CARBON ENRICHMENT OF AUSTENITE AND CARBIDE PRECIPITATION DURING THE QUENCHING AND PARTITIONING (Q&P) PROCESS

F.C. Rizzo¹, D.V. Edmonds², K. He², J.G. Speer³, D.K. Matlock³ and A. Clarke³

¹Department of Materials Science and Metallurgy; Pontificia Universidade Católica-Rio de Janeiro; RJ 22453-900, Brazil

²School of Process, Environmental and Materials Engineering; University of Leeds; Leeds LS2 9JT, United Kingdom

³Advanced Steel Processing and Products Research Center; Colorado School of Mines; Golden, CO 80401, USA

Abstract

A novel heat treatment process for obtaining superior properties in a variety of steel compositions has been recently proposed. The process, designated Quenching and Partitioning (Q&P), is based on the partial transformation of austenite into martensite, followed by partitioning of carbon under conditions preventing tempering reactions. During partitioning, escape of carbon from supersaturated martensite results in carbon enrichment of austenite, promoting stabilization of this phase during subsequent quenching to room temperature. The final microstructure can consist of ferrite, carbon enriched martensite and retained austenite, exhibiting interesting combinations of mechanical properties. Carbon enrichment of the austenite is dependent on the ability to prevent formation of carbides. In the present work, the kinetics of carbon escape from martensite is investigated for a high Si steel subjected to Q&P processing and the results discussed with regard to carbide precipitation and austenite stabilization.

Introduction

Development of advanced high strength steels has resulted in materials with superior combinations of strength and formability, such as the dual-phase, TRIP and complex steels. One important constituent of TRIP steels is the presence of metastable retained austenite that can transform to martensite during deformation and which is obtained by carbon enrichment of austenite during a carbide-free bainitic transformation. The possibility of improving the mechanical properties of such steels through an alternative route designated Quenching and Partitioning (Q&P) has recently been proposed [1]. In this new process, tempering reactions are suppressed by alloying with Al and/or Si, so that a substantial increase in the carbon concentration of austenite is attained by partitioning. Figure 1 shows a schematic diagram of the Q&P process and the corresponding evolution of the microstructure. A detailed description of the process and some preliminary results have been reported in the literature [2-5], indicating the potential for considerable improvement of properties if control of the microstructure is attained through optimization of the composition and processing conditions. Figure 2 illustrates the total elongation vs ultimate tensile strength for sub-sized samples subjected to the Q&P process and the favorable comparison with properties usually obtained for dual-phase, conventional TRIP and martensitic steels [3].



Fig 1 Schematic diagrams of the Q&P process, producing ferrite/austenite/martensite microstructures, as appropriate, from homogeneous austenite (Ci, C γ and Cm represent the carbon contents of the initial alloy, austenite, and martensite, respectively, and QT and PT are the quenching and partitioning temperatures, respectively). The process may start with an intercritical annealing below Ac₃ to produce a starting microstructure containing ferrite and carbon enriched austenite [1].

The amount of retained austenite after the first quenching, which is dependent on the quenching temperature (QT), will determine the potential level of carbon enrichment in the austenite during partitioning, if one assumes that formation of carbides is suppressed. Taking into account that this carbon enrichment will determine the stability of the austenite during the final quenching, a proper choice of QT plays an essential role in the development of the final microstructure. Therefore, a methodology to select the quenching temperature was developed assuming that all carbon leaves the ferrite (martensite) and partitions to the austenite [1-5]. The condition under which partitioning occurs has been called constrained carbon equilibrium (CCE), due to the restriction in movement of the ferrite/austenite interface and the assumption that only carbon equilibrates its chemical potential [5-8]. However, although equilibration of the carbon chemical potential occurs quite rapidly at the interface, concentration gradients may be present in both phases. The evolution of the carbon concentration profiles during partitioning will be determined here using the diffusivity of carbon in both phases, as well as the relative size of adjacent plates of ferrite and austenite and the overall scale of the microstructure. The escape of carbon from a supersaturated ferrite plate has been previously addressed by both analytical [9-10] and numerical techniques [11-12]. To provide a more realistic description of the partitioning during the O&P process and to allow a corresponding refinement of the quenching temperature selection methodology [13], the kinetics of carbon escape from the ferrite and its homogenization in the austenite have been modeled in the present work using DICTRA [14], following the numerical technique proposed by Hillert et al. [12]. Diffusivities for DICTRA calculations are obtained as a product of a thermodynamic and a kinetic factor. The thermodynamic factor is essentially the second derivatives of the molar Gibbs energy with respect to concentration, while the kinetic factor contains the atomic mobilities, which are stored in a kinetic database [15]. Therefore, the effect of Si and Mn on the diffusivity of carbon is automatically taken into account during the calculations.



