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The "Quenching and Partitioning" Process: Background and Recent Progress

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A new process concept, "quenching and partitioning" (Q&P) has been proposed recently for creating steel microstructures with retained austenite. The process involves quenching austenite below the martensite-start temperature, followed by a partitioning treatment to enrich the remaining austenite with carbon, thereby stabilizing it to room temperature. The process concept is reviewed here, along with the thermodynamic basis for the partitioning treatment, and a model for designing some of the relevant processing temperatures. These concepts are applied to silicon-containing steels that are currently being examined for low-carbon TRIP sheet steel applications, and medium-carbon bar steel applications, along with a silicon-containing ductile cast iron. Highlights of recent experimental studies on these materials are also presented, that indicate unique and attractive microstructure/property combinations may be obtained via Q&P. This work is being carried out through a collaborative arrangement sponsored by the NSF in the USA, CNPq in Brazil, and the EPSRC in the United Kingdom.

Keywords: *carbon partitioning, retained austenite, martensite*

1. Introduction

High strength ferrous alloys containing significant fractions of retained austenite have been developed in recent years, and have important commercial applications. In sheet steels, for example, carbon-enriched metastable retained austenite is considered beneficial because the TRIP phenomenon during deformation can contribute to formability and energy absorption. In gear and bearing surfaces, austenite is considered to provide damage tolerance in rolling/sliding contact fatigue applications. In thicker section structural applications, retained austenite may provide enhanced resistance to fracture. Similarly, austempered ductile cast iron materials develop favorable property combinations through a microstructure of fine ferrite plates in combination with carbon-rich retained austenite.

Steels with substantial amounts of carbon-enriched retained austenite are typically produced by transforming at low temperatures, leading to a microstructure containing "carbide-free bainite" that consists of bainitic ferrite laths with interlath retained austenite. Alloying additions such as Si or Al are made to suppress cementite precipitation that usually accompanies bainite formation. Recently, an alternative processing concept, "quenching and partitioning (or Q&P), has been developed for the production of austenite-containing steels, based on a new understanding of carbon partitioning hypothesized between martensite and retained austenite[1]. This paper reviews the fundamental elements of the process concept, and recent experimental investigations to examine the Q&P processing response of two commercial Si-containing steels and a commercial Si-containing ductile cast iron.

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2. Background and Q&P Fundamentals

2.1. Carbon partitioning concept

Carbon partitioning between martensite and retained austenite is usually ignored in quenched steels, because the temperature is normally too low for substantial amounts of carbon diffusion to occur after quenching, and because carbon supersaturation in martensite is ordinarily eliminated by a different mechanism, viz. carbide precipitation during tempering. Consequently, while carbon-enriched retained austenite has been identified in martensitic steels for some time[2], the thermodynamics of carbon partitioning between martensite and retained austenite has been scarcely considered. Recently, a model has been developed to address carbon partitioning from as-quenched martensite into austenite, under conditions where competing reactions such as bainite, cementite or transition carbide precipitation are suppressed[1]. The model predicts the "endpoint" of partitioning, when martensite (i.e. ferrite) is in metastable equilibrium with austenite.

Metastable equilibrium between austenite and ferrite is not a new concept[3], and equilibrium (e.g. orthoequilibrium) and paraequilibrium concepts are well understood at sub-critical temperatures for conditions where partitioning of slow-moving substitutional elements is either complete or absent, respectively. It must be recognized, however, that transformations occurring under equilibrium or paraequilibrium necessarily involve interface migration and thus require short range movements of iron and substitutional atoms, even when long-range substitutional diffusion is precluded as in the paraequilibrium case. When the position of the martensite/austenite interface is effectively

constrained, as we consider to apply for carbon partitioning between martensite and retained austenite at relatively low temperatures, then even short-range diffusional movements of iron and substitutionals are precluded, and it is not possible for a ferrite/austenite mixture to reach equilibrium in the Fe-C system (or paraequilibrium in multicomponent alloy systems). The metastable α/γ equilibrium in the case of an immobile or constrained interface, is therefore termed "constrained paraequilibrium" or CPE. Paraequilibrium and CPE derive fundamentally from the immobility of iron and substitutionals in comparison to carbon and other interstitials. Consequently, these two conditions are considered by the authors to be closely related, although this view is not held universally[4] and remains the subject of discussion[5].

