Quenching and Partitioning of low alloyed steels



Master Thesis

Tuan Nguyen Minh

Department of Materials Science and Engineering

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Supervisors Dr. M.J. Santofimia Dr. Ir. J. Sietsma Dr. L. Zhao



Technische Universiteit Delft

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Abstract

In this study, the Quenching and Partitioning (Q&P) process has been applied to obtain the steel microstructure with retained austenite. The heat treatment involves quenching austenite below the martensite start temperature, followed by a partitioning step to enrich the residual austenite with carbon and thus brings the stability to this phase. The two studied materials contain low concentration of carbon ($\sim 0.2 \text{ wt.\%}$) and different combinations of silicon and aluminum contents. Experimental measurements show that the maximum volume fraction of retained austenite can reach 0.10-0.20, depending on chemical composition of materials and applied heat treatment parameters. The estimation of retained austenite volume fraction with the fixed martensite/austenite interface model brings the inconsistent results to the measured values. Other kinetic processes, which could occur during partitioning treatment, are also discussed. It has been proved that, during the partitioning treatment, austenite is stabilized by a complex mechanism.

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Chapter 1 Introduction

The most prominent tendency in recently material researches is to produce high performance materials. For automobile application, steels have been developed with the goal to get higher combination of mechanical properties. The improvement of material properties has been achieved by alloying steels with various elements and applying suitable heat treatments. By these ways, different mechanical properties of steels can be obtained by changing the microstructure. The presence of different phases in microstructure can bring wider variation of the mechanical properties for steel, compared to single phase microstructure. The strength of steels is provided by martensite and/or bainite. On the other hand, ferrite and retained austenite support the ductility to the materials. The presence of retained austenite in microstructure can bring additional strength to material due to the strain hardening effect of this phase.

In this study, a new heat treatment, called Q&P process, to retain austenite in the microstructure of steels is investigated. The theories and recent progress of the Q&P heat treatment are presented in Chapter 2. The main features of some overlapping processes are also introduced at the end of this chapter. In Chapter 3, the background of experimental procedures, used to study materials, is described. The as-received stage and critical temperatures of studied materials are investigated in Chapter 4. Based on these investigations, the corresponding heat treatments for each material are designed. These heat treatments include interrupted treatment, Q&P treatment and isothermal bainitic treatment. Experimental results of microstructure, retained austenite and the change in length of the specimen corresponding to heat treatments are shown in Chapter 5 and Chapter 6. Based on experimental results, the possible processes and the influence of heat treatment parameters on the Q&P heat treatment are discussed in the same chapters. In Chapter 7, the difference between microstructures of the two studied materials is analyzed based on the chemical composition of steels. Finally, conclusions and recommendations are outlined in Chapter 8.

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Chapter 2 Background

2.1. Advanced high strength steels (AHSS)

Recently, under the pressure to reduce the weight of vehicles and to increase their strength and crash resistance, steel productions for automobile industry are required to have an innovative development. In order to fulfill these requirements, conventional high strength steels (HSS), which were used to produce body frame of vehicles, have been gradually replaced by Advanced High Strength Steels (AHSS). This tendency is driven by the advantages given by the new generation of steels. In comparison with HSS, AHSS have higher strength. While the tensile strength of HSS generally is lower than 700 MPa, typical grades of AHSS can produce up to 1500 - 1700 MPa of tensile strength. Although they have superior strength, the ductility of AHSS is still relatively high. The total elongation that some types of AHSS can reach is to 30 %. Figure 2.1 shows the relationship between tensile strength and total elongation of HSS (in grey) and AHSS (in color). As can be seen in this figure, with a wide range of mechanical properties AHSS are expected to have larger application. Various components of vehicle body frame could be made with these steels, from energy absorption parts to anti intrusion barriers.



Figure 2.1 Strength and ductility relationship of HSS (in grey) and AHSS (in color).

The high mechanical properties of AHSS originate from the microstructure of these materials. While microstructures of HSS are mostly single phase (ferrite, pearlite or bainite), AHSS have multi-phase microstructures. Based on the phases present in the microstructure, AHSS can be classified in several groups:

Dual phase (DP) steels: among AHSS, this group of steels is gaining the widest application. This is not only because they can be manufactured easily but also because of the excellent combination of properties they provide. Approximately, the tensile strength of these steels is in the range of 400 to 1000 MPa, while the total elongation is 5 - 30 %. Microstructure of these steels includes a matrix of ferrite and isolated martensite islands. While the continuity of soft ferrite phase provides the steels ductility, isolated hard martensite phase performs as strain concentration points and thus increases the work-hardening of these materials.

Complex phase (CP) steels: this type of steels can also be referred to multi-phase (MP) steels. With the same level of tensile strength of DP steels, CP steels always have higher yield strength. This property comes from the multi-phase microstructure of steels. Instead of using only martensite as hardening component, different microstructures such as pearlite, bainite and retained austenite are used in these steels.

TRIP steels: As can be referred from their names, the highest combination of strength and ductility of these steels is brought by the transformation induced plasticity (TRIP) effect. This effect is gained by purposely retaining a significant amount of carbon enriched austenite during material processing. Conventionally the heat treatment of these steels includes intercritical annealing to obtain a ferrite/austenite microstructure, fast cooling and holding at intermediate temperature for bainite formation from austenite and quenching to room temperature. During the bainite formation, the carbon diffusion from bainitic ferrite plates enriches untransformed austenite and thus part of this phase is retained after the last quench. The presence of bainite and martensite increases the strength and toughness of materials while the ductility is mostly provided by intercritical ferrite and carbon enriched austenite.

Martensitic steels: compared to all other groups of AHSS, martensitic steels have the highest strength. The tensile strength of these steels can reach 1600 MPa due to the presence of

almost solely martensite in microstructure. However this group of steels has the lowest ductility, less than 15 % of total elongation.

Although in the last few years various steels of the groups above have been broadly used in manufacturing, efforts to produce higher quality AHSS have been carried out. A new class of AHSS that based on twinning induced plasticity (TWIP) effect of austenite based microstructure has recently been developed. Current studies indicate that these steels can produce the elongation of 60–80 % with the strength is higher than 1000 MPa. However, various problems with the high alloying content (for example 17-24 wt.% of manganese) of these steels need to be solved before their industrial application.

On the other hand, it has been suggested that high mechanical properties could be obtained with martensite/austenite microstructure in steels. A recently developed heat treatment to gain this microstructure and its theoretical background are explained in the next section.

2.2. The Q&P process

2.2.1. Heat treatment

For a long time, quenching and tempering (Q&T) has been used as an effective treatment to improve the combination of mechanical properties of steels [1,2]. But the presence of retained austenite has not been an object of interest during application of Q&T since the volume fraction of austenite is insignificant and even vanishes after tempering. However in 2003, knowing that silicon, aluminum and some other alloying elements can suppress the formation of cementite and bring the stability for austenite during tempering [3], Speer et al. [4,5] proposed a new heat treatment which resembles to conventional Q&T. This new treatment is called "Quenching and Partitioning" (Q&P) in order to distinguish it from conventional Q&T, in which carbide formation and austenite decomposition are typical, rather than the stabilization of austenite.

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Figure 2.2 Schematic illustration of the Q&P process and the microstructure corresponding to each stage of this heat treatment.

A schematic illustration of the Q&P process and the microstructure corresponding to each stage of this heat treatment is presented in Figure 2.2. The Q&P process mainly includes three successive steps: annealing treatment, quenching step and partitioning step. In the annealing treatment the heating to a intercritical temperature (T_i) between austenite start (Ac_i) and austenite finish (Ac_3) temperatures is implemented to obtain two phase ferrite/austenite microstructure (α/γ). A temperature higher than Ac_3 can also be used to get a full austenite state. The time to hold at the T_i temperature is the intercritical time (t_i) . After the intercritical treatment, the quenching step is carried out by fast cooling to a certain quench temperature (T_0) between the martensite start (M_s) and the martensite finish (M_t) temperatures. It is expected that there is no other phase transformation during the quenching step, except the part of austenite transforming to martensite (α_M^I). In this situation, the carbon concentrations of martensite and austenite are equal to the carbon concentration of austenite at intercritical stage $(x_{\gamma} = x_{\alpha_{1j}}^{I} = x_{i})$. The time at which the material is kept at the T_{Q} temperature is t_{Q} . In the third stage of the Q&P process, an isothermal treatment called partitioning step is applied. The temperature of partitioning step (T_P) can be equal to (1-step) or higher (2-step) than T_O . During the holding at T_P temperature for a partitioning time (t_P) , with the absence of competitive processes (tempering of martensite and/or bainite formation) the diffusion of carbon from martensite to austenite enriches the austenite $(x_{\gamma} > x_i > x_{\alpha_M^l})$. Due to this

partitioning process, the stability of austenite is increased. However, during the last quench to room temperature, some less stable austenite is transformed to martensite (α_M^{II}).

2.2.2. Expectations of the Q&P process

Speer et al. [4] suggested that the Q&P process can be applied to many available materials. Since silicon, aluminum and other alloying elements are already present to suppress the formation of carbide, TRIP sheet steels, high strength carbide-free bainite grades, austempered ductile iron and even martensitic steels can be treated by this new heat treatment. The authors expected that by this way the design of new materials for the Q&P process is not necessary. According to Speer and coworkers, the Q&P heat treatment can bring more advantages to the material processing:

- A potentially high fraction of carbon enriched austenite can be obtained by applying the Q&P process since during the partitioning of carbon the volume fraction of austenite does not change. On the contrary, the carbon enrichment of austenite during isothermal bainitic treatment in the conventional TRIP-process requires a partial transformation of austenite.
- Theoretically, it can be expected that, with the Q&P heat treatment, the carbon concentration of retained austenite is higher than the concentration obtained with conventional isothermal bainitic treatment.
- During the Q&P process, fractions and morphologies of phases (ferrite, martensite and austenite) are introduced to materials in the annealing treatment and quenching step. On the other hand, the stabilization of austenite occurs during the partitioning step. Therefore the fraction, distribution and carbon concentration of phases in microstructure can be independently controlled.
- In the Q&P process, since martensite transformation occurs by athermal mechanism, only the quench temperature is required to control the volume fraction of austenite and

martensite. The variation of the partitioning temperature changes the diffusivity of carbon in martensite and austenite and thus the homogeneous time of carbon in austenite.

• Although the characteristic phases of Q&P microstructure are austenite and martensite, ferrite can also be introduced by an intercritical treatment. While the microstructure of current AHSS is mostly based on ferrite/martensite or ferrite/bainite mixtures, the appearance of controllable ferrite, austenite and martensite in the same microstructure suggests for a wider strength/ductility properties of Q&P steels.

2.2.3. The Carbon Constrained Equilibrium (CCE)

Before the work of Speer et al., the existence of carbon enriched austenite in martensitic microstructure had been known for long time [6-8]. The diffusion of carbon from supersaturated ferrite plates to untransformed austenite in bainite formation, which resembles to the partitioning of carbon from martensite to austenite, was investigated by kinetic modeling [9]. However none of these studies went further in the use of the partitioning of carbon in other conditions (for example during austenite formation at high temperature or bainite formation at lower temperature) was well understood, current knowledge could not be used to argue for this stabilization of austenite.

According to Speer and coworkers, the diffusion of carbon from martensite to austenite occurs without any migration of interface. Thus it is necessary to develop a thermodynamic model in which the equilibrium is achieved uniquely by carbon diffusion from martensite to austenite. The model is later called Carbon Constrained Equilibrium (CCE) [4,10-12]. Thermodynamically, this model is described by two conditions: (a) the equal chemical potentials of carbon in martensite and austenite

$$\mu_C^{\alpha_M} = \mu_C^{\gamma} \tag{1.1}$$

and (b) the conservation of iron and substitutional atoms in each phase. Figure 2.3 shows two possibilities of carbon concentrations in martensite and austenite which can satisfy CCE condition of Fe-C binary system.



Figure 2.3 Schematic illustration of two possibilities of carbon concentration in martensite and austenite which can satisfy CCE condition of Fe-C binary system.