Figure 2. Total elongation vs. ultimate tensile strength for TRIP, Dual phase (DP), martensitic (M), and Q&P sheet steel products [3].

Numerical Calculation Results and Discussion

Initial calculations were performed using DICTRA, taking as a reference a 0.19C-1.59Mn-1.63Si wt% steel fully austenitized at 900°C, quenched to 293°C to produce 68% martensite and partitioned at 400°C. Plate-shaped regions for both martensitic ferrite and austenite are assumed. The thicknesses of the ferrite and austenite plates used in the simulations were 0.30 and 0.14 microns, respectively. These dimensions were obtained from direct observation by transmission electron microscopy and represent an average value from measurements carried out in several samples subjected to this treatment [16],.

Figure 3 shows an example of the resulting microstructure, illustrating the adjacent austenite/ferrite plate (lath) morphology. In Figure 3b the $(200)\gamma$ dark field image shows the presence of thin retained austenite laths.



(a)



(b)

Figure 3 Bright field (a) and (200) γ Dark field (b) of a 0.19C-1.59Mn-1.63Si steel sample subjected to partitioning at 400 C during the Q&P process, illustrating the lath morphology.

The simulation was done assuming that, due to the presence of silicon, no tempering reaction occurs and all available carbon diffuses into the austenite. Results for calculations of the carbon distribution in both phases for selected partitioning times, ranging from 10^{-4} to 10 seconds, are shown in Figure 4. The initially uniform C distribution is rapidly altered at the ferrite/austenite

interfaces to equilibrate the carbon activity, resulting in steep concentration gradients in both phases. For the particular geometry chosen, the results indicate that ferrite is depleted quite rapidly.



Figure 4. Carbon concentration profiles (weight %) in the ferrite (Fer) and austenite (Aus) during partitioning at 400C, for a 0.19C-1.59Mn-1.63Si steel. The thickness of the ferrite and austenite plates represent average values experimentally measured for each phase by TEM observation. For these conditions, carbon depletion of the ferrite occurs below 0.1 seconds while the austenite takes around 10 seconds to reach a uniform concentration.

Most of the diffusion process in this phase takes place below 10^{-1} seconds and after this time has elapsed the average carbon concentration of both phases have approached their final value, as indicated by Figure 5. Nonetheless, the complete homogenization of the austenite plate will only take place after around 10 seconds, a duration one hundred times longer.¹ In the subsequent analysis of the diffusion process, the interface, the ferrite and the austenite phases will be treated separately.

¹ For a 0.6wt% C steel, considering the same dimensions, the partitioning times are slightly longer, although in the same range.



Figure 5. Average carbon concentration as a function of time for (a) ferrite (0.30μ) and (b) austenite (0.14μ) adjacent plates during partitioning at 400°C, for a 0.19C-1.59Mn-1.63Si steel. After 0.1 seconds the carbon enrichment of the austenite is almost complete.

Carbon activity and flux at the interface

When partitioning starts, assuming an initially uniform composition, the carbon activity is much higher in the supersaturated martensite (ferrite). This results in a quick adjustment of the carbon concentration at the interface in both phases, to equilibrate the carbon activity. Assuming that the interface does not move at the temperature of partitioning, the flux of carbon that leaves the ferrite must be equal to the flux of carbon entering the austenite. The flux of carbon across the interface, as a function of time, is shown in Figure 6a, indicating a sharp drop to very low values, in less than 10^{-3} seconds,. While the carbon flux varies, a corresponding adjustment of the carbon activities and concentrations at the interface stakes place. Figure 6b illustrates the calculated variation of the carbon activity at the interface with time, which is the same for both phases.



Figure 6. Variation of (a) carbon flux and (b) carbon activity at the interface during partitioning. Time has been plotted in a log scale to allow the observation of the whole process.

The corresponding carbon concentrations of the ferrite and austenite at the interface are indicated in Figure 7. As the carbon flux decreases, the carbon concentrations at the interface as calculated by DICTRA first rise to a plateau value and then remain approximately constant until the carbon flux from the ferrite becomes so small that austenite cannot hold its carbon concentration at the interface. At this point, the carbon concentration of the austenite at the interface starts falling, to accommodate the decreasing carbon flux. The concentration of the ferrite at the interface keeps adjusting to maintain the same carbon activity in both phases, as indicated in Figure 7.