Constrained paraequilibrium is essentially defined by one thermodynamic requirement, and one key matter balance constraint. First, carbon diffusion is completed under constrained paraequilibrium conditions when the chemical potential of carbon is equal in the ferrite and austenite. Ignoring effects of alloying on carbon activity, this requirement may be represented using results of Lobo and Geiger[6,7] for the Fe-C binary system as follows:

$$x_C^{\gamma} = x_C^{\alpha} \cdot e^{\frac{76,789 - 43.8T - (169,105 - 120.4T)x_C^{\gamma}}{RT}} \quad (1)$$

where x_C^{α} and x_C^{γ} represent the mole fractions of carbon in ferrite and austenite. The relevant thermodynamics are embedded in Equation 1. This thermodynamic condition may be understood by comparing the schematic Gibbs molar free energy *vs.* composition diagram in Figure 1a representing metastable equilibrium in the Fe-C system, with constrained paraequilibrium in Figure 1b.

In (ortho) equilibrium, or paraequilibrium in higher order alloys, there are unique ferrite and austenite compositions (x_{EQ}^{α} and x_{EQ}^{γ}) satisfying the common tangent construction whereby the chemical potentials of both carbon and iron are equal in both phases ($\mu_C^{\alpha} = \mu_C^{\gamma}$ and $\mu_{FE}^{\alpha} = \mu_{FE}^{\gamma}$). (In paraequilibrium, the same construction would apply if the vertical axis at the composition of pure iron were replaced by the appropriate composition in multicomponent space representing the relative fractions of iron and substitutional elements in the alloy). In constrained paraequilibrium, the thermodynamic condition that the chemical potential of carbon is equal in both phases requires only that the tangents to the ferrite and austenite free energy curves must intersect the carbon axis at a single point. This condition can be satisfied by an infinite set of phase compositions[8], and examples of two such conditions are given in Figure 1b, one which is associated with phase compositions ($x_{CPE}^{\alpha\text{-}II}$ and $x_{CPE}^{\gamma\text{-}II}$) having a higher carbon concentration than the equilibrium phase compositions, and one associated with phase compostions ($x_{CPE}^{\alpha\text{-}I}$ and $x_{CPE}^{\gamma\text{-}I}$) having lower carbon levels than equilibrium. The actual CPE phase compositions must also satisfy the unique matter balance constraint associated with the stationary α/γ interface. This second constraint requires that the number of iron (and substitutional) atoms is conserved in each phase during carbon partitioning. Mathematically, this matter balance for iron may be represented by:

$$f_{CPE}^{\gamma}(1 - x_{C_{CPE}}^{\gamma}) = f_i^{\gamma}(1 - x_C^{alloy}) \quad (2)$$

where x_C^{alloy} is the overall carbon content of the steel (in atom fraction, recognizing also that in Fe-C binary alloys, $1 - x_C = x_{FE}$), $f_i^{\gamma}$is the mole fraction of retained austenite before partitioning begins, and f_{CPE}^{γ} and $x_{C_{CPE}}^{\gamma}$ represent the austenite amount and carbon concentration, respectively, at constrained paraequilibrium when carbon partitioning is complete. (A small change in austenite fraction is consistent with transfer of carbon atoms across the interface). Constrained paraequilibrium is achieved when Equations 1-2 above, and Equations 3-4 below are satisfied, where the mass balance for carbon is represented by:

$$f_{CPE}^{\alpha} x_{C_{CPE}}^{\alpha} + f_{CPE}^{\gamma} x_{C_{CPE}}^{\gamma} = x_C^{alloy} \quad (3)$$

and the relationship between the phase fractions of α and γ is simply:

$$f_{CPE}^{\alpha} + f_{CPE}^{\gamma} = 1 \quad (4)$$

Example CPE calculations have been reported previously[1], where it was shown that most of the carbon in the steel is expected to partition to the austenite, and quite high levels of carbon enrichment are possible. The dependence of the metastable CPE condition on alloy carbon content, temperature, and the as-quenched austenite and martensite phase fractions was also illustrated. While the detailed calculations are not difficult, it was found that *the austenite composition at constrained paraequilibrium can be closely approximated by assuming that virtually all of the carbon in the martensite partitions to the austenite*, and then applying the appropriate carbon matter balance based on the amount of retained austenite present after quenching[9].

