Effect of Mn-Enriched Cementite on Austenite Formation During Intercritical Annealing

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INTRODUCTION

Intercritical annealing (IA) heat treatments are implemented to a variety of steels with the general intent to form austenite and generate composite final microstructures. The austenite may or may not be retained upon cooling from IA. The processing of continuous annealed dual-phase (DP) steels, for example, is intended to generate ferrite-martensite microstructures as the intercritical austenite transforms upon cooling. More recently, IA heat treatments have been extensively studied in application to medium-manganese (Mn) steels, where the general intent is to form intercritical austenite that is retained upon cooling. The stabilization of austenite in Medium-Mn steels is predominantly facilitated by the greater Mn content (4-10 wt pct), relative to DP steels (1.5-2.0 wt pct), which partitions to intercritical austenite, along with carbon (C), during IA and enables the austenite to be retained as a meta-stable phase. During deformation of medium-Mn steels, the meta-stable austenite may exhibit deformation induced martensite transformation, often referred to as transformation-induced plasticity (TRIP).

Different levels of Mn and C enrichment in the austenite can cause dramatic differences in mechanical behavior; low-enriched austenite transforms with little strain and corresponds to greater work-hardening and ultimate tensile strength, while highly-enriched austenite transforms more gradually with strain and corresponds to greater elongation. With mechanical properties having a strong dependence on the level of solute enrichment in the retained austenite, it is of considerable interest to predict not only the austenite fraction during IA, but C and Mn solute distributions in the austenite as well. The diffusion of Mn is relatively slow in austenite, thus redistribution of Mn within austenite during IA may be considered negligible. The Mn distribution within a region of retained austenite is expected to reflect the Mn concentration that was incorporated as the austenite interface advanced during growth, and compels the need for understanding austenite nucleation and growth mechanisms during IA to predict solute enrichment.

The presence of cementite is a feature that is often mentioned as having significant influence on the nucleation and growth of austenite. From studies on austenite formation in DP steels, Speich et al. suggested the most potent site for austenite nucleation was at a ferrite-pearlite interface when the microstructure prior to IA consisted of ferrite and pearlite. They suggested that austenite nucleated at and consumed pearlite colonies before continued growth into the surrounding ferrite and proposed a sequence of austenite growth that included 1) austenite growth consuming pearlite, 2a) continued growth of austenite into ferrite controlled by C redistribution in austenite (relevant for higher intercritical temperatures), 2b) continued growth of austenite into ferrite controlled by Mn diffusion through ferrite (relevant for lower intercritical temperatures), and finally 3) slow equilibration of Mn in austenite. Calculations for growth of austenite during IA were published by Ågren which utilized the analytical framework suggested by Speich et al. The calculations for austenite fraction as a function of IA time from the models agreed well with experimental data for longer times; however, the models were not in good agreement with...
observations from short IA times. The calculations suggested greater austenite fractions at short IA times than measured experimentally. Ågren posited that the assumption of near instantaneous dissolution of pearlite and austenite growth, as suggested by Speich et al., may not be accurate due to Mn partitioning between ferrite and cementite in pearlite, which could cause the dissolution of pearlite to be Mn-diffusion controlled rather than C-diffusion controlled.

Other researchers that studied austenite formation from ferrite and spheroidized cementite microstructures have similarly suggested that austenite nucleation at cementite-ferrite interfaces is most predominant. Etsay et al. proposed that austenite nucleated on cementite particles residing at ferrite grain boundaries and grew along the ferrite boundary to encompass other cementite particles. From experimental observations, they noted a resistance to cementite dissolution even when the cementite was enveloped by austenite. The resistance to dissolution of cementite was suggested to be caused by Mn partitioning to the cementite during subcritical annealing. The enrichment of Mn in cementite has been verified by various researchers that studied similar steels and has been attributed to causing slow dissolution of cementite.

Considering the effect of Mn enrichment in cementite, Navara et al. proposed an austenite nucleation and growth sequence that differed substantially from those previously mentioned. They suggested that Mn enrichment in cementite caused cementite-ferrite interfaces to be less potent nucleation sites and that the predominant austenite nucleation site was ferrite grain boundaries; a conclusion also reached by Yang et al. Navara et al. argued that Mn enrichment in cementite must reduce the activity of C in cementite, which resulted in a stabilizing effect and a reduction in the potency of the cementite-ferrite interface as a nucleation site for austenite. Additionally, they posited that austenite nucleation occurring at ferrite grain boundaries is stimulated by Mn-enriched zones adjacent to ferrite boundaries caused by diffusion-induced grain boundary migration.