In Figure 2.3, the same intersection of G-curve tangents with C-vertical axis represents the equal chemical potentials of carbon in austenite and martensite ($\mu_C^{\gamma} = \mu_C^{\alpha_M}$). Since the same condition is not required for iron, a difference in chemical potential of this element can be observed ($\mu_{Fe}^{\gamma} \neq \mu_{Fe}^{\alpha_M}$). It can be recognized that every couple of carbon concentrations in martensite and austenite ($x_{CCE}^{\alpha_M}$, x_{CCE}^{γ}) which can fulfill the constraint of equal carbon chemical potential could also be an end point of the partitioning. Therefore at a certain partitioning temperature, there is an infinite set of possible martensite and austenite compositions. However the possible martensite/austenite composition couple becomes unique when the CCE condition is applied for a certain treatment. Because the interface between austenite and martensite is stationary, the number of atoms of iron and other substitutional elements are conserved during partitioning. This matter balance can be presented as:

$$f_{CCE}^{\gamma}(1 - x_{C_{CCE}}^{\gamma}) = f_{i}^{\gamma}(1 - x_{C_{i}}^{\gamma})$$
(1.2)

where f_i^{γ} and f_{CCE}^{γ} are mole fractions of austenite before and after partitioning. $x_{C_i}^{\gamma}$ and $x_{C_{CCE}}^{\gamma}$ are carbon concentrations in atomic fraction of austenite before and after the partitioning, respectively. Since only carbon diffuses from martensite to austenite during the partitioning, the total amount of this element is also conserved:

$$f_{CCE}^{\gamma} x_{C_{CCE}}^{\gamma} + f_{CCE}^{\alpha_M} x_{C_{CCE}}^{\alpha_M} = x_{C_i}^{\gamma}$$

$$(1.3)$$

where $f_{CCE}^{\alpha_M}$ and $x_{C_{CCE}}^{\alpha_M}$ are mole fraction and carbon concentration in atomic fraction of martensite after the partitioning. In addition, the relation between mole fractions of phases after partitioning can be given by:

$$f_{CCE}^{\gamma} + f_{CCE}^{\alpha_M} = 1 \tag{1.4}$$

By solving these four equations, the end-point of the carbon partitioning under the CCE condition can be determined.

It is known that the martensite transformation is an athermal kinetic process [13]. The mole fraction of martensite formed on quenching (f_{α_M}) depends on the undercooling below M_s temperature. This relation is usually represented by the Koistinen-Marburger (KM) equation [14]:

$$f_{\alpha_M} = 1 - \exp\left(A\left(M_s - T_Q\right)\right) \tag{1.5}$$

where A is a constant, M_s and T_Q are martensite start and quench temperatures, respectively. For convenience, M_s temperature is normally estimated by empirical equations, for example [15]:

$$M_s(^{o}C) = 539 - 423x_C - 30.4x_{Mn} - 7.5x_{Si} + 30x_{Al}$$
(1.6)

where x_C , x_{Mn} , x_{Si} and x_{Al} are the concentrations in weight percent of carbon, manganese, silicon and aluminum in austenite. If KM equation is combined with CCE conditions, the influence of the quench temperature on the mole fraction and carbon concentration of retained austenite after quenching and partitioning can be determined. This relation is shown in Figure 2.4.

As can be seen in this figure, there is an "optimum" quench temperature at which the mole fraction of retained austenite after partitioning is maximum. By the similar calculations, heat treatment parameters of the Q&P process for different materials have been selected in the literature [5,16,17]. In general, the variations of the retained austenite mole fraction with the quench temperature obtained from experiments and predicted by CCE calculations have the

same tendency. However, the obtained mole fraction of retained austenite in most of the cases is smaller than the CCE predicted value [18].



Figure 2.4 The variation of the retained austenite fraction with the quench temperature. Before the Q&P treatment, material contains 50 % ferrite and 50 % austenite [5].

When Speer et al. developed the CCE model to argue for the diffusion of carbon from martensite to austenite, they assumed that all competitive processes including carbide precipitation and bainite formation were ideally suppressed. This assumption is not always achieved in practice and the competitive processes are discussed later.

Rizzo et al. studied the kinetics of carbon partitioning under the CCE condition for a steel which has composition of 0.19%C-1.59%Mn-1.63%Si [19] by simulation with DICTRA software. In their investigations, plates of martensite and austenite with the thickness 0.30μ m and 0.14μ m respectively were supposed to be placed side-by-side. The partitioning of carbon between these phases was investigated at 400 °C. Results of these calculations, shown in Figure 2.5, indicated that the total depletion of carbon in martensite occurs within the first 0.1 s, while the homogenization in austenite requires approximately 10 s of the partitioning time. The slow diffusion of carbon in austenite causes a thin layer with high carbon concentration at martensite/austenite interface at the initial stages of the partitioning step.



Figure 2.5 Carbon concentration profiles (wt.%) in martensite (Fer) and adjacent austenite (Aus) during the partitioning at 400 °C for time ranging from 10⁻⁴ to 10 s, calculated by DICTRA assuming CCE conditions [19].

2.2.4. Recent progress

The Q&P process was firstly verified by an experimental investigation with a medium-carbon, high-silicon microalloyed bar steel [20]. The presence of a significant amount of carbon enrichment retained austenite indicated that the partitioning of carbon from martensite to austenite did occur during the heat treatment. This conclusion was confirmed by other studies with a medium-carbon bar (grade 9260) steel [16], TRIP sheet steels [5,17,21] and austempered ductile cast iron [18,22]. The study with grade 9260 steel has shown that the volume fraction of retained austenite increased immediately after the holding the material at quench temperature for 120 s [16]. This result suggested that the partitioning occurs rapidly after quenching. Evidence for the presence of carbon enriched austenite has been given by both XRD measurement and directed TEM observation. In their studies, Edmonds et al. [23-25] have shown that with the full austenite microstructure before the partitioning the carbon enriched austenite has film morphology and situates between martensite laths.

During the studies of the Q&P process responding to different materials, it has been recognized that, in most of the cases, volume fraction and carbon concentration of retained

austenite could not reach the values predicted by the CCE model. These results suggested the presence of competitive processes occurring during the partitioning treatment. Clarke et al. [26] compared the measured volume fraction of retained austenite which could be obtained by either carbon partitioning from martensite or carbide-free bainite formation. The result indicated that the measured high fraction of austenite could not be yielded solely by the carbide-free bainite formation. That means the carbon partitioning did occur during the isothermal treatment. However due to the overlap of other kinetic processes, the final austenite volume fraction was reduced below the theoretically predicted level of CCE calculations.

In a study about the Q&P process responding to an Al-TRIP steel [5], it has been reported that the volume fraction of retained austenite predicted by CCE calculation was achieved in experiments. However, the study also showed that the Q&P microstructure contained features resembling to carbide-free bainite.

The presence of carbide in the Q&P microstructure has been found by TEM investigations. Edmonds et al. [23,24] have shown the presence of carbides in different materials after the partitioning. It has been reported that in grade 9260 steel, carbide precipitation occurred immediately after quenching [23]. The presence of cementite after the partitioning at high temperature (500 °C) indicated that alloying elements successfully suppressed the formation of this carbide at lower temperature. However, the appearance of epsilon carbide after partitioning at low temperatures was clearly confirmed by electron diffraction analyses. By comparing the thickness of retained austenite films between martensite laths after partitioning at 250 °C and 400 °C, authors indicated that the formation of thinner films observed after the partitioning at lower temperature had origin from the precipitation of epsilon carbide in the martensite. They suggested that the precipitation of epsilon carbide was the main reason for the reduction of obtained volume fraction of retained austenite below the CCE calculated values.

An investigation of the Q&P process responding to Si-TRIP steels with high resolution dilatometry indicated that there was an isothermal phase transformation during the holding at quench temperature [27]. In their study, Kim et al. observed an increase in the length of the

specimens when they were held at the quench temperature. Since the occurrence cannot be explained by a pure process of the carbon partitioning from martensite to austenite, authors proposed that the observed dilatation was the result of an isothermal phase transformation occurred during partitioning. However the nature of this transformation has not been identified unambiguously as the continued growth of athermal martensite, the nucleation of isothermal martensite or bainite formation.

During the microstructure investigation of material responding to Q&P heat treatment, Zhong et al. [28] found that after the partitioning at 480 °C for 6 s the martensite/austenite interface had straight appearance. However, with a longer holding time (80 s) this characteristic was replaced by curved interface. Authors suggested that in this situation the partitioning of carbon occurred with the migration of interface. Therefore the CCE condition could not be strictly applied.

The suggestion was then further discussed with the consideration about the relative speed of the carbon diffusion and the interface migration [29]. It was assumed that the partitioning of carbon from martensite to austenite is significantly faster than the migration rate of the interface. In this situation, the carbon diffusion occurs first and is followed by the austenite/martensite interface migration when the partitioning time is kept longer. The moving direction of interface is controlled by volume fractions and carbon concentrations of phases before the partitioning step. If the migration rate of interface is competitive with the rate of the carbon partitioning, interface is predicted to move in one direction and change to the opposite side during the partitioning step.

The predictions recently have been illustrated by a numerical modeling [30]. It has been shown that the initial seconds of partitioning lead to a sharp increase in the carbon content in the austenite close to the martensite/austenite interface. Due to the carbon content at this region is higher than the equilibrium value, the migration of interface from austenite to martensite takes place. However, the carbon diffusion afterward allows the reduction of the concentration at interface lower than the equilibrium value and thus the interface migrates from martensite to austenite. The homogenization of carbon in austenite leads to further

movement of the interface until the establishment of the equilibrium carbon content in both phases.

In a different study, phase field modeling has been used to investigate the partitioning of carbon under the moving interface condition [31]. This investigation was implemented with two different quench temperatures; 125 °C and 175 °C. Microstructure before the partitioning step included ferrite, austenite and martensite. During the cooling from the intercritical stage to the quench temperature, epitaxial ferrite was formed in the austenite close to the ferrite/austenite interface. This transformation led to the presence of high carbon enriched austenite region near to the ferrite/austenite interface. On the other hand, the lower carbon concentration region inside austenite grain transformed to martensite during the quench. It has been shown that the moving directions of ferrite/austenite and martensite/austenite interface depend on the quenching temperature. With lower quench temperature, the prior-partitioning austenite grain size is smaller while fraction of martensite is larger. During the partitioning step the fast diffusion of carbon from martensite increases the local carbon concentration of austenite above the equilibrium value. The homogenization of carbon in austenite accompanied by interface migration from austenite to ferrite and martensite afterward reduces the carbon concentration of austenite to equilibrium value. On the contrary, the large prior partitioning austenite grain size and small fraction of martensite produced by higher quench temperature keeps the carbon concentration of austenite below equilibrium value during the partitioning. The equilibrium concentration of carbon in austenite is then achieved by interface migration from ferrite and martensite to austenite.

The initial investigations of mechanical properties have shown that the gap between strength/ductility properties of DP, TRIP and martensitic steels could be filled by Q&P steels. As can be seen in Figure 2.6 compared to martensitic steels, Q&P steels have equivalent or even higher ductility. On the other hand, the low tensile strength of DP and TRIP steels is improved by applying Q&P heat treatment. Furthermore, an investigation of the mechanical properties of a steel with composition 0.19%C-1.59%Mn-1.63%Si after Q&P heat treatment suggested that the Q&P process after intercritical annealing resulted on TRIP effect of the austenite [23].

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Figure 2.6 Total elongation vs. ultimate tensile strength for TRIP, DP, M and Q&P sheet steels products [21].

It can be seen that although the presence of the carbon partitioning from martensite to austenite is confirmed by various investigations, this process is frequently overlapped by other competitive processes. Both of austenite stabilization process (bainite formation) and carbide precipitations were detected. The expectation of Speer et al. about the application of the Q&P process for TRIP composition steels [4] has not been completely successful. In addition, some features involving the Q&P process (such as the isothermal martensite transformation and the migration of martensite/austenite interface) have not been well resolved. Following these, the tendencies of future investigations about the Q&P process will be focused on the application of this heat treatment on new Q&P tailoring materials and the characterization of kinetic processes occurring during the partitioning treatment.

2.3. Overlapping processes

As mentioned before, in practice the partitioning of carbon from martensite to austenite is frequently overlapped by other kinetic processes. Because these processes consume austenite and carbon, they have a great influence on the kinetics of carbon partitioning from martensite to austenite. In this section, two important competitive processes, bainite formation and tempering of martensite, are considered.

2.3.1. Bainite formation

It has been pointed out in section 2.2.2 that the retained austenite volume fraction obtained with isothermal bainitic treatment in principle is smaller than that obtained with the Q&P process. This occurrence has origin from the nature of bainite formation. The carbon enrichment of austenite during bainitic treatment requires a partial transformation of austenite. Therefore the available austenite for carbon partitioning is reduced. In order to understand further about this competitive process, a description of bainite formation is necessary. Since, in the case carbide formation is suppressed, bainite formation can also bring the stability to austenite, more attention will be given to the role of carbon in this kinetic process.



Figure 2.7 Schematic illustration of bainite formation in steels [32].

Bainite formation occurs when austenite is cooled with intermediate rate meaning not fast enough to form martensite or slow enough to directly decompose as ferrite and cementite. Similar to the martensite formation, bainite formation has diffusionless mechanism. During the transformation, parallel and carbon supersaturated plates of ferrite grow rapidly with the holding time. The aggregates of these plates are called sheaves and the individual plates are called subunits. On the contrary to the martensite transformation, bainitic ferrite plates forms at somewhat higher temperature where the diffusion of carbon atoms from supersaturated ferrite plate to adjacent austenite regions can occur within fraction of seconds [32]. However depending on the activation energy provided by temperature, not all carbon atoms in ferrite plate can diffuse to austenite region. In this situation, the precipitation of carbide in ferrite plate as small and rod-shape particles is more preferred. Bainite microstructure which contains carbide in ferrite plates is called lower bainite. On the other hand, if carbon is totally rejected to austenite before the carbide precipitation in ferrite plate occurs the microstructure is called upper bainite. The difference between morphologies of upper and lower bainite can be observed in Figure 2.7.

The diffusion of carbon from bainitic ferrite plates increases the carbon concentration of untransformed austenite regions. In plain carbon steels, since the high carbon enrichment state cannot be held by austenite, cementite is precipitated in these regions as thin and parallel layers. With a lower carbon enrichment state, these layers are replaced by small and discrete particles along ferrite plates.



Figure 2.8 Schematic illustration of the origin of T_{θ} construction on Fe-C binary system [13].

However, if material contains a sufficient amount of alloying elements which could retard the formation of cementite (for example silicon and aluminum) the state of the high carbon concentration of austenite is conserved. Depending on the carbon concentration in austenite after the last quench to room temperature, carbon enriched austenite or martensite regions are present between ferrite plates instead of cementite. The high carbon concentration of austenite

also keeps this phase from the further bainite formation. This occurrence comes from the thermodynamic nature of bainite formation. Because bainite formation is diffusionless process, the reduction of energy when austenite transforms to ferrite without the change of carbon concentration is the required condition. Following this, the bainite formation is unfavorable when the free energy of ferrite is greater or equal than that of austenite. Corresponding to each carbon concentration, there is a temperature at which bainite formation cannot occur. A locus of carbon concentration and this temperature forms T_0 curve. Figure 2.8 schematic shows the origin of T_0 curve on Fe-C binary system.

2.3.2. Tempering of martensite

Whereas bainite formation closely relates to austenite, most of the events during tempering come from martensite. Normally the reheating martensite kinetics of plain carbon steels can be divided as several distinct but overlapping stages [3,13,33,34]:

Carbon redistribution: Due to the instability of martensite, carbon atoms swiftly segregate to lattice defects such as dislocations and lath boundaries after quenching. The gathering of carbon atoms around lattice defects leads to the formation of clusters. However the redistribution of carbon does not totally finish with quenching. Thus in the early stage of heating (60-120 °C), the further segregation and clustering of carbon in martensite can occur.

Stage 1: During this first stage of the tempering (120-195 °C), the precipitation of transition carbides (η/ϵ) reduces the supersaturation state of martensite. However if the carbon concentration in martensite is lower than 0.2 wt.%, the presence of these carbides is less favorable than the segregation and clustering of carbon.

Stage 2: In the second stage of tempering (200-300 °C), retained austenite is decomposed. Generally, the productions of retained austenite decomposition are ferrite and cementite. But in some specific situations, the presence of χ -carbide (Fe₂C₅) and ferrite or even bainite and cementite has been reported.

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Stage 3: The tempering of martensite at around 350 °C leads to the formation of cementite (θ). This carbide appears as well oriented particles. Three favorable sites for the nucleation of cementite are: at the interface of epsilon carbide and the matrix, along the twin/lath boundaries and the interface between martensite and austenite.

Stage 4: The coarsening of cementite in this last stage occurs between 300-400 °C, while the recovery of martensite lath and the spheroidization of cementite takes place up to 600 °C.

Under the influence of alloying elements, the kinetics of carbide precipitation during tempering is changed. For a long time, it has been known that with the presence of a significant amount of silicon, the third stage of tempering is retarded to higher temperature and with longer time [35,36]. The effect is believed to come from the difference in solubility of silicon in transition carbides and cementite [37]. Since they have high solubility of silicon, transition carbides are easily formed whenever an equivalent carbon concentration is reached. On the contrary, cementite has very low silicon solubility. Therefore the nucleation and growth of cementite are normally controlled by the slow diffusion of silicon to adjacent ferrite regions [35,37]. In a similar way, aluminum can suppress the formation cementite. However the effect of this element is weaker and less known than that of silicon [38].

2.4. Objective

The objective of this study is to investigate the Q&P heat treatment responding to two different steels. These new materials have been developed with the aim to minimize the presence of competitive processes (including cementite precipitation and bainite formation) during the partitioning. A modification of alloying element (manganese, silicon and aluminum) content from typical TRIP steels has been applied. Various initial conditions of the partitioning treatment are produced by changing the intercritical temperature and the quench temperature

Chapter 3 Experimental procedures

In order to achieve the given objective, various experimental techniques were used to investigate the Q&P process of materials. These techniques include: dilatometry, X-ray diffraction, optical microscopy and scanning electron microscopy.

3.1. Dilatometry

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In this study, heat treatments were implemented by a high resolution dilatometer. This instrument gives an accurate control of the treatment schedule and a direct observation of the elongation of material during the treatment. The specimens for dilatometry experiments have a rod shape with 4 mm in diameter and 10 mm in length. These specimens were machined from hot rolled slabs with the length of specimen parallel to the rolling direction. A Bähr 805A/D dilatometer which configuration is presented schematically in Figure 3.1 was used in this study. Inside the instrument, the specimen is held by two quartz push rods. During thermal cycle, heating is carried out by high frequency induction coil under vacuum level ($\sim 10^{-4}$ mbar) while cooling is achieved by fluxing argon or helium gas. The real temperature of specimen is measured by an S-type thermocouple which is spot welded on its surface. The change in length of specimen is detected by Linear Variable Displacement Transducer (LVDT).



Figure 3.1 Schematic representation of dilatometer configuration.

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The kinetics of the phase transformations corresponding to the applied heat treatment schedule can be obtained by analysis of the change in the specimen length detected by the dilatometer. Figure 3.2(a) shows a typical dilatometric curve of austenite formation from ferrite and cementite during heating. In this figure, the two linear parts of the dilatometric curve are regarded as thermal expansions of material. On the contrary, the temperature range in which the length of the specimen varies non-linearly is the phase transformation region. By fitting the linear parts of dilatometric curve, the first deviation of experimental curve from the fitting line is determined as critical temperature of transformation. The procedure is called "the onset method". In this study, the onset method was used to determine Ac_1 , Ac_3 and M_s temperatures of austenite and martensite transformations.



Figure 3.2(a) The dilatometric curve of austenite formation during the heating and (b) the kinetic curve extracted by lever rule of this transformation.

In the situation where phase transformation only involves two phases, as in the case of the martensite transformation, the kinetic curve can be extracted from the dilatometric curve. By applying the lever rule for dilatometric curve with two end-points extrapolated from fitting lines, the change of phase volume fraction with temperature and time can be obtained.

In general, the extraction of the kinetics of phase transformation from the dilatometric curve involving more than two phases is more complicated. For example, the formation of austenite during heating as shown in Figure 3.2(a), includes the transformation of ferrite and the dissolution of cementite. Because the dissolution of cementite is finished before the completion of the ferrite transformation to austenite, during the heating from Ac_1 to Ac_3 the

contribution of cementite to the elongation of the specimen needs to be withdrawn from the extraction procedure at the temperature called Ac_1 '. However, the determination of the temperature at which cementite is totally dissolved (Ac_1) is not always feasible. Furthermore, the subtraction also requires the information of volume fraction and thermal expansion coefficient of cementite which are difficult to determine by few experiments. Thus for simplicity, it is possible to assume that the volume fraction and the contribution of cementite to the strain behavior of the specimen are insignificant. Following this assumption, the extraction method with lever rule can be applied for austenite formation process shown in Figure 3.2(a). The kinetic curve of this process is presented in Figure 3.2(b). As will be shown later in section 3.1, the maximum volume fraction of carbide in the low carbon steels used in this study is less than 3.5 %. Therefore the assumption about minor effect of cementite on austenite formation during heating is acceptable.

3.2. Dilatometric calculations

Even if the kinetic curve can be easily extracted from the dilatometric curve by lever rule, the interpretation of this data to a real phase transformation is not simple. Inversely, the estimation of the change in length or volume of the specimen with a certain phase transformation is more feasible. In this way, the kinetic processes occurring during a heat treatment is evaluated by comparing the measured strain with values predicted by calculation. In this section, methods to calculate the strains of some kinetic processes which can occur during the partitioning step of the Q&P process are given.

In principle, the volume change of the specimen during a phase transformation comes from the variation of molar fractions and atomic volumes of phases. The relative change in volume of specimen ($\Delta V/V$) is given by:

$$\frac{\Delta V}{V} = \frac{\sum f_i^a V_i^a - \sum f_i^b V_i^b}{\sum f_i^b V_i^b}$$
(2.1)

where f_i and V_i are for molar fraction and atomic volume of phase *i*. The superscripts *b* and *a* are represented for the stage before and after phase transformation. For simplicity, it is assumed that the volume change of the specimen during the phase transformation is isotropic.

Thus the change in volume of specimen is related with the relative change of the specimen length ($\Delta l/l$) as follow:

$$\frac{\Delta l}{l} \approx \frac{1}{3} \cdot \frac{\Delta V}{V} = \frac{1}{3} \cdot \frac{\sum f_i^a V_i^a - \sum f_i^b V_i^b}{\sum f_i^b V_i^b}$$
(2.2)

In general, the atomic volume of each phase depends on its lattice parameters. For orthorhombic lattice systems, this value is determined by:

$$V_i = \frac{a_i \cdot b_i \cdot c_i}{N_i} \tag{3.1}$$

where a_i , b_i , c_i are lattice parameters of phase *i*. N_i is the numbers of iron atoms in an unit cell of the same lattice. While transformations are often investigated at high temperature, lattice parameters of phases are mostly measured at room temperature. Therefore the thermal expansion of lattice parameters needs to be taken into account:

$$a_i^T = a_i (1 + \beta_i (T - T_0))$$
(2.4)

$$b_i^T = b_i (1 + \beta_i (T - T_0))$$
(2.5)

$$c_i^T = c_i (1 + \beta_i (T - T_0))$$
(2.6)

where β_i is the linear thermal expansion coefficient of phase *i*, T_0 is the temperature at which lattice parameter was measured (usually room temperature) and *T* is the investigated temperature. At a temperature of *T*, the atomic volume of the phase *i* is given as:

$$V_i^T = \frac{a_i^T b_i^T c_i^T}{N_i} \approx \frac{a_i \cdot b_i \cdot c_i}{N_i} \cdot (1 + 3 \cdot \beta_i (T - T_0))$$
(2.7)

(

Generally, lattice parameters of a phase are greatly influenced by the chemical composition, but this relation is not always available for all alloying elements of steel. Therefore only the effect of carbon on the lattice parameters is considered in the calculations below. Table 3.1 shows crystallographic data and the thermal expansion coefficient of the different phases. In the following, the changes in length of the specimen corresponding to specific phase transformations are presented.