The results of the constrained paraequilibrium model suggested a new process, whereby austenite is formed at high temperature (either by full austenitization or intercritical heat treatment), followed by cooling to a temperature carefully selected (between M_s and M_f) to control the fractions of martensite and retained austenite, and finally by a thermal treatment that accomplishes the desired carbon partitioning to enrich the austenite with carbon and stabilize some (or all) of it to room temperature. This process sequence and the corresponding microstructural changes are illustrated schematically in Figure 2 [10]. The process assumes that carbon supersaturation is relieved by diffusion into retained austenite, and is referred to as quenching and

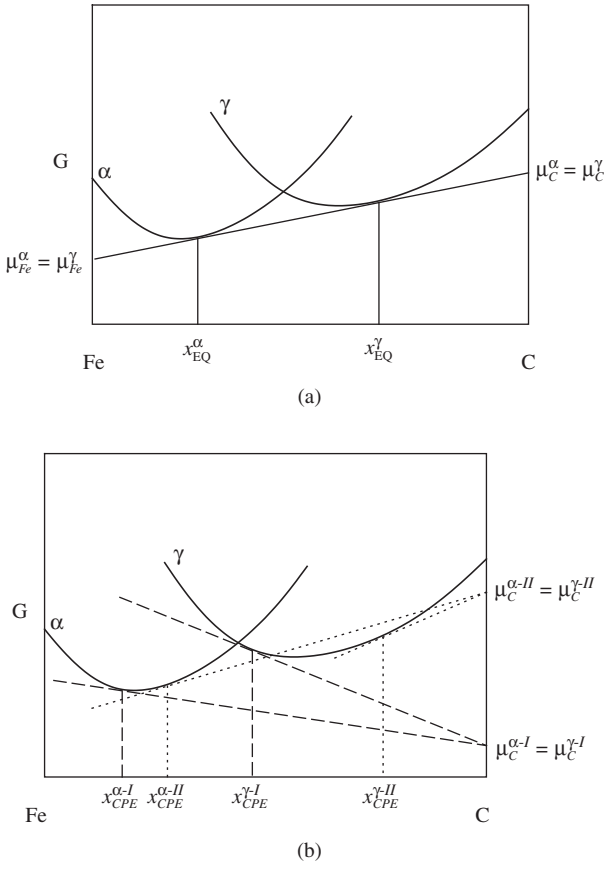


Figure 1. Schematic molar Gibbs free energy *vs.* composition diagrams illustrating metastable equilibrium at a particular temperature between ferrite and austenite in the Fe-C binary system. a) equilibrium (EQ), and b) two possible constrained paraequilibrium conditions (I and II).

partitioning, or Q&P, to distinguish it mechanistically from conventional quenching and tempering (Q&T) of martensite, where carbide precipitation and decomposition of retained austenite (to ferrite plus cementite) are typical. The example in Figure 2 indicates an initial full austenitization step, although intercritical annealing is also envisioned for formable sheet products containing an equiaxed ferrite component in the microstructure. During intercritical annealing, a smaller initial fraction of austenite would be present with a higher initial carbon content.

The quenching and partitioning heat treatment was envisioned to have application to high-strength austenite containing TRIP sheet steel products, replacing an isothermal bainitic heat treatment of low-carbon steels containing substantial additions of Si, Al, or P to suppress carbide formation. Some suggested advantages of Q&P include the potential for greater carbon enrichment of austenite, decoupling of the (bainitic) ferrite growth kinetics from the carbon partitioning process, and increasing strength via formation of substantial quantities of lath martensite in the microstructure. Other opportunities were identified to employ retained austenite through Q&P processing of higher strength bar steels or even austempered ductile cast iron. Finally, it was suggested that a specific CPE phase composition (where the austenite composition approximates T_o) might even represent a viable steady state boundary condition at the α/γ interface during bainitic ferrite growth, providing a model for the bainite transformation mechanism that is both "fully" diffusional and "fully" martensitic[1].

2.2. Importance of suppressing carbide precipitation

The absence of carbide formation is a fundamental element of the constrained paraequilibrium model, since the existence of metastable equilibrium between ferrite and austenite is precluded if the more stable ferrite plus iron carbide equilibrium can be achieved. Any carbide formation effectively "consumes" carbon, since these carbon atoms are no longer available to enrich the austenite. Thus, it is necessary to understand and control carbide precipitation processes that may occur during any partitioning treatments associated with the Q&P process.

It is well known that cementite formation can be eliminated or suppressed through additions of silicon[11,12], and also that aluminum and even phosphorus can produce a similar effect[13]. Such elements thus play a critical enabling role in the Q&P process. It is also well known in the martensite tempering literature that silicon suppresses cementite formation, or delays the transition from early-stage tempering (where ε or η carbides are present), to later-stage tempering (where θ-Fe_3C is present)[14-16]. In martensite, fine transition carbides are usually not considered detrimental, whereas cementite can be of more concern. Thus, the greater emphasis has been on understanding when transition carbides are replaced by cementite formation[16,17], rather than on the *initiation* of transition carbide precipitation. For Q&P processing, however, any transition carbide precipitation diminishes the potential for carbon enrichment of austenite, and it is necessary to develop a better understanding of the *onset* of transition carbide formation, including composition and processing effects[9,18].

Precipitation of transition carbides *within* retained austenite during martensite tempering has not been documented. Since the chemical potential of carbon is much higher in as-quenched martensite than in the retained austenite, it is reasonable to conclude that carbide nucleation would be more likely in bcc ferrite than in austenite[9,19]. The α/γ interface is also a favored site for carbide formation. In the Q&P process, high carbon supersaturation of the martensite prior to partitioning could conceivably drive transition carbide formation to a greater extent than would be possible during bainite growth at the same temperature if bainitic ferrite grows with a much lower carbon content than the austenite. (In this context, it should be noted that the carbon supersaturation of bainitic ferrite *during growth* remains a subject of controversy). In any event, the extent to which carbide formation is suppressed will be a critical factor influencing the microstructures that are achievable using the Q&P process, and further studies are needed to establish more clearly the influences of alloying and processing on the carbide precipitation behavior and kinetics in these steels.

2.3. Process design (selection of quenching temperature)

A methodology for designing the quench temperature to achieve the maximum possible retained austenite fraction after Q&P processing, was developed in a recent publication[9]. The model ignores partitioning kinetics, and assumes that all of the carbon partitions from martensite to austenite, and that carbide precipitation is avoided completely. The model results are shown in Figure 3, for a 0.19%C,

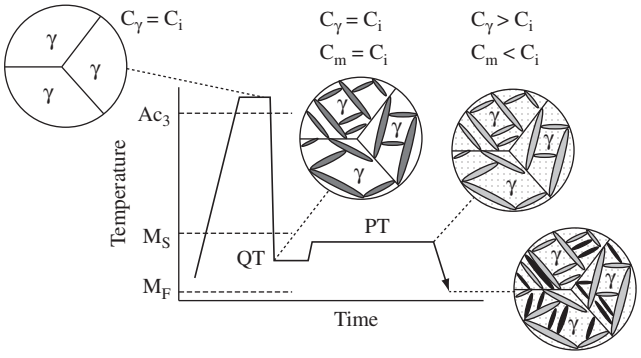


Figure 2. Schematic illustration of the Q&P process for producing of austenite-containing microstructures. C_i, C_γ, C_m represent the carbon concentrations in the initial alloy, austenite, and martensite, respectively. QT and PT are the quenching and partitioning temperatures[10].

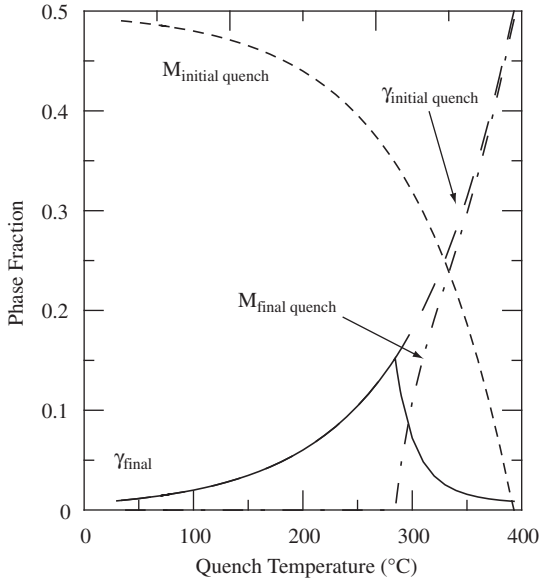


Figure 3. Predicted Q&P microstructure components for experimental steel containing 50% intercritical ferrite, *vs.* quench temperature, assuming full partitioning prior to final quenching to room temperature. The final austenite fraction at room temperature is given by the solid bold line. Dashed lines represent the austenite and martensite (M) present at the initial quench temperature, and the additional martensite formed during the final quench to room temperature. For this example, $M_{initial\ quench} + M_{final\ quench} + \gamma_{final} = 0.5$, and the intercritical ferrite fraction is 0.5.

1.96%Al, 1.46%Mn, 0.02%Si (by weight) TRIP sheet steel composition, assuming that intercritical annealing was conducted to achieve a microstructure containing 50% austenite and 50% ferrite prior to quenching. In this figure, the *final* austenite fraction after partitioning and cooling to room temperature is plotted (bold solid line) *vs.* the quenching temperature prior to partitioning. The austenite and martensite fractions at the quench temperature are also plotted, along with the fraction of "fresh" martensite that forms during final cooling.

The model first estimates the fractions of austenite and martensite at the quench temperature (QT in Figure 1) based on the undercooling below M_s, according, for example, to the Koistinen-Marburger[14] relationship:

$$f_m = 1 - e^{-1.1\times10\text{-}2(M_s - QT)} \quad (5)$$

where f_m is the fraction of austenite that transforms to martensite upon quenching to a temperature QT below the M_s temperature, and M_s for the applicable austenite composition can be estimated from published correlations. (For processing where intercritical annealing is conducted rather than full austenitization, the initial carbon concentration of the austenite is controlled by the intercritical annealing temperature, and may be estimated by assuming that nearly all of the carbon in the steel is contained in the austenite, since the carbon solubility in ferrite is very low). After completion of (full) partitioning between martensite and austenite subsequent to quenching, the carbon concentration in the remaining austenite may be estimated, and the final phase fractions may be predicted after final cooling, again applying the Koistinen and Marburger relationship to the carbon-enriched austenite.

The model results indicate an "optimum" quenching temperature that yields a maximum amount of retained austenite. Above the peak temperature, substantial austenite fractions remain after the initial quenching step, but the austenite stability is too low during final quenching, and increasing amounts of fresh ($M_{final\ quench}$) martensite are found at higher quench temperatures, reducing the final austenite fraction at room temperature. Below the peak temperature too much austenite is consumed during the initial quench prior to carbon partitioning, and the carbon content of the retained austenite is greater than needed for stabilization at room temperature. The peak is found at the particular quench temperature where martensite formation is just precluded during the final quench, whereby the austenite has an M_s temperature of room temperature after full partitioning. This methodology provides guidance for experimental processing design, and allows the effects of changes in a variety of processing variables to be explored and predicted. Partitioning kinetics are not predicted in this simple model, however, and development of a more sophisticated model will require further understanding of the length-scale of the microstructure over which partitioning occurs, and the kinetics of carbide precipitation processes that may occur.

3. Highlights of Recent Progress

3.1. Medium-carbon bar steels

Initial investigation of the Q&P processing concept verified the presence of significant amounts of carbon enriched austenite in a 0.35%C, 1.3%Mn, 0.74%Si (wt. pct.) microalloyed bar steel, despite the apparent formation of some transition carbides during the partitioning treatment[10]. More recently, the Q&P processing response of a 0.6%C, 2%Si (grade 9260) steel was examined by Gerdemann, and compared to the results of conventional austempering or quenching (to room temperature) and tempering[20]. Wafers (28.5 mm in diameter by 2.5 mm thick) were austenitized in molten salt for 15 minutes at 900 °C, quenched into a molten tin-bismuth bath at temperatures ranging between 150 and 210 °C, and equilibrated for 120 seconds before partitioning at temperatures between 250 and 500 °C in molten salt for times ranging between 10 and 3600 seconds, and finally, quenched to room temperature. The quenching temperatures were designed using the methodology described above.

The results showed that substantial levels of retained austenite could be achieved by Q&P processing of the 9260 alloy, approaching 30% by volume. The relationship between the amount of retained austenite and the quench temperature is reproduced here in Figure 4, for conditions involving a 10 seconds partitioning treatment at 500 °C. The figure shows that the amount of austenite measured by X-ray diffraction was in qualitative agreement with model calculations, although the measured austenite fractions were lower than the maximum amounts predicted.

Partitioning at lower temperature (250 °C) led to partitioning treatment times that would be more appropriate for industrial processing of bulk specimens (e.g. 45 to 60 minutes), whereas much shorter times were associated with the maximum austenite fractions at higher temperature (e.g. 10 seconds at 400 °C). Some encouraging property results were noted in this study, such as hardness levels in excess of HRC58 in combination with austenite fractions approaching 10%. In contrast, substantial austenite levels were not achievable by conventional quenching and tempering, and lower hardnesses were associated with bainitic processing (austempering). The combination of high hardness along with a significant retained austenite fraction is considered to be of possible interest for gear or bearing applications, where "damage tolerance" under pitting or contact fatigue conditions is enhanced by austenite that is present in the microstructure[21].

Microstructure characterization is currently underway, and Figure 5 shows an example resulting from quenching to 190 °C, and holding in the bath for 120 seconds. Transmission electron microscopy (TEM) shows the martensite substructure in bright field (Figure 5a), along with finely dispersed retained austenite in dark field (light regions in Figure 5b). This heat-treatment condition is associated with much more retained austenite (> 6%) than is obtained by quenching directly to room temperature (< 2%), illustrating that partitioning has already begun during the 120 seconds equilibration at the quench temperature (190 °C)[20].

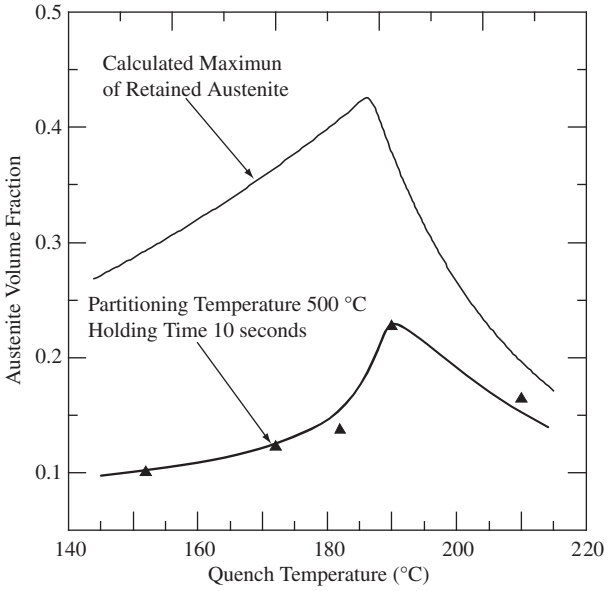
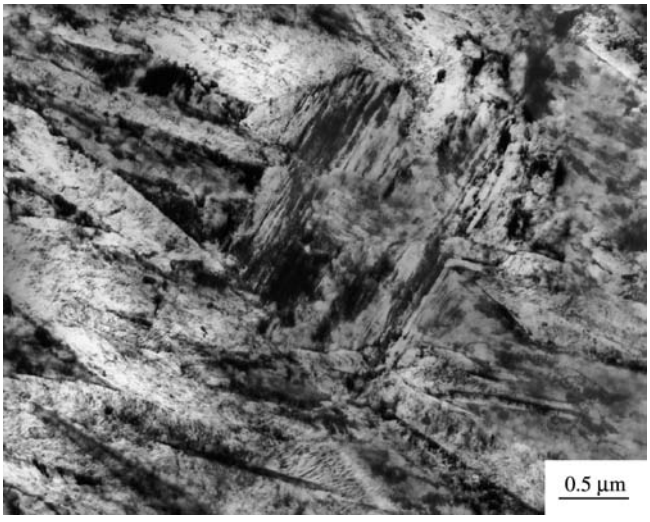


Figure 4. Final volume fraction of retained austenite depending on the quench temperature at a partitioning temperature of 500 °C, and calculated austenite volume fraction over this quench temperature range[20].

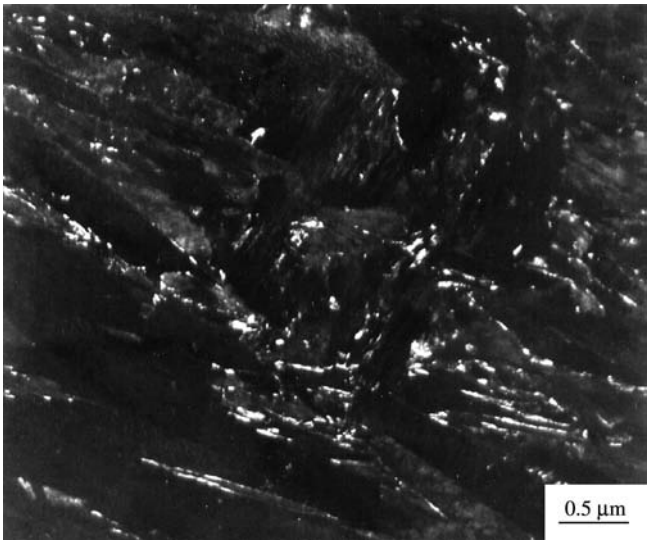
3.2. TRIP sheet steels

High strength sheet steels containing significant fractions of retained austenite have been developed in recent years, and are the subject of growing commercial interest[23,24]. Carbon-enriched metastable retained austenite is considered beneficial because the TRIP phenomenon during deformation can contribute to formability and energy absorbtion. These steels are typically produced by intercritical annealing followed by austempering, with additions of Si, Al, or P to suppress carbide formation that usually accompanies the bainite transformation. Initial studies on the Q&P processing response[9] of TRIP sheet steel showed that substantial amounts of austenite could be obtained via Q&P processing, with measured retained austenite fractions similar to the predicted maximum of 15% in this 0.19%C, 1.96%Al, 1.46%Mn steel. Because of concerns related to uncertainty in the effects of aluminum on the M_s temperature, and overlapping of the carbon partitioning and bainite transformation mechanisms owing to accelerated austenite decomposition kinetics associated with aluminum additions, more recent studies have been conducted using a 0.19%C, 1.63%Si, 1.59%Mn TRIP sheet steel[18]. Transformation response and mechanical behavior are both being assessed, and initial results have been very encouraging. Variations in quenching temperature were examined, along with selected variations in partitioning time and temperature, using either "1-step" or "2-step" Q&P processing. In 1-step processing, partitioning is carried out at the quenching temperature, while 2-step processing involves reheating to a selected partitioning temperature that differs from the quench temperature.

New microstructures that extend the strength levels of current TRIP steels resulted from Q&P processing, as shown in the results of Figure 6, comparing the measured strength and formability (ductility) combinations with current "state-of-the-art" sheet grades including dual-phase (ferrite-martensite), austempered TRIP (bainite), and martensitic steels. (The data used in this figure are discussed further in reference[18].) Much additional opportunity remains to explore available property combinations, and optimize retained austenite fractions and austenite stability, as well as to understand the operative fundamental mechanisms and explore industrial processing capabilities. Scanning electron microscopy, as illustrated in the example of Figure 7, shows the presence of intercritical ferrite (dark featureless areas), along with a mixture of martensite and fine retained austenite. The fine substructure in the Q&P heat treated condition is apparently responsible for the elevated strength levels and distinguishes the resulting Q&P microstructure from bainite produced by conventional austempering at the same temperature as partitioning is accomplished in Q&P[18].



(a)



(b)

Figure 5. TEM bright field (a) and $(002)_\gamma$ dark field (b) images showing martensite and retained austenite in 9260 alloy quenched to 190 °C and equilibrated for 120 seconds before final cooling to room temperature[22].

3.3. Austempered ductile cast iron

Austempered ductile iron (ADI) contains substantial levels of silicon, and is usually processed by heating into the austenite-plus-graphite phase field, followed by austempering at a lower temperature to transform the austenite to "ausferrite," which is essentially bainitic ferrite with carbon-enriched retained austenite. This microstructure provides ADI with high strength in combination with ductility and toughness that is sufficient for many applications. Because of the high-silicon levels and the importance of retained austenite, Q&P was considered to offer a potential heat treating alternative for ADI, and a team of 4th year undergraduate students at Colorado School of Mines

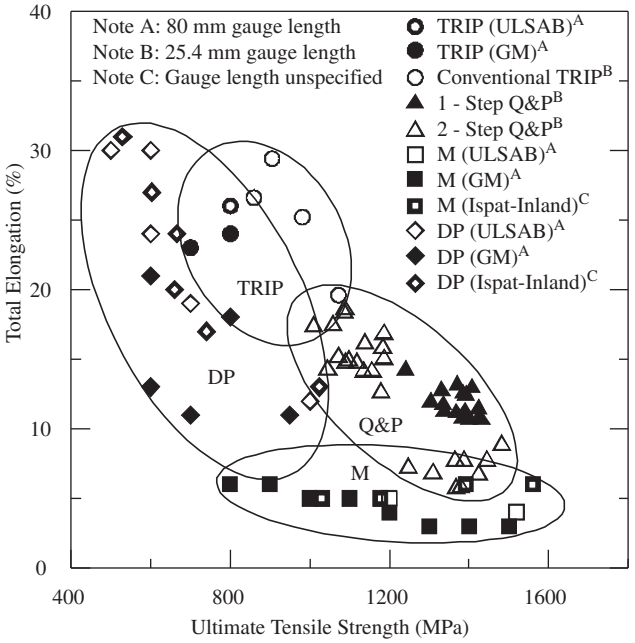


Figure 6. Total elongation *vs.* ultimate tensile strength for TRIP, Dual phase (DP), martensitic (M), and Q&P sheet steel products[18].

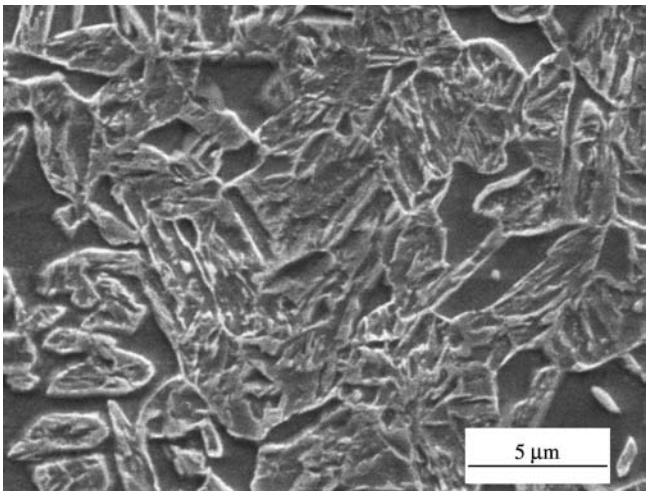


Figure 7. Microstructure of Si-TRIP sheet steel containing 8.4% austenite, processed by intercritical annealing (75% γ + 25% α) followed by quenching to 200 °C and partitioning at 400 °C for 10 seconds. Etched in 2% nital.

has recently examined the response of a commercial 3.7%C, 2.5%Si, 0.34%Mn, 0.17%Cu ductile cast iron grade to Q&P processing, as part of a "capstone" materials-design course project[25]. A limited number of quenching (137, 157, and 172 °C) and partitioning temperatures (230, 270, 310, 350, and 390 °C) was assessed in this work, while the "austenitizing" temperature (850 °C) and partitioning time (1800 seconds) were held constant. The quenching temperatures were selected for austenite compositions predicted at 850 °C using Thermo-Calc software[26] to estimate the austenite/graphite equilibrium condition.

The results again showed that substantial fractions of carbon-enriched austenite could be retained via Q&P processing, although the austenite levels were found to be lower than obtained via austempering under the processing conditions evaluated. The strengths were greater in the Q&P condition, while the ductility and room-temperature impact properties were lower. Further experimentation and process optimization is needed to determine whether Q&P represents an advantageous alternative in this application.

4. Concluding Remarks

The Q&P process concept has been reviewed, along with the fundamental thermodynamics of carbon partitioning between martensite (i.e. carbon-supersaturated ferrite) and austenite. A methodology for predicting the amount of retained austenite as a function of quenching temperature was described, based on the assumptions that full partitioning of carbon is achieved, and that carbide precipitation is fully suppressed. Recent experimental studies have confirmed that Q&P provides a viable means to create microstructures containing carbon-enriched retained austenite, and attractive property combinations have been achieved in a variety of materials. Carbon concentrations in the austenite vary with partitioning treatment parameters, and were found to reach levels in the 1.5% to 1.7% range for the materials examined here. In most cases, the measured austenite fractions and austenite carbon concentrations are less than values predicted from theory. Thus it appears that partitioning is generally interrupted before the hypothesized "constrained paraequilibrium" condition. Carbide precipitation is a likely means by which austenite enrichment and retention are reduced, especially in light of the substantial carbon supersaturation of martensite, and X-ray diffraction has confirmed the presence of carbides in some microstructures[10,18]. Further work is currently underway by the project team to characterize better the carbide precipitation behavior and other features of the microstructure using high-resolution TEM techniques. Initial results have already confirmed the presence of ε-carbide in the 9260 bar steel after quenching to 150 °C and partitioning for 3600 seconds at 250 °C[22]. Clearly, substantial work remains to understand the fundamental transformation characteristics of these alloys during Q&P processing, and to optimize the chemical compositions, microstructures and properties, although the results to date are of great encouragement.

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