Overall, Navara et al. suggested that cementite particles did not have a significant effect on austenite nucleation in the so-called Manganese-Partitioning Dual-Phase Steels that they studied. Despite differing assertions regarding austenite nucleation sites, this conclusion from Navara et al. is in good agreement with another from Garcia and Deardo which stated that remarkably similar austenite-ferrite microstructures could be obtained from very different initial ferrite-cementite structures.

Many studies on austenite formation during IA have included DICTRA™ simulations for austenite growth. These simulations did not consider the presence of cementite in the initial simulation structure, ostensibly with the assumption that any cementite would rapidly dissolve upon IA. The absence of cementite in the DICTRA™ simulations leads to a commonly predicted feature where austenite growth occurs in two stages during IA. The first stage of growth has often been termed negligible-partitioning local-equilibrium (NPLE) and refers to a rapid increase in austenite fraction that occurs without Mn enrichment which is corresponded to much better agreement with in situ high-energy X-ray diffraction results for austenite fraction during short IA times (~1000 s) relative to simulations that included solute C in ferrite – This suggests that initial austenite formation is Mn-diffusion controlled rather than C-diffusion controlled. Additionally, a study by Gouné et al. suggested that cementite dissolution during IA can be Mn-diffusion controlled, which limits the availability for C to contribute to austenite growth. Similar to Navara et al., Gouné et al. suggested that Mn enrichment in cementite causes a decrease in the chemical potential of C in cementite.

The present study expands on some of the ideas from Navara et al. and Gouné et al. and applies them to considerations for austenite growth and cementite dissolution during IA of a 0.2C-4.5Mn steel that was previously tempered and cold-rolled. The analytic framework proposed here follows the fundamental methodology promoted by Hillert et al. and considers local equilibrium at the interfaces. The present work does not make an attempt at quantitative predictions regarding rates of phase transformations, which would require greater consideration of the kinetics involved with diffusing alloy elements and interface migration, but suggests the diffusive species that limit phase transformation rates. Experimental results suggest austenite formation and cementite dissolution occurred by Mn-diffusion-controlled processes. A straightforward modelling framework is discussed which utilized chemical potential calculations from Thermo-Calc® and provides insight on driving forces for partitioning of C and how Mn enrichment can cause slow dissolution of cementite during IA.

METHODS

The material discussed here was a 0.19C-4.39Mn steel that was vacuum cast as a 35 cm × 13 cm × 13 cm ingot. The ingot was reheated to 1180 °C for 2 h and hot-rolled to a thickness of 4 mm and air cooled. The hot-rolled plate was then annealed for 16
h at 550 °C and cold-rolled to a final thickness of 1 mm. Samples extracted for IA heat treatments had dimensions of 4 mm x 10 mm and 10 mm x 20 mm; these samples were later analyzed with microscopy and X-ray diffraction (XRD), respectively. The IA heat treatments were conducted in a TA Instruments DIL 805A dilatometer under vacuum; samples were heated at 50 °C·s⁻¹ to 660 °C and held for various IA times before cooling at 20 °C·s⁻¹.

Samples for field-emission scanning electron microscopy (FESEM) analysis were hot-mounted in Bakelite, polished using standard metallographic procedures, and etched with a 1 pct Nital solution (1 pct nitric acid in ethanol) for approximately 5 s. Micrographs were captured using a 15 kV accelerating voltage and working distance of 10 mm with a JEOL 7000 FESEM. Lift-out samples that were analyzed with scanning transmission electron microscopy (STEM) were extracted from cross-sections perpendicular to the rolling direction with ion-milling using an Oxford Instruments OmniProbe and a focused-ion-beam (FIB) in a FEI Helios Nanolab 600i. These lift-outs had cross-sections normal to the transverse-rolling direction of approximately 10 x 10 μm and were thinned using the FIB to produce electron transparent samples. STEM characterization was conducted in an FEI Talos F200X operating in scanning mode with a 200 keV accelerating voltage. Images of the microstructures were captured with the bright-field (BF) STEM detector; corresponding Mn distribution maps and line-scans were collected with energy-dispersive X-ray spectroscopy (EDS). The EDS maps and line-scans were quantified using the Cliff-Lorimer k-factor approach for thin films using Bruker Esprit microanalysis software. A three-point moving-average smoothing function was applied to the line-scan EDS data, using MATLAB®, to reduce noise.