Table 3.1 Crystallographic data for the different phases.					
Phase	Lattice parameter (Å)	$\beta_i(\mathrm{K}^{-1})$	Ni	Ref.	
Bcc α-Fe	<i>a</i> = 2.8664	1.244×10 ⁻⁵	2	[39,40]	
Bct α_M	$a = 2.8664 - 0.014w_C$ $c = 2.8664 + 0.115w_C$	1.244×10 ⁻⁵	2	[39,40]	
Fcc γ-Fe	$a = 3.556 + 0.0453 w_C$	2.065×10 ⁻⁵	4	[39,40]	
Orthorhombic θ (Fe ₃ C)	a = 4.5246 b = 5.0885 c = 6.7423	0.840×10 ⁻⁵ (at 350°C)	12	[41]	

3.2.1. Carbide precipitations from martensite

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It has been shown in section 2.3.2 that the precipitation from martensite includes several types of carbide. Since the precipitation of cementite is the most important stage, in this section only the relative change in length of the specimen corresponding to this precipitation is analyzed. Schematically, the precipitation of cementite can be presented by the reaction:

$$\alpha_M \rightarrow \alpha + \theta$$

In this description, it is assumed that, after the precipitation, all carbon atoms rest in cementite whereas martensite is totally recovered to bcc lattice. Before the precipitation of cementite, the concentration in atomic fraction of carbon in martensite is x_C and the atomic fraction of iron in the same phase is $(1 - x_C)$. The redistribution of carbon and iron atoms after the cementite precipitation can be given as:

$$\alpha_M \rightarrow \alpha + \theta$$

Carbon $x_C \qquad 0 \qquad x_C$
Iron $1 - x_C \qquad 1 - 4x_C \qquad 3x_C$

If before the precipitation of cementite the microstructure of material contains f_{α_M} molar fraction of martensite, the fractions of iron atoms that belong to ferrite and cementite can be determined as:

$$f_{\alpha} = \frac{1 - 4.x_C}{1 - x_C} f_{\alpha_M}$$
(2.8)

$$f_{\theta} = \frac{3.x_C}{1 - x_C} \cdot f_{\alpha_M} \tag{2.9}$$

The relative change in length of the specimen corresponding to this precipitation process is:

$$\frac{\Delta l}{l} = \frac{1}{3} \cdot \frac{f_{\alpha}V_{\alpha} + f_{\theta}V_{\theta} - f_{\alpha_M}V_{\alpha_M}}{\sum f_i^b V_i^b}$$
(2.10)

3.2.2. Carbon partitioning from martensite to austenite

$$\alpha_{M} + \gamma \to \alpha_{CCE} + \gamma_{CCE}$$

After the partitioning of carbon from martensite to austenite, the carbon concentration and thus the atomic volume of involving phases change. In general situation, these variations originate from the diffusion of carbon from martensite to austenite and the migration of austenite/martensite interface. However the estimation of the change in molar phase fraction and carbon concentration requires a sophisticated calculation. For simplicity in this section, these variations are only calculated with a fixed interface condition by applying CCE model mentioned in section 2.2.3. The relative change in length of specimen under this condition is:

$$\frac{\Delta l}{l} = \frac{1}{3} \cdot \frac{f_{\alpha_{CCE}} V_{\alpha_{CCE}} + f_{\gamma_{CCE}} V_{\gamma_{CCE}} - f_{\alpha_M} V_{\alpha_M} - f_{\gamma} V_{\gamma}}{\sum f_i^b V_i^b}$$
(2.11)

3.2.3. Upper bainite formation

With the presence of silicon, aluminum and some other alloying elements the stability of austenite is increased. Instead of the precipitation of carbide, high carbon enriched austenite regions are present between ferrite plates. This partial transformation of austenite can simply be represented by:

$$\gamma \to \alpha_b + \gamma_b$$

It is known that the upper bainite formation is finished when the carbon concentration in untransformed austenite reaches the value defined by T_0 curve. The molar fractions of bainitic ferrite and carbon enriched austenite after the transformation can be predicted by lever rule:

$$f_{\alpha_b} = \frac{x_C^{\gamma_b} - x_C^{\gamma}}{x_C^{\gamma_b} - x_C^{\alpha_b}} f_{\gamma}$$
(2.12)

$$f_{\gamma_b} = \frac{x_C^{\gamma} - x_C^{\alpha_b}}{x_C^{\gamma_b} - x_C^{\alpha_b}} f_{\gamma}$$
(2.13)

where $x_C^{\alpha_b}$, x_C^{γ} and $x_C^{\gamma_b}$ are carbon concentrations of bainitic ferrite, austenite before and after bainite formation, respectively. The relative change in length of the specimen after bainite formation is:

$$\frac{\Delta l}{l} = \frac{1}{3} \cdot \frac{f_{\alpha_b} V_{\alpha_b} + f_{\gamma_b} V_{\gamma_b} - f_{\gamma} V_{\gamma}}{\sum f_i^{\ b} V_i^{\ b}}$$
(2.14)

3.3. X-ray diffraction

In order to investigate the volume fraction and the carbon concentration of the retained austenite, X-ray diffraction measurements were carried out. Specimens were prepared by standard grinding and polishing to 1 μ m diamond. Diffraction experiments were performed by a Bruker type D8-Advance diffractometer equipped with a Bruker Vantec Position Sensitive Detector (PSD) using Co-K α radiation. The diffractometer was operated at 45 kV and 35 mA. Scanning range of 20 was 30° to 135° with a step size of 0.05°. In this range, the reflections of γ {111}, γ {200}, γ {220}, γ {311} and γ {222} austenite peaks and α {110}, α {200}, α {211} and α {220} ferrite peaks were recorded. Figure 3.3 shows a typical XRD pattern of an experimental specimen in which all the reflection peaks of the phases are present.



Figure 3.3 A typical X-ray diffraction pattern of experimental specimen.

From measured diffraction patterns, volume fraction of retained austenite was determined by the "direct comparison method" [42,43] ignoring the presence of carbides. Although specimens contain both ferrite and martensite, under this experimental condition the distinction for reflection peaks of these two phases has not been observed. Therefore it could be considered that all α peaks belong to a unique bcc phase. Because of the overlap of $\gamma_{\{111\}}$ austenite and $\alpha_{\{110\}}$ ferrite peaks, volume fraction calculations were performed using $\gamma_{\{200\}}$, $\gamma_{\{220\}}$ and $\gamma_{\{311\}}$ austenite peaks and $\alpha_{\{200\}}$, $\alpha_{\{211\}}$ and $\alpha_{\{220\}}$ ferrite peaks. The volume fraction of retained austenite determined by multi peaks is given by:

$$f_{\gamma} = \frac{\frac{1}{q} \sum \frac{I_i^{\gamma}}{R_i^{\gamma}}}{\frac{1}{q} \sum \frac{I_i^{\gamma}}{R_i^{\gamma}} + \frac{1}{p} \sum \frac{I_j^{\alpha}}{R_i^{\alpha}}}$$
(2.15)

where I_i^{γ} and I_j^{α} are integrated intensities of austenite and ferrite, R_i^{γ} and R_j^{α} are constants determined for individual reflection peak of the particular phases, q and p are the numbers of ferrite and austenite peaks used to determine volume fraction of austenite. The values of this constants corresponding to reflection peaks which were used to determined volume fraction of austenite are shown in the Table 3.2 [43]:

Table 3.2 R-values for reflection peaks of ferrite and austenite.

		Ferrite			Austenite	•
Peak index – <i>hkl</i>	200	211	220	200	220	311
R-value – R_{hkl}	14.8	32.4	15.4	39.2	21.6	31.9

For each austenite reflection peak, the lattice constants were determined by:

$$a_{hkl} = \frac{\lambda}{2.\sin\theta} \cdot \sqrt{h^2 + k^2 + l^2}$$
(2.16)

where a_{hkl} is the lattice constant corresponding to the $\gamma_{\{hkl\}}$ reflection peak in Angstrom. λ is the wavelength of the radiation in Ångstrom. θ is the reflection angle. The obtained values were later used to determine the accurate lattice constant by the Cohen's method [42]. The carbon concentration in the retained austenite was estimated by the equation [39]:

$$a_{r} = 3.556 + 0.0453x_{C} + 0.00095x_{Mn} + 0.0056x_{Al}$$

$$(2.17)$$

where a_{γ} is the lattice parameter of austenite in Ångstroms, x_C , x_{Mn} , x_{Al} are concentrations of carbon, manganese and aluminum in weight percent. Since the variation of the lattice parameter with different silicon content in austenite was not detected in previous study [44], the influence of this element on the lattice parameter of austenite is ignored.

3.4. Optical microscopy

For optical microscopic investigations, dilatometric specimens were sectioned in half with a diamond wheel blade with rotation speed at 2200 rpm and cutting speed at 0.1 mm/s. During sectioning, specimen and blade were cooled by fluxing water. The specimens were then grinded using P800, P1000, and P1200 abrasive papers. These steps were followed by polishing with 6, 3 and 1 μ m diamond suspension oils.

Depending on the investigation purposes, different etchants were used. For general observations, specimens were etched by 2 % nital (2 ml HNO₃ + 98 ml ethanol) for 8-10 s. Normally with this etchant ferrite and martensite can be distinguished by their different contrasts. While martensite is dark or brown, ferrite appears as white and light regions. However, in this study the difference between ferrite and martensite was not always feasible. Figure 3.4(a) is a typical example of this situation. Whereas the boundaries between these two phases are clearly observed, the grains themselves could not be well differentiated.

A better contrast was achieved by using color metallography. LePera's etchant [45] has been used successfully to differentiate multi-phase microstructures of steels [46]. The recipe of this etchant contains two equal volumes of 1 g Na₂S₂O₅ in 100 ml water and 4 g picric acid in 100 ml ethanol. The etching procedure starts soaking specimen in 2% nital for 3 s and followed by dipping in LePera's etchant for 8 s. After etched, specimen is cleaned by ethanol. Microstructure after tint etched with LePera's solution is presented in Figure 3.4(b). This is the same microstructure as which is shown in Figure 3.4(a). Because the specimen was preetched with 2 % nital, the dark boundaries between ferrite and martensite can be recognized. Martensite is white and brighter regions whereas the brown ones is ferrite. With the improvement of contrasts, fraction of phases can be determined by area measurement method with the help of IQmaterials software.



(a) (b) Figure 3.4 Two phase (ferrite - martensite) microstructure of one of the studied steels after etched with (a) 2 % nital and (b) LePera's etchant.

3.5. Scanning electron microscopy

A similar sample preparation procedure described in section 3.4 was applied for scanning electron microscopy (SEM) experiments. In all experiments, specimens were etched with 2 % nital for 8-10 s. The instrument used in these investigations is a JEOL JSM-6500F Field Emission Gun Scanning Electron Microscope (FEG-SEM) operating at 15 kV with working distance of 10 mm.
Chapter 4 Materials and Heat treatments

4.1. Materials

4.1.1. Chemical compositions

The chemical composition of the steels used in this study is presented in Table 4.1. These two materials have compositions resembling to typical TRIP-steels. Both contain low carbon concentration. However, manganese contents in these steels are relatively higher than that in normal TRIP-steels. With this difference, it is expected that the transformation of austenite to ferrite during the cooling is retarded to lower temperature and the nucleation of bainitic ferrite during isothermal treatment is delayed to longer time. On the other hand, difference in concentrations of silicon and aluminum can be observed. This indication suggests a difference on the kinetics of the processes happening in the material during the application of similar heat treatment, especially the carbide precipitation in the partitioning step.

Table 4.1 Chemical composition of the studied steels (wt.%).									
Steel	C	Mn	Si	A 1	Ni				
HSi	0.195	3.5	1.54	0.006	0.08				
LSi	0.198	3.5	0.45	0.22	0.06				

4.1.2. As-received microstructures

The materials were prepared by laboratory vacuum induction furnace. After casting, materials were hot rolled to a final thickness of 4.5 mm. For dilatometric study, experimental specimens were prepared by the procedure mentioned in section 2.1.

Figure 4.1 shows an optical micrograph of the HSi steel at as-received state. Brown and darker regions in the microstructure are martensite whereas the white ones are ferrite. Both phases have fine and blocky morphologies. Small and well dispersed particles in the microstructure suggest the presence of carbide.



Figure 4.1 Optical micrograph of the HSi steel at as-received state (etchant: 2 % nital) (F: ferrite, M: martensite).

An investigation with SEM (Figure 4.2(a)) showed that the initial microstructure has more phases than those observed with OM. Bainite and isolated austenite/martensite regions can be seen in the same prior austenite grains. In the ferrite matrix, small and bright particles which resemble to the fine and dispersed spots observed in optical micrograph can be distinguished. It is believed that these particles are coarsened carbide which is formed during tempering of martensite. When bainite structure is observed with a higher magnification (Figure 4.2(b)), it has been found that there is a different form of carbide in bainitic ferrite plates. This carbide is rod-shaped and well oriented particles. Based on this feature, the observed structure is identified as lower bainite.



(a) (b) Figure 4.2 SEM micrograph of the HSi steel at as received state (a) with a low magnification and (b) in a bainite region with a high magnification (F: ferrite, M: martensite, B: bainite, C: carbide).

Figure 4.3 is an optical micrograph of the LSi steel at as received state. Three main features of this micrograph which can be identified are ferrite, martensite and coarsened carbide. However, isolated martensite regions does not homogeneously distribute in microstructure. Ferrite and martensite appear in this microstructure as alternative strips. This distribution of phases indicates that the microstructure of the LSi steel contains bands. These bands can be also observed in SEM micrograph as the one showed in Figure 4.4(a). At this level of magnification, it can be recognized that lower bainite is included in austenite/martensite bands. Sheaves of bainite can be seen in Figure 4.4(b).



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Figure 4.3 Optical micrograph of the LSi steel at as-received state (etchant: 2 % nital) (F: ferrite, M: martensite, C: carbide).



(a) (b) Figure 4.4 SEM micrograph of the LSi steel at as received state (a) with a low magnification and (b) in a bainite region with a higher magnification (F: ferrite, M: martensite, B: bainite, C: carbide).

4.1.3. Phase diagrams and T_0 curves

For each material, critical temperatures and volume fractions of phases corresponding to different degrees of transformations are important information for the design of the heat treatment schedules. In general, these values are not easily obtained by normal experimental measurements. However, they can be known from thermodynamic calculations. The equilibrium phase diagrams of HSi and LSi steels calculated by Thermo-calc software [47] are presented in Figure 4.5. Although behaviors of the two materials with the change of temperature are similar, critical temperatures of the LSi steel are lower than those of the HSi steel.



Table 4.2 Calculated equilibrium critical temperatures of austenite transformation in HSi and LSi steels.

Steel	<i>Ae</i> ₁ (°C)	<i>Ae</i> ₁'(°C)	<i>Ae</i> 3 (°C)
HSi	627	679	784
LSi	613	671	770

Table 4.2 shows calculated equilibrium critical temperatures of these materials, where Ae_1 ' is the temperature at which cementite is totally dissolved. The transformation of austenite can be separated in two periods. The first is from Ae_1 to Ae_1 '. In this period, due to the cooperative transformation of ferrite and cementite volume fraction of austenite increases rapidly with temperature. However in the second period (from Ae_1 ' to Ae_3) the growth of austenite solely from ferrite is slower than that in the former period. The thermodynamic calculations have shown that, at equilibrium condition below Ae_1 temperature, both HSi and LSi steels contain approximately 3.5 % cementite.

In principle, Q&P heat treatments do not involve bainite formation. However this transformation can occur in practice during the partitioning step as a competitive process. An investigation of T_0 curves for the studied materials therefore is necessary. The T_0 curves of HSi and LSi steels calculated by Thermo-calc are shown in Figure 4.6. In these calculations, the chemical composition of the full austenized state corresponding to each material was used.



Figure 4.6 Relations between carbon concentration of austenite and temperature of (a) HSi and (b) LSi steels defined by T_0 curves.

4.1.4. Ac_1 and Ac_3 temperatures

Although they could be predicted accurately by thermodynamic calculations, equilibrium critical temperatures are rarely applied for practical heat treatment. These temperatures are only achieved with very slow heating or cooling condition. Instead, the critical temperatures measured with a certain heating rate (Ac_1 and Ac_3 with the heating rate of 2 °C/s) were used in this study. Figure 4.7 shows dilatometric curves in the heating part of HSi and LSi steels. To obtain these curves, materials were heated to 900 °C with the rate of 2 °C/s. During the heating, because the dissolution of cementite is finished earlier than all of ferrite transforms to austenite, the rates of austenite formation before and after Ac_1 ' temperature are different. This temperature can be determined by finding the point where the contraction rate of the specimen length between Ac_1 and Ac_3 is suddenly changed. As can be seen in Figure 4.7(a), the Ac_1 ' temperature of the HSi steel can be extracted easily from the dilatometric curve and its

corresponding derivative curve. However the similar temperature could not be obtained from the dilatometric and its corresponding derivative curves of LSi steel. The absence of Ac_1 ' temperature on the dilatometric curve of LSi steel which should originate from the banded microstructure of this material will be discussed more detail in section 7.1.



Figure 4.7 Dilatometric curve and its corresponding derivative curve of (a) the HSi steel and (b) the LSi steels during heating to 900 °C with the rate of 2 °C/s.

By applying the onset method mentioned in section 2.1, critical temperatures (Ac_1 , Ac_1 ' and Ac_3) of each material were determined. Results of these analyses are summarized in Table 4.3. It can be recognized that the errors of critical temperatures of HSi steel are smaller than those of LSi steel. Since banded structure has been observed in LSi steel, the larger variation of critical temperatures could be due to the less homogeneous stage of alloying elements.

Steel	Ac_1 (°C)	<i>Ac</i> ₁ ' (°C)	<i>Ac</i> ₃ (°C)
HSi	722 ±4	754±5	825±4
LSi	695±11	-	789±7

 Table 4.3 Experimental critical temperatures of austenite transformation in HSi and LSi steels with the heating rate of 2 °C/s.

4.2. Heat treatments

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4.2.1. Intercritical and interrupted heat treatments

Since the investigation of the Q&P process is carried out with different intercritical conditions, the estimation of phase fractions at each temperature is necessary. Figure 3.8 presents kinetic curves which have been extracted from the dilatometric curves showed in Figure 4.7. From these curves, the chosen intercritical temperatures to obtain 0.50 and 0.40 of austenite with the HSi steel are 770 °C and 760 °C, respectively. Since both of these temperatures are above Ac_1 ' temperature, it is expected that microstructure of the HSi steel after intercritical treatments does not contain carbide. With the intercritical temperatures of 740 °C and 730 °C, the volume fractions of austenite in the microstructure of the LSi steel are estimated as 0.50 and 0.40, respectively. For both of these materials, the chosen intercritical time is 600 s. Due to the isothermal transformation of ferrite to austenite, the volume fractions of austenite obtained after intercritical treatment are expected to be higher than 0.50 and 0.40.



From section 2.2, it has been shown that in the Q&P heat treatment the microstructure and the stabilization of austenite are separately controlled. During annealing and quenching different morphologies could be introduced to microstructure of material. Therefore not only the volume fraction but also the distribution of phases in the microstructure of the material during the intercritical treatment needs to be studied. The investigation of the phase morphology is carried out by analyzing microstructures of interrupted heat treatments during the heating and holding at the intercritical temperature. The schedules of these interrupted heat treatments are shown in Figure 4.9. In these schedules, all specimens were heated with the rate of 2 °C/s and

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cooled with the rate of 50 °C/s. The holding time at interrupted temperatures is 3 s while these periods for the intercritical temperature are 3, 30 and 300 s.



Figure 4.9 Interrupted heat treatment schedules for (a) HSi steel and (b) LSi steel.

4.2.2. Selection of quenching temperatures

In order to control volume fraction of austenite during the first quench, the athermal kinetics of the martensite transformation needs to be investigated. Specimens after intercritically treated at predefined temperature for 600 s were quenched to room temperature at a cooling rate of 50 °C/s. The dilatometric curve corresponding to the quenching part was then analyzed by the lever rule method to obtain the change in volume fraction of martensite with temperature. The extracted kinetic curve was fitted by Koistinen – Marburger (KM) equation (eq(1.5)) with two parameters (A and M_s^{KM}). Values of these parameters are given in Figure 4.10 and Figure 4.11.

The kinetic curves of martensite transformation for both two steels were well fitted with KM equation. However with the formation of martensite from less than 10 % of the intercritical austenite, the discrepancy between experimental data and the fitting curve can be observed. This difference has origin from the gradual growth of martensite from austenite during the quench which in turn is due to the inhomogeneous distribution of carbon in austenite. While most of austenite contains approximately same carbon amount, there is a small fraction of this phase having a lower carbon concentration. During the quench, this low carbon content austenite transforms to martensite before the martensite formation from the austenite which has higher carbon concentration. This occurrence leads to the difference of M_s temperatures

determined by the onset method and the fitting KM equation. With the onset method, the M_s temperature of poorer carbon austenite is detected. On the contrary, the transformation of the main part of austenite is below the M_s temperature determined by the fitting KM equation. Based on the fitting curves, the quench temperatures for the Q&P heat treatment of both materials were chosen as 240 °C and 215 °C. It can be seen that with these quench temperatures the fraction of intercritical austenite transforming to martensite is significantly larger than 10 %.



Figure 4.10 The change in volume fraction of martensite during the quench after the intercritical treatment at (a) 770 °C and (b) 760 °C.



Figure 4.11 The change in volume fraction of martensite during the quench after the intercritical treatment at (a) 740 $^{\circ}$ C and (b) 730 $^{\circ}$ C.

4.2.3. The Q&P heat treatments

With the aim to investigate the influence of initial conditions prior the partitioning step on the Q&P process, three series of heat treatments were designed for each material. The difference of initial conditions for partitioning step was produced by changing intercritical temperature (T_i) and quench temperature (T_Q) . The schedule of each series is presented in Figure 4.12. In all the experiments, the heating and cooling rate were kept constant. The heating rate of the intercritical treatment is 2 °C/s while the cooling rate of quenching steps is 50 °C/s. The holding time at intercritical stage is 600 s. To avoid the precipitation of carbide after hold at T_Q temperature for 5 s, specimens were fast heated to T_P temperature with the heating rate is 10 °C/s. In each series, several partitioning periods which are 3, 10, 100, 1000 and 5000 s were used.

Because the effect of the partitioning temperature was not investigated in this study, a fixed value of this parameter was applied for all heat treatments. In principle, the partitioning temperature is constrained by the diffusion of carbon between phases and the stability of these phases. This temperature needs to be high enough to activate the diffusion of all carbon atoms from martensite to austenite. However, if the partitioning temperature is too high austenite can decompose directly to ferrite and cementite before it is enriched. Thus the partitioning temperature in this study was chosen as 350 °C.



Figure 4.12 Heat treatment schedule of the Q&P process.

For each material, the values of intercritical and quench temperatures applied for different heat treatments are given in Table 4.4.

		HSi steel			LSi steel	
T_i (°C)	770	770	760	740	740	730
T_Q (°C)	240	215	215	240	215	240

Table 4.4 Heat treatment parameters in different series of HSi and LSi steels.

4.2.4. Isothermal bainitic treatments

Because the partitioning step is implemented at 350 °C, bainite formation could occur during the same holding period. An investigation of isothermal microstructure which is probably bainite is necessary. Following this, the (dis)similarity between the isothermal and the Q&P microstructures can be revealed. The isothermal treatment schedule applied for HSi and LSi steels are presented in Figure 4.13. Except for the absence of the first quenching step, the similarity between the isothermal treatment and one of the three Q&P heat treatments applied for each material can be recognized.



Figure 4.13 Isothermal treatments for HSi and LSi steels. Excluding the absence of the first quenching step, the isothermal treatment resembles to one of the three Q&P heat treatments applied for each material.

Chapter 5 Q&P process of the HSi steel

5.1. Evolution of microstructure

5.1.1. Microstructure after direct quench

Microstructures of the HSi steel after direct quench at the cooling rate of 50 °C/s from the two chosen intercritical temperatures 770 °C and 760 °C, are presented in Figure 5.1. As expected, microstructures after heat treatments include two main phases: ferrite and martensite. The absence of retained austenite in these microstructures is proved by XRD investigations. There is also no evidence for the presence of carbide.



Figure 5.1 Microstructure of the HSi steel after direct quench from (a) 770 °C and (b) 760 °C (F: ferrite, M: martensite).

The morphologies of ferrite and martensite in these microstructures are not similar to those in the usual intercritical microstructures of low carbon steels. In the normal situation, austenite appears as isolated blocky islands in boundaries and corners of ferrite grain matrix. At higher annealing temperature, these islands are coarser and connected as a net of austenite. The growth of austenite into ferrite grains continues until the whole microstructure is occupied by austenite. On the contrary, in Figure 5.1, ferrite has plate-like shape. The parallel arrangement of these plates can be observed clearly. The appearance of austenite and ferrite as thin and parallel alternative plates suggests that this morphology can replace the blocky shape of the intercritical austenite currently applied for TRIP steels. In the new microstructure, parallel

plates of austenite and ferrite are present as isolated colonies in the matrix of ferrite. Different from the normal TRIP microstructure obtained after isothermal bainitic treatment, the new microstructure is produced directly from the intercritical annealing. Following this, the thickness of ferrite and austenite plates can be adjusted by changing intercritical temperature. The new microstructure is expected to improve the combination of mechanical properties of these steels. The ductility of material is still given by ferrite matrix like in TRIP steels. However, the presence of plate-like austenite with adjustable thickness in the microstructure reduces the mean free path of dislocation glide and thus increases the resistance of material to the strain. Due to this promising advantage, the evolution of these morphologies during intercritical annealing was investigated by the interrupted heat treatment which the schedules have been given in section 4.2.1.

Figure 5.2 shows microstructures after interrupted heat treatments. In the first micrograph (Figure 5.2(a)), the microstructure after annealing at 710 °C mostly contains ferrite (brown regions). Small and white regions in this micrograph were identified as austenite and martensite. The differentiation of these two phases cannot be revealed by optical microscopic observations. Most of austenite/martensite regions have a blocky shape. The presence of thin and parallel regions of austenite/martensite can also be observed. With the higher annealing temperature (730 °C) the formation of austenite/martensite as plates is more abundant, as can be seen in Figure 5.2(b). But ferrite is still the main characteristics of this microstructure. The increase of the temperature to 750 °C brings a rapid change of microstructure (Figure 5.2(c)). Ferrite is only observed as long islands in the matrix of austenite/martensite. When intercritical temperature for longer periods (30 and 300 s) leads to the reduction of the density of ferrite plates in a colony and the thickness of individual plates (Figure 5.2(e) and (f)). In some regions, ferrite is only present as small and dark particles.



The investigation above clearly shows the directional growth of austenite during intercritical treatment. According to previous studies of Yi et al. [48] about the austenitization of martensite microstructure, the mechanism for the formation of observed microstructures can

be explained as follows. During the heating martensite is tempered. Because of the

accumulation of dislocations at martensite lath boundaries, in the early stage of tempering carbon atoms in martensite migrate to these locations. This segregation of carbon provides suitable sites for the precipitation of carbide along the lath boundaries. Due to the favorable energy, the nucleation of intercritical austenite consequently occurs at the interface of these carbide grains and prior martensite laths. Therefore, the growth of austenite grains at the prior martensite laths is faster than at other locations.

The presence of carbon enriched austenite layers between bainitic ferrite plates in initial microstructure could also be a cause for the directional growth of austenite during the intercritical treatment. The existence of carbon enriched austenite layers between bainitic ferrite plates in the initial microstructure of the HSi steel has been shown in Figure 4.2. During heating, this austenite is believed to decompose into ferrite and cementite. The precipitation of cementite along prior austenite layers has the same influence on the nucleation and growth of intercritical austenite as in the case of inter-lath carbide presented above.

Table 5.1 Volume fractions and carbon concentrations of phases after the intercritical treatment.

<i>T_i</i> (°C)	f_{lpha}	x_c^{α} (wt.%)	f_{γ}	x_C^{γ} (wt.%)
770	0.10±0.05	~10 ⁻³	0.90±0.05	0.22±0.01
760	0.41±0.02	~10 ⁻³	0.59±0.02	0.33±0.01

By applying quantitative metallography, as described in section 2.4, volume fractions of phases after direct quench were measured. Since the length of specimen decreases linearly during the cooling from intercritical to martensite start temperature, the volume fraction of intercritical ferrite is not changed in this period. On the other hand, the completion of the martensite transformation after the quench to room temperature is proved by XRD measurements which did not show any trace of austenite. Therefore the volume fractions of phases at the intercritical stage can be determined indirectly from the microstructure measurements at room temperature. Results of these measurements are presented in Table 5.1. In this table, the carbon concentration of ferrite was estimated by calculations with Thermo-

calc software. And the carbon concentration of austenite was determined by the carbon balance between ferrite and austenite in material.

5.1.2. Microstructures after the first quench

Although the microstructures of the HSi steel after quenching from T_i to T_Q temperature cannot be directly observed, it is possible to estimate the volume fractions and carbon concentrations of phases at this state. In the previous section, volume fractions and carbon concentrations of ferrite and austenite at intercritical state have been determined. Moreover, it was proved that kinetics of martensite transformation can be described accurately with the KM equation by fitting experimental data (section 4.2.2). Hence, a combination of these data can be used to calculate the volume fraction of phases at any quench temperature. Because of the diffusionless mechanism of martensite transformation, martensite after quenching has the same carbon concentration as intercritical austenite.

Table 5.2 presents the volume fractions and carbon concentrations of phases after quenching to predefined temperatures (240 °C and 215 °C). In this Table, the larger volume fraction and carbon concentration of ferrite corresponding to the lower T_i temperature treatment can be observed. However after the quench to the same T_Q temperature (215 °C), the obtained volume fractions of austenite are approximately equal. This is a good advantage for the investigation of the influence of the intercritical temperature on kinetic processes during the partitioning step.

<i>T_i</i> (°C)	<i>Т</i> _{<i>Q</i>} (°С)	f_{lpha}	x_C^{α} (wt.%)	f_{r}	$\frac{x_C^{\gamma}}{(\text{wt.\%})}$	f_{α_M}	$\frac{x_C^{\alpha_M}}{(\text{wt.\%})}$
770	240	0.10±0.05	~10 ⁻³	0.50±0.03	0.22±0.01	0.40±0.02	0.22±0.01
770	215	0.10±0.05	~10 ⁻³	0.25±0.01	0.22±0.01	0.65±0.04	0.22±0.01
760	215	0.41 ± 0.02	~10 ⁻³	0.23±0.01	0.33±0.01	0.36±0.01	0.33±0.01

Table 5.2 Volume fractions and carbon concentrations of phases after the first quench.

5.1.3. Microstructures after partitioning step

Although some differences in volume fractions and carbon concentrations of phases after the first quenching step between heat treatment schedules have been listed in Table 5.2, the microstructure evolutions of the HSi steel during partitioning treatment have been found similar. For simplicity, the investigation of microstructure in this section is only focused on one heat treatment schedule. Specimens in this schedule were intercritically treated at 770 °C and quenched to 240 °C before partitioning at 350 °C for different periods of time. The difference in microstructure between heat treatment schedules will be described whenever it is found.



(b) (c) Figure 5.3 Microstructure of the HSi steel after partitioning at 350 °C for 3 s (F: ferrite, A/M: austenite/martensite, C: carbide).

Figure 5.3 shows SEM micrographs of the HSi steel after partitioning at 350 °C for 3 s. In Figure 5.3(a), the microstructure includes three main features: ferrite, austenite/martensite and bainite. Austenite and martensite are the most abundant phases in the microstructure. Since the interactions of the etchant (2 % nital) with austenite and martensite are the same, the differentiation between these two phases cannot be made. These phases are the main characteristics of the microstructure. In the austenite/martensite matrix, ferrite has a plate-like shape, similar to the feature seen in the direct quench microstructure. A higher magnification observation of these plate-like regions, presented in Figure 5.3(b), indicates that there is no carbide inside ferrite plates. The appearance of bainite structure can also be seen in Figure 5.3(c). Instead of dispersing in the whole microstructure, this feature is only found as isolated colonies within large austenite/martensite regions. The presence of small and bright particles in bainite sheaves suggests that the precipitation of carbide occurred inside bainitic ferrite plates. Thus the observed structure is lower bainite.



Figure 5.4 Microstructures of the HSi steel after partitioning at 350 °C for 10 s (F: ferrite, A/M: austenite/martensite, C: carbide).

As can be seen in Figure 5.4(a), after 10 s of partitioning, the microstructure of the material still resembles the one shown in Figure 5.3(a). In this microstructure, there are long strips of austenite/martensite. The presence of these strips suggests that the microstructure of the HSi steel contains bands. Although the evidence for the existence of banded structure in this material has not been revealed in as-received and directed quench microstructure, bands have been found in the as-received microstructure of the LSi steel. Thus the origin and influence of the banded structure on the microstructure formed during partitioning will be discussed later

in section 6.1.1 during the investigations of the LSi steel. Within the austenite/martensite bands, isolated lower bainite regions are clearly observed, as shown in Figure 5.4(b). Because of the unambiguous presence of carbide in bainitic ferrite plates, the existence of lower bainite structure in this material after the partitioning treatment is proved.

Microstructure of HSi steel after partitioning at 350 °C for 100 s is presented in Figure 5.5. The microstructure contains plate-like ferrite and austenite/martensite. Lower bainite was not observed in this microstructure. Compared to the same feature in the microstructures after shorter partitioning time, ferrite plates are better defined with straight and parallel boundaries. Most of austenite/martensite regions between ferrite plates have a thickness less than 0.5 μ m. An investigation with a smaller region of microstructure (Figure 5.5(b)) showed that there is no evidence for the presence of carbide in ferrite plates.



(a) (b) Figure 5.5 Microstructure of the HSi steel after partitioning at 350 °C for 100 s (F: ferrite, A/M: austenite/martensite).

Microstructures of the HSi steel after partitioning at 350 °C for 1000 and 5000 s are shown in Figure 5.6. From Figure 5.6(a), it can be seen that the microstructure of the material after 1000 s of partitioning is similar to that shown in Figure 5.5(a). However ferrite plates in this microstructure are thicker. While a similar feature is also observed in the microstructure of material after 5000 s of partitioning (Figure 5.6(b)), the presence of banded structure and lower bainite has been revealed.

From all of these results, the evolution of the microstructure of the HSi steel during partitioning could be summarized as: The main features of the microstructure are ferrite and austenite/martensite. In the austenite/martensite matrix, ferrite presents as parallel and thin plates. During the partitioning step, increase in the number of plates and the thickness of each plate has been observed. Besides the presence of the main features, lower bainite structure has also been found. This structure locates in austenite/martensite bands which are not frequently found in the microstructure of the HSi steel.



Figure 5.6 Microstructures of the HSi steel after partitioning at 350 °C for (a) 1000 s and (b) 5000 s (LB: lower bainite).

It has been shown that during the partitioning treatment the number of plates and the thickness of ferrite plates increase with holding time. The well defined orientation of ferrite plates suggests the resemblance of this feature with upper bainite structure. In order to investigate upper bainite microstructure in the studied material and the (dis)similarity with partitioning microstructure, an isothermal bainitic treatment was implemented. Detail of this heat treatment schedule has been presented in section 4.2.4. Figure 5.7 shows the microstructure of the HSi steel after intercritical annealing at 770 °C and isothermal treatment at 350 °C for 1000 s. Ferrite plates and the austenite/martensite region between these plates are clearly revealed in this figure. Several blocky austenite/martensite islands which have the origin in the in homogeneity of the material can also be observed in the same microstructure has been shown. This result suggests that the occurrence of bainite microstructure cannot be neglected.



Figure 5.7 Microstructure of the HSi steel after isothermal bainitic treatment at 350 °C for 1000 s.

5.2. Retained austenite

Figure 5.8 shows XRD patterns of the HSi steel after quenching from two intercritical temperatures, 770 °C and 760 °C. In these patterns, no diffraction peaks of austenite are present. This absence of austenite peaks indicates that the direct quench specimens contain insignificant or even no volume fraction of retained austenite.



Figure 5.8 X-ray diffraction patterns of the HSi steel after the quench from the intercritical temperatures of (a) 770 °C and (b) 760 °C.

Figure 5.9 shows the variations of retained austenite volume fraction, carbon concentration and their product with partitioning time for different heat treatment schedules. In Figure 5.9(a), the evolution of retained austenite in all heat treatment schedules has the same tendency. While the absence of retained austenite in direct quench specimens has been shown in Figure 5.8, the volume fraction of this phase increases rapidly with partitioning time. After holding at 350 °C for 3 s, the volume fractions of retained austenite in all heat treatment schedules are from 0.04 to 0.08. When partitioning time is increased to 100 s, the measured volume fractions of this phase are as high as 0.18 to 0.19. Between 100 s and 5000 s, the variation of retained austenite volume fraction with all heat treatment schedules is less significant.



Figure 5.9 The variations with partitioning time of (a) retained austenite volume fraction (b) carbon content in this phase and (c) the product of these two values.

The changes in carbon concentration of retained austenite with partitioning time are more complicated than that of retained austenite volume fraction. For the treatments with the intercritical temperature of 770 °C and the quench temperature of 240 °C, the measured carbon content in retained austenite after the partitioning treatment for 3 s was 0.79 wt.%. Equivalent carbon concentrations were also detected in the specimens for 10 s and 100 s at the

partitioning temperature. When the time was extended to 1000 and 5000 s, the carbon concentration gradually increased to 0.9 wt.%.

In the case the material is annealed at 770 $^{\circ}$ C and quenched to 215 $^{\circ}$ C, carbon content in retained austenite continuously increased from 0.60 to 0.87 wt.% with the holding time from 3 to 1000 s. However, similar to the heat treatment schedule with the quench temperature of 240 $^{\circ}$ C carbon concentration in retained austenite did not further increase when partitioning time was extended to 5000 s.

There was a fast increase of carbon concentration in retained austenite when the material was annealed at 760 $^{\circ}$ C before quenching to 215 $^{\circ}$ C and partitioning at 350 $^{\circ}$ C. Along to the extension of the partitioning time from 3 s to 10 s, the carbon concentration in retained austenite increased by 0.2 wt.%. The carbon concentration of 0.78 wt.% was kept stable from 10 s to 1000 s of partitioning time. After the longest partitioning treatment (5000 s), the measured carbon concentration in retained austenite was 0.88 wt.%.

The evolution of the total carbon amount in austenite during partitioning step of all heat treatment schedules, shown in Figure 5.9(c), can be separated into two periods. Within the first 100 s of the partitioning treatment, the carbon amount in retained austenite increases rapidly. After 3 s of the holding time, retained austenite in all specimens contains 0.03-0.04 wt.% of carbon. However when holding time is lengthened to 100 s this value increases to 0.13-0.14 wt.%. During the second period from 100 to 5000 s, the change of carbon amount in retained austenite is less than that of the period before. The largest increase of this value is from 0.14 to 0.16 wt.%.

The increase of carbon amount in retained austenite with partitioning time indicates that during this heat treatment austenite is stabilized. It is known that the carbon enrichment of austenite reduces the M_s temperature of this phase during the martensite transformation. Therefore with the same quench temperature, meaning room temperature in this situation, the decrease of M_s temperature leads to a higher volume fraction of retained austenite after the last quench. Table 5.3 shows the volume fraction, carbon concentration and their product

before and after the partitioning step for 5000 s in different heat treatments. The increase of carbon concentration in austenite after all partitioning treatments can be clearly observed in this table. After the partitioning step, the measured carbon concentration with all heat treatment schedules is approximately 0.90 wt.%. The increase of carbon amount in austenite after the partitioning treatment can also be observed in this table. In all heat treatments, the holding at 350 °C for 5000 s brings the carbon amount in austenite larger than the amount this phase contains after the first quench step. These results indicate the existence of carbon diffusion from an external source. Since after the first quench step microstructure of the HSi steel contains ferrite, martensite and austenite the observed increase of carbon amount in austenite must be related to the partitioning of carbon from martensite.

Table 5.3 Austenite volume fraction, carbon concentration and their product before and after the partitioning for 5000 s in different heat treatments.

		Afte	r the first qu	iench	After the partitioning			
<i>T_i</i> (°C)	<i>То</i> (°С)	f_{γ}	x_c^{γ} (wt.%)	$f_{\gamma}.x_{c}^{\gamma}$ (wt.%)	f_{γ}	x_{C}^{γ} (wt.%)	$f_{\gamma}.x_{c}^{\gamma}$ (wt.%)	
770	240	0.50±0.03	0.22±0.01	0.11±0.01	0.16±0.01	0.90±0.05	0.15±0.02	
770	215	0.25±0.01	0.22±0.01	0.06±0.00	0.16±0.01	0.86±0.05	0.14±0.02	
760	215	0.23±0.01	0.33±0.01	0.08±0.00	0.18±0.01	0.89±0.05	0.16±0.02	

5.3. Dilatometric analysis

Figure 5.10(a) shows dilatometric curves of Q&P heat treatments with different partitioning periods after quenching from 770 °C to 240 °C. As can be seen in this figure, quenching processes were well controlled by dilatometer. All the specimens are quenched to the same desired temperature. During the heating period from T_Q to T_P , a linear expansion of specimens showed that dilatometer did not detect any phase transformation in the same period. However, an isothermal dilatation was observed when specimens were held at T_P temperature. With longer partitioning periods, larger increases in the length of specimens were detected. The difference in partitioning time also results in the change in the material behavior during the last quench. After holding for 3 s, 10 s and 100 s at 350 °C, the transformation of austenite to martensite was observed during the fast cooling from T_P to room temperature. However with

longer holding periods (1000 and 5000 s), only the thermal contraction was observed in the dilatometric curve when the specimen was quenched.

By applying the onset method, the M_s temperatures corresponding to the last quench of specimens which were partitioned for 3, 10 and 100 s were determined. For the specimens which were partitioned for 1000 and 5000 s, the similar procedure cannot be applied because the M_s temperature is below room temperature. The results are presented in Figure 5.10(b). For comparison, the M_s temperature of the specimen which was directly quenched from intercritical temperature is also given in the same figure at 0 s of the partitioning time. The fast reduction of M_s temperature with partitioning time can be observed clearly in this figure. The reason of this reduction of M_s temperature has been mentioned in the previous section. This is a clear evidence for the stabilization of austenite during the partitioning step.



Figure 5.10 (a) Dilatometric curves of the Q&P heat treatments and (b) the reduction of martensite start temperature with different partitioning periods.

The dilatation of material during partitioning in different heat treatment schedules is presented in Figure 5.11. With all heat treatment schedules, the change in length of specimen with partitioning time is not linear. 90 % of detected dilatation evolves in the first 500 s of partitioning. Although the specimen length increases less when the holding time is extended to 5000 s, the visible slope of dilatometric curve indicates that the length of specimen can further increase if partitioning time is kept longer. Qualitatively, the shape of these dilatometric curves reflects the variation of volume fraction or carbon amount of retained austenite. This similarity suggests that there is a relationship between this isothermal dilatation and the evolution of retained austenite during partitioning step. On the other hand, a difference between the magnitude of dilatation corresponding to the variation of intercritical and quenching temperatures can also be observed. After 5000 s of holding time, the largest difference in dilatation magnitude is between the two heat treatments which have the same intercritical temperature (770 °C) but the quenching temperatures are 240 °C and 215 °C. Since the volume fractions of intercritical ferrite in these heat treatments are equal, the observed dilatation suggests the evolution of austenite and martensite.



Figure 5.11 The isothermal dilatations with partitioning time of the HSi steel in different heat treatment schedules.

5.4. Processes during partitioning step

Since the change in microstructure, volume fraction of retained austenite and also the length of specimen must be the results of kinetic processes in material, it is necessary to analyze possible evolution of phases during the partitioning step.

Table 5.2 shows volume fractions and carbon concentrations of phases before the partitioning treatment. At this stage, the microstructure of the HSi steel includes intercritical ferrite, martensite and austenite. Because in the range between T_Q and T_P temperature ferrite is a stable phase, there is no phase transformation involving this phase. On the contrary, martensite and austenite can evolve in several different ways in the same temperature range. Results from XRD measurements have shown that austenite is carbon enriched during the partitioning step. The carbon diffusion from martensite to austenite has also been pointed out by the same analyses. However behind this enrichment, there is a complex kinetic process. By

separately analyzing each kinetic process which could occur during partitioning treatment, the stabilization mechanism of austenite could be revealed. During these analyses, the method already mentioned in section 3.2 is used to estimate the relative change in length of the specimen during the partitioning step. This relative change in length of specimen, volume fraction and carbon concentration of austenite predicted for each kinetic model are then compared with corresponding experimental values. Directly, these comparisons will be carried out with the measured results of 5000 s partitioned specimens. Since the martensite transformation during the last quench was not observed in these specimens, the interference of this transformation on the investigation is not considered.

5.4.1. Carbon partitioning from martensite

The existence of the carbon partitioning from martensite to austenite has been proved by XRD analyses in section 5.2. Based on the condition of the material before the partitioning step, given in Table 5.2, the volume fraction and carbon concentration of phases after partitioning have been calculated by the CCE model (section 2.2.3). In these calculations, the fitting KM equations, shown in section 4.2.2, were used to estimate the volume fraction of austenite after the first and the last quench. Figure 5.12 shows the relationships between the first quench temperature and the retained austenite volume fraction after partitioning treatment with two intercritical temperatures 770 °C and 760 °C. As can be seen in this figure, due to the diffusion of carbon during the partitioning, the volume fractions of phases are changed. Compared to the state after the first quench, volume fraction of austenite after partitioning treatment with both intercritical temperatures increases less than 0.01. For an intercritical temperature of 770 °C, CCE calculation predicts that the "optimum" quench temperature is 207 °C bringing the stability for 0.22 fraction of austenite. The similar volume fraction of retained austenite is also found for the heat treatment with lower intercritical temperature (760 °C). But in this case the "optimum" quench temperature (760 °C).

The predicted volume fraction and carbon concentration of phases after Q&P heat treatment for the schedules shown in section 4.2.3 are presented in Table 5.4. During the calculation with the CCE model it is assumed that all carbon atoms from martensite diffuse to austenite. Therefore after the partitioning treatment there is no distinction between intercritical ferrite and carbon depleted martensite. In Table 5.4, the total volume fraction of these two phases is presented by unique f_{α} values. For convenience, the retained austenite volume fraction, carbon concentration and the change in length of specimen measured after 5000 s of partitioning treatment are also given in the same table.



Figure 5.12 The relationship between the quench temperature and the retained austenite volume fraction in the HSi steel with different intercritical temperatures (a) 770 °C and (b) 760 °C.

 Table 5.4 Volume fraction, carbon concentration and the relative change in length of the specimen after carbon partitioning from martensite.

			Calculation for carbon partitioning						Experiment			
<i>T₁</i> (°C)	<i>T</i> _Q (°C)	f_{α}	x_c^{α} (wt.%)	f _r	x_c^{γ} (wt.%)	f_{α_M}	$\frac{x_C^{\alpha_M}}{(\text{wt.\%})}$	Δ <i>l/l</i> (%)	f _y	x_C^{γ} (wt.%)	Δ <i>l / l</i> (%)	
770	240	0.51	~10 ⁻³	-	-	0.49	0.40	0.02	0.16±0.01	0.90 ± 0.05	0.12	
770	215	0.75	~10 ⁻³	0.05	0.78	0.20	0.78	0.03	0.16±0.01	0.86±0.05	0.08	
760	215	0.77	~10 ⁻³	0.09	0.85	0.14	0.85	0.03	0.18±0.01	0.89±0.05	0.11	

As can be seen in Table 5.4, the retained austenite volume fraction estimated by the CCE calculation in all heat treatment schedules is smaller than that obtained in experiments. In the simulation for the intercritical temperature of 770 °C and quench temperature of 240 °C, there is no retained austenite after the last quench. Furthermore in all three heat treatments, CCE calculation predicted that there is a martensite transformation during the last quench. Due to this transformation, a large fraction of carbon enriched austenite is transformed to martensite. However, as mentioned previously, after 5000 s of partitioning treatment, there is no transformation detected by dilatometer. On the other hand, the carbon concentration in retained austenite obtained from CCE calculations for all heat treatments is also smaller than

the measured values. In general, the difference between measured and calculated carbon concentration in retained austenite is much larger than 0.05 wt.% which is the error of experimental measurements.

By applying equation (2.11), the relative changes in length of specimen during partitioning steps have been determined. These values are given in Table 5.4. The dilatometric calculations show that during partitioning treatments the relative changes in length of specimen are slightly increased. The estimated dilatation is from 0.02-0.03 %. But in the experiments, the measured dilatation is much larger than this predicted value. The smallest dilatation measured in the heat treatment with intercritical temperature of 770 °C and quenching temperature 215 °C is 0.08 %. From the inconsistence between calculated and measured results, it is seen that the carbon diffusion from martensite to austenite under the fixed interface condition cannot account for the evolution of austenite during the partitioning step.

5.4.2. Bainite formation

The difference in measured and CCE calculated values of austenite volume fraction suggested that during the partitioning step the stabilization of austenite does not come alone from the diffusion of carbon from martensite under the fixed interface condition. The partial transformation of austenite to bainite can also bring the stability to the untransformed part of this phase. Under the investigated time and temperature range, austenite can decompose to upper and/or lower bainite. However, from microstructure investigations, it has been known that lower bainite is a minor feature in the microstructure of the HSi steel. This structure is only observed with the presence of bands. On the contrary, it has also been pointed out the similarity between upper bainite and the Q&P microstructure. Therefore, in this section only upper bainite is considered. For simplicity, it is assumed that tempering and carbon diffusion from martensite does not occur during the partitioning step.

It is known that upper bainite formation is ceased whenever the concentration of austenite in T_0 curve is reached. The end point of this transformation can be predicted by applying lever rule (equations 2.12-2.13). At 350 °C, the concentration of austenite in T_0 has been

determined as 1.04 wt.% (section 3.1.3). This carbon concentration is approximately 0.1 wt.% higher than the measured value. However the difference could be understood in several ways. It should be due to the statistic error in carbon concentration measurement. Furthermore, it is no sure that bainite formation, in the case it happened, was completed after 5000 s of holding time. On the other hand, the carbon concentration defined by T_0 is calculated by just thermodynamic data. The influence of other factors such as internal stress has not been taken into account during calculation.

Volume fraction and carbon concentration of phases after bainite formation with different heat treatment schedules are given in Table 5.5. Because it is assumed that all of carbon atoms in ferrite plates diffuse to untransformed austenite, the difference between intercritical ferrite and bainitic ferrite is ignored. The total volume fraction of these two types of ferrite is presented in Table 5.5 as a unique f_{α} value. In all heat treatment schedules, the calculated volume fraction and carbon concentration of austenite are smaller than the experimental results. The smallest difference observed in the heat treatment with intercritical temperature of 770 °C and quenching temperature of 240 °C is 0.06. The relative changes in length of specimen corresponding to upper bainite formation in different heat treatments have been determined by equation (2.14). Results of these calculations are shown in Table 5.5. For all three heat treatment schedules, the calculated dilatations are 2-4 times larger than the measured values.

		(Calculation for upper bainite formation							Experiment			
<i>T</i> _i (°℃)	<i>То</i> (°С)	f_{α}	x_{C}^{α} (wt.%)	f _r	x_C^{γ} (wt.%)	f_{α_M}	$\begin{array}{c} x_{C}^{\alpha_{M}} \\ \text{(wt.\%)} \end{array}$	Δ <i>l/l</i> (%)	- f _y	x_{C}^{γ} (wt.%)	Δ <i>l/l</i> (%)		
770	240	0.49	~10 ⁻³	0.10	1.04	0.41	0.22	0.50	0.16±0.01	0.90±0.05	0.12		
770	215	0.30	~10 ⁻³	0.05	1.04	0.65	0.22	0.25	0.16±0.01	0.86±0.05	0.08		
760	215	0.57	~10 ⁻³	0.07	1.04	0.36	0.33	0.20	0.18±0.01	0.89±0.05	0.11		

 Table 5.5 Volume fraction, carbon concentration and the relative change in length of the specimen after upper bainite formation.

As mentioned before, the difference in carbon concentration between experiment and calculation could be due to the ambiguousness about the time when bainite formation finishes.

In the case bainite formation needs longer time than 5000 s to finish, both calculated carbon concentration and volume fraction of austenite might be achieved in practice if partitioning time is kept longer. However, bainite formation alone cannot account for the increase of carbon amount in austenite shown in section 5.2 and also the small dilatation measured from experiments. Thus austenite could be stabilized by both carbon diffusion from martensite and upper bainite formation. On the other hand, the calculation in section 5.4.1 only predicts the with carbon concentration the fixed austenite volume fraction and retained austenite/martensite interface assumption. Recently, the more complicated calculations of carbon diffusion from martensite to austenite under the moving interface condition have been carried out with numerical and phase field methods. Results of these calculations indicate that volume fractions of phases can vary significantly during partitioning step. Thus the austenite stabilization under this condition needs to be further analyzed.

5.4.3. Carbide precipitation

The analysis would be incomplete if carbide precipitation were not discussed. Although lower bainite formation is also accompanied by carbide precipitation in bainitic ferrite plates, this process has already been mentioned in previous section. Thus the precipitation here is carbide formation from martensite and directly from austenite. Because these two processes often appear during tempering, it is convenient to consider them at the same time.

It is known that epsilon carbide could be precipitated early after quench. Since not all carbon atoms are attracted by the formation of this carbide, a significant amount of carbon is still kept in martensite. Previous studies indicated that the carbon concentration of martensite with the presence of epsilon carbide is 0.20-0.25 wt.% [3]. With an equivalent carbon concentration before partitioning, the precipitation of epsilon carbide in martensite is not expected to occur during partitioning treatment. In Table 5.2, the heat treatments with intercritical temperature of 770 °C bring a carbon concentration in martensite of 0.22 wt.%. Thus the epsilon carbide in these heat treatments could not be expected to form. For lower intercritical temperature (760 °C), the carbon concentration in martensite is 0.33 wt.%. There might have a small fraction of epsilon carbide in this situation.

A different form of carbide which could precipitate with long time or high temperature treatment is cementite. However with a relatively high content of silicon in composition, it is believed that this precipitation especially in austenite is effectively suppressed. In this study, the presence of cementite was not found by XRD investigation. In addition, microstructure observation with SEM did not bring any evidence for the presence of carbide except for the lower bainite structure. Furthermore, if carbon atoms are assumed to present at either austenite or cementite and nowhere else the maximum volume fraction of the latter phase after 5000 s of the holding time in all Q&P heat treatment is less than 0.8 %. From these results, it can be said that carbide precipitation is insignificant during partitioning step.

5.5. Influence of heat treatment parameters

5.5.1. The quench temperature

During the discussion about the partitioning of carbon from martensite to austenite in section 5.4.1, the relationship between the first quench temperature and the retained austenite volume fraction has been given. According to the CCE calculation shown in Figure 5.12, the reduction of the first quench temperature from 240 °C to 215 °C after intercritical treatment at 770 °C increases the retained austenite volume fraction from 0.00 to 0.05. This effect can be referred to: The reduction of the first quenching temperature decreases the volume fraction of austenite and increases the carbon amount in martensite. Under the influence of these two effects the carbon concentration of austenite after partitioning step increases. The higher carbon enrichment brings more stability for austenite by decreasing M_s temperature. And thus a larger fraction of austenite is retained after the last quench.

The decrease of austenite volume fraction before partitioning treatment caused by the reduction of the first quenching temperature has been shown in Table 5.3. However contrary to the prediction of CCE calculation, the retained austenite volume fraction obtained after 5000 s of partitioning step does not change when the quench temperature is reduced. In both heat treatments the volume fraction of austenite after the partitioning step for 5000 s is 0.16. The observation with Figure 5.9(a) shows that the equal retained austenite volume fraction can also be found with all other partitioning periods. This inconsistence between CCE

calculation and experimental observation again suggests that carbon diffusion from martensite under the fixed interface condition is not the only process occurring during partitioning step.

However since the austenite volume fraction obtained after the quench to lower temperature (215 °C) is smaller the ratio of this austenite is stabilized during the holding at 350 °C is larger. For clearer indication, the evolutions of retained austenite volume fraction with partitioning time in two heat treatment schedules are presented in Figure 5.13. In this figure, the volume fraction of retained austenite is normalized to the volume fraction of austenite after the first quench step $(\frac{f_r}{f_{\gamma 0}})$. For all partitioning periods the ratios of retained austenite obtained with lower quenching temperature are higher.



Figure 5.13 The evolutions of retained austenite ratio with partitioning time in different heat treatments.

The higher ratio of retained austenite with the lower quench temperature observed above suggests that there is a different relationship between the quench temperature and the retained austenite volume fraction besides which pointed out by CCE model. It has been shown that upper bainite formation could occur during the partitioning treatment. But the calculation with this transformation alone did not bring the agreement with experimental measurements. On the other hand the migration of austenite/martensite interface during the carbon diffusion cannot be ignored especially in the case the holding time is as long as 5000 s. Therefore the reduction of the quench temperature might also influence these processes.

For upper bainite formation, it is known that the volume fraction of carbon enriched austenite depends on the carbon concentration of this phase before and after the transformation. This relation can be clearly observed from equation (2.13). Since the partitioning temperature in two heat treatments is kept constant at 350 °C, the carbon concentrations in austenite after the upper bainite formation defined by T_0 curve are not different. However, the variation of the carbon concentration in austenite before bainite formation could produce the dissimilarity in austenite volume fraction after the transformation. It has been suggested that both carbon diffusion from martensite and upper bainite formation occur during the partitioning treatment. The increase of carbon concentration in austenite after partitioning of the heat treatment with lower quench temperature has been shown by CCE calculations. It is assumed that during the partitioning treatment austenite obtained with lower quench temperature always contains a larger amount of carbon. Because the volume fractions of phases after upper bainite formation depend on the carbon concentration of the austenite prior to transformation, the lower quench temperature always is reatment.

Recently, the partitioning of carbon under the moving austenite/martensite interface has been studied by phase field modeling [31]. In this study, the partitioning of carbon in two Q&P heat treatments which are only different in the quench temperatures is investigated. It has been pointed out that the volume fraction of austenite after partitioning treatment increases or decreases depending on the quench temperature. For the lower quench temperature, during the holding at partitioning temperature the volume fraction of austenite increases. On the contrary, at a higher quench temperature the volume fraction of this phase decreases during the partitioning treatment. In these two cases, the same volume fraction of austenite is reached when the holding time is kept longer.

From analyses above, the relation between the quench temperature and the retained austenite volume fraction in two heat treatment schedules has been discussed. CCE calculation predicts the increase of retained austenite volume fraction when the quench temperature is reduced from 240 °C to 215 °C. However in practice after 5000 s of partitioning treatment in both heat treatments the measured volume fraction of retained austenite is 0.16. During the partitioning treatment the ratio of retained austenite obtained with lower quench temperature is higher. The inconsistence between CCE calculation and experiment suggests the existence of a

different relation between the quench temperature and the retained austenite volume fraction besides that is predicted by CCE model. The upper bainite formation and the carbon partitioning under the moving austenite/martensite interface can also be affected by the reduction of the quench temperature.

5.5.2. The intercritical temperature

From Table 5.1, it has been shown that the volume fraction of intercritical austenite decreases while the carbon concentration in this phase increases with the reduction of the intercritical temperature from 770 °C to 760 °C. Due to the increased carbon concentration in austenite when the intercritical temperature is decreased, the M_s temperature of austenite is also reduced. During the first quench to the same temperature (215 °C), the volume fraction of lower intercritical temperature austenite transforming to martensite is smaller. This indication can be observed in Table 5.2.

From this table, the large difference of the intercritical ferrite volume fractions between heat treatments can be recognized. