], D. R. Coughlin[2], D. L. Williamson[3], K. D. Clarke[2], A. J. Clarke[2], J. G. Speer[1], D. K. Matlock[1], E. De Moor[1]

[1]Advanced Steel Processing and Products Research Center, Colorado School of Mines, Golden, CO
[2]Los Alamos National Laboratory, Materials Science and Technology Division, Los Alamos, NM
[3]Department of Physics, Colorado School of Mines, Golden, CO

Quenching and partitioning (Q&P) is a novel steel heat treatment that produces microstructures of martensite and retained austenite (Fig.1) [1]. Q&P consists of quenching to a temperature (QT) between the martensite start and finish temperatures, partitioning at a temperature the same or greater than the QT, followed by quenching to room temperature (RT). The goal of the heat treatment is to partition carbon (C) from martensite to austenite, thereby stabilizing the austenite prior to the final quench. Competing reactions such as transition carbide formation can reduce the extent of C partitioning, resulting in less retained austenite and mechanical property variations. The small volume fractions, carbide thicknesses below ~50 nm, and numerous overlapping peaks makes X-ray diffraction characterization of transition carbides challenging. In contrast, Mössbauer spectroscopy (MS) with correlative transmission electron microscopy (TEM) is better suited for identifying and quantifying carbides. Most MS studies on transition carbides have focused on quenched and tempered microstructures in binary Fe-C steels with high C, extensive amounts of carbides, and MS spectra primarily comprised of resonance from a limited number of unique Fe sites [2]. Q&P steels with lower C and carbide fractions, alloying additions of Manganese (Mn), Silicon (Si), and other elements, and significant amounts of retained austenite in the microstructures have more complex MS spectra, requiring more precise analysis methods.

A 0.38C-1.54Mn-1.48Si wt.% steel underwent austenitization, quenching to 225 °C and partitioning at 400 °C for 10 or 300 s. Microstructural characterization using a Philips CM200 TEM operated at 200 kV indicates the presence of η-carbides (Fig.2). The $(110)_\eta$ super lattice reflections in the selected area diffraction pattern in Fig.2b arise from the ordering of C atoms in the octahedral sites of the orthorhombic η-carbide structure [2,3]. The MS spectra in Fig.3 were acquired at RT with a ^{57}Co-Rh source and a spectrometer operating in the triangular constant acceleration mode. Resonance due to martensite, austenite and η-carbide are present in the MS spectra. Five sextets with varying hyperfine fields and other sextet fitting parameters accounted for the total resonance of the complex distribution of Fe sites in the martensite [3]. Resonance due to Fe sites in austenite with zero C first or second nearest neighbors (A(0,0)) and with zero C first but with n (n=1, 2, 3 or 4) C second nearest neighbors (A(0,n)) were fit with two singlets [4]. Resonance due to Fe sites in austenite with one or two C first nearest neighbors (A(c)) was fit with a quadrupole split doublet [4]. The MS spectra also reveal magnetic six line resonances from two different Fe sites in η-carbide: 1) Fe sites with three C nearest neighbors corresponding to stoichiometric η-carbide, $C(\eta_s)$, and 2) Fe sites with two nearest C neighbors corresponding to non-stoichiometric η-carbide, $C(\eta_{ns})$, [3]. Fig.4 shows the MS spectrum of the 300 s sample on an expanded scale. The influence of both η-carbide components on the spectrum is evident near the resolved 2 and 5 lines (labeled in Fig.3) of each resonance in Fig.4. η-carbide fractions increase with increasing partitioning time. A correction [3] accounted for the saturation of the absorption spectrum due to sample thicknesses of ~30 μm, which disproportionately attenuates the martensite and austenite resonance relative to η-carbide. We calculated the recoilless fraction for η-carbide, a fundamental parameter in quantitative MS analysis, to be 0.88. The recoilless fraction of η-carbide is significantly greater than that for martensite and austenite (~0.81), making use of this parameter important for quantitative MS investigations [3]. The total fractions of η-carbide, including η_s and η_{ns} components, were 1.4±0.3 and 2.4±0.3 at.% after partitioning for 10 and 300 s, respectively. Therefore, η-carbides consume a significant portion (~24 and 41%) of the bulk C [5].

References:
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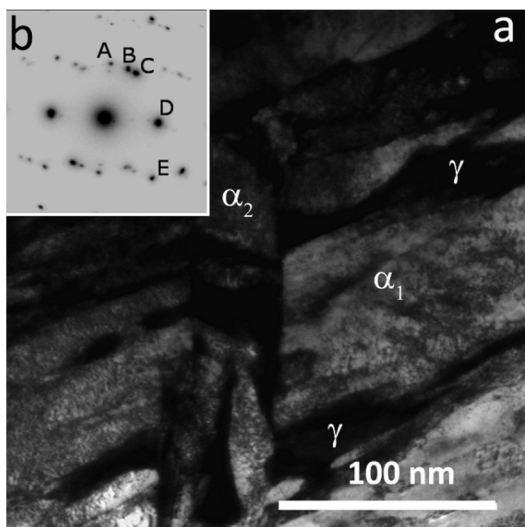
Fig.1 (a) Bright-field (BF) TEM image of two martensite variants with zone axes of $[-111]_{\alpha1}$ and $[001]_{\alpha2}$ and an austenite film with a zone axis of $[011]_{\gamma}$ after partitioning at 400°C for 300 s. (b) Inset SAD pattern: A = $(-110)_{\alpha2}$, B = $(-11-1)_{\gamma}$, C = $(110)_{\alpha1}$, D = $(11-1)_{\gamma}$, $(101)_{\alpha1}$, $(110)_{\alpha2}$, and E = $(200)_{\alpha2}$.
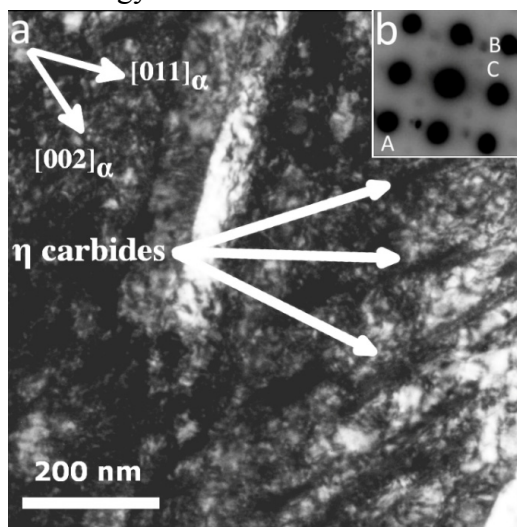

Fig.2 (a) $[-100]_{\alpha}$ zone axis BF TEM micrograph showing η-carbides within the martensite matrix in a sample partitioned for 10 s at 400 °C, and (b) $[-100]_{\alpha}$ SAD pattern corresponding to the image in (a) where A=$(0-20)_{\alpha}$, B=$(210)_{\eta}$, and C=$(110)_{\eta}$ indicate superlattice reflections.
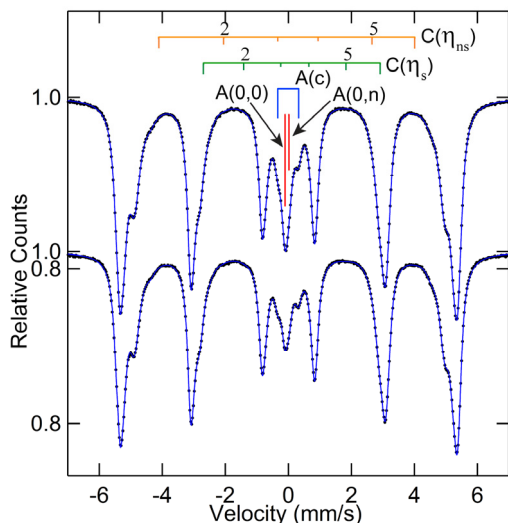

Fig.3 MS spectra: relative counts as a function of source velocity for samples partitioned at 400 °C for 10 (top) and 300 s (bottom). The stick diagrams represent the A(0,0), A(0,n), A(C), $C(\eta_s)$ and $C(\eta_{ns})$ resonances and are not to scale. Martensite components have been removed for clarity.
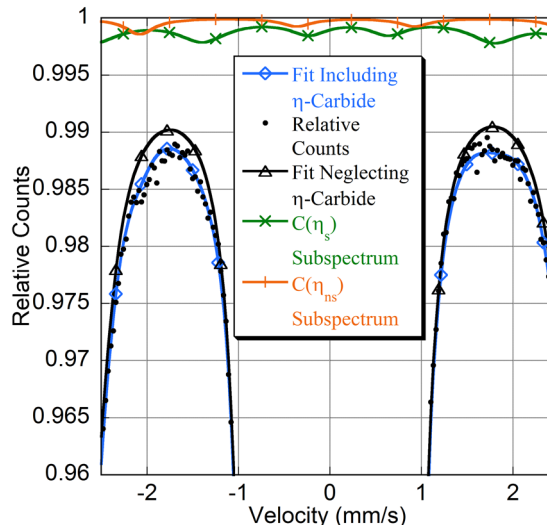

Fig.4 Expanded scale MS spectrum for the sample partitioned for 300 s from Fig.3. Relative counts, η_s-and η_{ns}-carbide subspectra, and fit including and neglecting η-carbide for the sample partitioned at 400 °C for 300 s. The quality of fit improves with the inclusion of the η_s-and η_{ns}-carbide subspectra.