Retained austenite fractions were assessed in samples after heat treatments with XRD. Samples were prepared for XRD by grinding with successively finer abrasive pads up to 1200 grit before chemically thinning in a 1:50:50 solution of hydrofluoric acid, hydrogen peroxide, and deionized water. A PANalytical Empyrean X-Ray diffractometer with a Cu source (Kα1 λ=15.41 nm) was utilized to collect XRD spectra. Scans were conducted over a range of 40-120 degrees and illuminated a maximum sample area of 4.7 mm x 10.8 mm. PANalytical X’Pert HighScore Plus® software was used to fit the X-ray spectra and determine the integrated intensity of peaks. The volume fraction of retained austenite was calculated from XRD according to Case 1 described by Jatczak 36.

The TCFE12 data base of Thermo-Calc® was used to make thermodynamic calculations for compositions and chemical potentials. Phases included in the calculations were ferrite, cementite, and austenite which correspond to the Thermo-Calc® notations BCC_A2, CEMENTITE_D011, and FCC_A1, respectively.

RESULTS

Experimental Characterization
The microstructure after cold rolling, prior to intercritical annealing, is shown in Figures 1 and 2. Figure 1 shows an FESEM micrograph of the deformed ferrite matrix with distributed cementite particles that have lighter contrast. Figure 2(a) shows a BF-STEM micrograph of the cold-rolled microstructure and the corresponding EDS map in Figure 2(b) indicates high levels of Mn enrichment in the cementite particles.

Figure 1. FESEM micrograph of the microstructure corresponding to the cold-rolled condition. Bright-contrast constituent labelled ‘θ’ is presumed to be cementite.
Figure 2. (a) BF-STEM micrograph and (b) STEM-EDS map of Mn distribution in the cold-rolled condition.

Figure 3. X-ray diffraction results for retained austenite fraction after various IA times at 660 °C.

Figure 3 shows XRD results for retained austenite fractions from the cold-rolled condition as well as after IA with different isothermal hold times up to 1000 s and shows that the retained austenite fraction increased with increasing IA time. The microstructure after IA at 660 °C for 500s is shown in Figure 4 with the different constituents labelled; undissolved cementite is the brightest constituent, retained austenite and/or martensite/austenite (MA) constituent corresponds to the intermediate contrast areas, and ferrite is the darker constituent.

Figure 4. FESEM micrograph of the microstructure after IA at 660 °C for 500 s. Bright-contrast constituent labelled ‘θ’ is presumed to be cementite; regions consistent with retained austenite and/or MA constituent are labelled ‘γ/MA’.

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Figure 5. (a) and (c) BF-STEM micrographs and (b) and (d) STEM-EDS map of Mn distribution after IA at 660 °C for 1000 s. (c) and (d) correspond to blue, dotted boxed region in (a). Red arrows in (a) and (c) correspond to EDS line-scans in Figure 6.

Micrographs collected with STEM and STEM-EDS results after IA at 660 °C for 1000 s are shown in Figure 5. BF-STEM images are shown in Figures 5(a) and 5(c); the corresponding STEM-EDS maps are displayed in Figures 5(b) and 5(d). Figures 5(c) and 5(d) show a higher magnification of the red, boxed region identified in Figure 5(a). Line-scan results from STEM-EDS, which correspond to the red arrows in Figures 5(a) and 5(c), are shown in Figures 6(a) and 6(b). The STEM-EDS results indicate Mn enrichment of approximately 7-10 wt pct in many of the grains, which are presumed to be retained austenite and/or MA constituent. Some small particles with higher Mn enrichment are also shown, presumed to correspond to undissolved cementite.
The experimental results indicate that Mn-enriched austenite formed during IA despite incomplete dissolution of Mn-enriched cementite. The IA temperature (660 °C) was greater than the equilibrium cementite solvus temperature predicted by Thermo-Calc® (647 °C) and thus the eventual dissolution of cementite is expected. After the 16 h tempering at 550 °C and cold-rolling, cementite was observed to have considerable Mn-enrichment. Cementite particles observed in ferrite after IA had lower Mn concentrations relative to the cold-rolled condition, which suggests that Mn had partially diffused out of the cementite during IA.

### Thermo-Calc® Model

The schematic shown in Figure 7(a) depicts austenite nucleation at a deformed-ferrite grain boundary in relation to cementite upon IA; this scenario is considered for the thermodynamic model presented here. The corresponding local equilibrium (LE) compositions of ferrite, cementite, and austenite from Thermo-Calc® are listed in Table 1. The initial compositions at the ferrite-cementite interface reflect equilibrium calculations at 550 °C, which is expected to have remained largely unchanged upon cold-rolling and heating to 660 °C.

Later, after IA for some time required to develop Mn gradients in the microstructure, the compositions at the ferrite-cementite interface approach LE levels; the calculation for these compositions utilized suppression of the austenite phase in Thermo-Calc®. The concentration at the austenite-ferrite interface reflects LE at 660 °C. This calculation considered a composition of Fe-0.05C-3.2Mn to reflect the ferrite matrix after tempering at 550 °C.

<table>
<thead>
<tr>
<th></th>
<th>$\gamma$-(\alpha) Interface (LE)</th>
<th>$\alpha$-(\theta) Interface (Initial)</th>
<th>$\alpha$-(\theta) Interface (LE)</th>
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<td>$\alpha$</td>
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The C chemical potentials at 660 °C from Thermo-Calc® are plotted against Mn concentration in Figure 7(b) for the austenite-ferrite and ferrite-cementite interfaces. The corresponding initial and LE chemical potentials of C for the ferrite-cementite interface are indicated by the red, dotted lines and the LE chemical potential of C for the austenite-ferrite interface is indicated by the blue, dashed line. Figure 7(b) indicates that the initial chemical potential of C at the ferrite-cementite is lower than at the austenite-ferrite interface; however, after LE conditions are established, the chemical potential of C increases to a level greater than at the austenite-ferrite interface.
Plots of the Mn distribution and chemical potentials of C among austenite, ferrite, and cementite during IA are shown in Figure 8 and provide additional context regarding the effect of Mn gradients on the chemical potential of C in cementite. The initial Mn enrichment in cementite causes the chemical potential of C in cementite to be lower than at the austenite-ferrite interface, shown in Figures 8(a) and 8(b). Figure 8(c) depicts the Mn distribution as Mn diffuses out of cementite. Near the ferrite-cementite interface, the LE Mn concentration in cementite is 31.6 wt pct (Table 1). The corresponding chemical potential of C, plotted in Figure 8(d), indicates that the chemical potential of C at the ferrite-cementite interface is greater than at the austenite-ferrite interface, this causes a driving force for C to migrate from cementite to austenite, suggesting that dissolution of cementite occurs as Mn diffuses out of cementite.

DISCUSSION

Our prior work considered various DICTRA™ simulations for austenite growth during IA and resulted in predictions for austenite formation that occurred by NPLE-type or PLE-type phase transformations depending on initial conditions used in the simulations. The simulations showed that austenite formed with NPLE conditions was associated with a Mn distribution where the center of the austenite was Mn-deficient, and the outer region was Mn-enriched. Alternatively, austenite that formed with Mn-diffusion-controlled, PLE conditions had a relatively uniform Mn distribution. For mechanical property modeling efforts that aim to consider austenite stability from different IA heat treatment simulations, the predicted Mn distribution in austenite should be of considerable interest. This highlights the need to ensure heat treatment simulation efforts accurately predict austenite growth mechanisms.
The present work compared initial assumptions for a similar DICTRA™ simulation to experimental characterization, and explored the thermodynamic conditions that result in gradual cementite dissolution and PLE-type growth of austenite during IA. The thermodynamic model suggests that Mn enrichment in cementite caused temporary stabilization of cementite above the equilibrium solvus temperature until Mn diffusion out of cementite caused the chemical potential of C to be greater than in austenite. The model is consistent with EDS results in Figures 5 and 6 which indicate Mn-enriched cementite particles after IA for 1000 s. While cementite dissolution was Mn-diffusion-controlled, austenite formed at a rate controlled by Mn diffusion through ferrite; this enabled significant fractions of austenite to form prior to complete cementite dissolution and is consistent with the XRD results in Figure 3 and the microstructure shown in Figure 4 after IA for 500 s. The model suggests that the formation of austenite proceeded by a Mn-diffusion-controlled, PLE-type phase transformation mechanism and not by NPLE-type growth, as C was only able to partition to austenite as Mn diffused out of the cementite.

CONCLUSIONS

Experimental results indicate formation of Mn-enriched austenite during IA and slow dissolution of Mn-enriched cementite. Thermodynamic assessments suggest that Mn enrichment caused cementite to be transiently stabilized above the equilibrium solvus temperature until Mn diffused out of the cementite. The Mn enrichment in cementite mediated dissolution and caused C migration from cementite to austenite to be dependent on Mn diffusion. Austenite formation occurred predominantly through a Mn-diffusion-controlled, PLE-type transformation as Mn migrated through ferrite toward the austenite-ferrite interface.

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REFERENCES


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