Figure 7. Carbon concentration (wt%) at (a) ferrite and (b) austenite interfaces as a function of time during partitioning of a 0.19C-1.59Mn-1.63Si wt% steel at 400 °C. At any given time the concentrations at the ferrite and austenite interface correspond to the same carbon activity.

Carbon diffusion in the ferrite

The time required to decarburize the ferrite plates is quite relevant, since it will determine if the addition of silicon will be sufficient to suppress the carbide precipitation in this phase [15-19]. Figures 4 and 5 indicate that ferrite is largely depleted in around 0.1 seconds. However, the driving force for carbide precipitation in a given region of the ferrite lath starts decreasing much earlier, when its carbon concentration begins to fall. Therefore, the period of time available for carbide precipitation in the ferrite may be estimated by the time necessary for impingement of the diffusion fields in the center of the plate. This situation can also be represented by the moment at which the flux of carbon reaches the center of the plate. The upper part of Figure 8a shows how the carbon concentration in the center of the ferrite plate varies with time during partitioning, while the lower part shows the flux of carbon. It is clear that most of the diffusion in the ferrite plate takes place between 10⁻³ and 10⁻¹ seconds. After that, only local adjustments of the interface composition will occur to maintain CCE during the later homogenization of the austenite. Consequently, with regard to the period available for carbide precipitation, it seems reasonable to consider it as approximately 10⁻³seconds (for the geometry assumed here), before the carbon flux in the center of the plate begins to be significant.

Carbon diffusion in the austenite

While the final carbon concentration of austenite after homogenization (in the present case, this condition of constrained carbon equilibrium involves an austenite composition around 0.6wt%C) is determined by the amount of martensite formed in the first quench, the calculations shown in Figure 4 indicate that a substantially greater enrichment of carbon occurs at the austenite interface (close to 2wt%C). Even though carbon enrichment of the austenite has been almost completed after 10^{-1} seconds (Figure 5), at this point most of the carbon is concentrated in a thin layer close to the interface and the majority of the austenite plate still has its original carbon composition. The stabilization of the austenite will occur progressively, from the interfaces to the center of the plate, following the inward advance of the region with carbon concentration corresponding to an M_s at room temperature. Figure 8b shows the variation with time of the time for full stabilization can be estimated. From Figures 4 and 8 one can see that diffusion in the bulk of the ferrite plate is virtually complete before the start of meaningful diffusion in the center of the austenite plate, for the geometry and partitioning temperature chosen in the present case.



Figure 8. Carbon flux and concentration in the center of (a) ferrite and (b) austenite plates as a function of time. The diffusion process in the ferrite center is essentially completed before the onset of substantial diffusion in the austenite center.

When considering different starting microstructures, the relative dimensions of the phases will influence these times accordingly during the carbon partitioning. Taking into account the parabolic dependence of the diffusion process, any change in the size of a constituent phase (due to change in scale, morphology or shape) will require a time squared variation in the partitioning conditions to produce the same result. The temperature of the partitioning treatment will also influence the kinetics of carbon escape from the ferrite and austenite stabilization and is under present consideration for the optimization of the Q&P processing conditions.

Conclusions

Based on experimental microstructural information obtained by TEM, the carbon escape from a 0.30 microns ferrite plate and enrichment of a 0.14 microns austenite plate during the partitioning treatment of the Q&P process has been simulated for a 0.19C-1.59Mn-1.63Si steel partitioned at 400°C. The results suggest the following conclusions:

- 1. For the scale of microstructure investigated, carbon depletion from the ferrite occurs quite rapidly, in around 10^{-1} seconds, while the austenite takes much longer, around 10 seconds, to achieve a uniform concentration.
- 2. During partitioning at 400°C, depletion of carbon from ferrite occurs quite rapidly and the carbon concentration in the center of the plate starts to decrease after 10⁻³ seconds. After this time the driving force for carbide precipitation is gradually reduced.
- 3. Carbon enrichment of the austenite will promote, initially, a substantial increase in the carbon concentration at the interface and a progressive stabilization of the plate, advancing from the interface to the center. Full stabilization is achieved when the composition of the central region reaches a carbon concentration corresponding to an M_s at room temperature.

Acknowledgements

This research programme is being conducted under an international collaboration supported in the authors' respective countries by NSF *Grant* # 0303510 (USA), EPSRC *Grant ref: GR/S86501* (UK) and CNPq *Grant Institutional Process* # 69.0053/03-7 (Brazil). _Support of the sponsors of the Advanced Steel Processing and Products Group at CSM is also acknowledged_: POSCO is acknowledged for providing experimental materials. The authors are also grateful to members of their respective research groups.

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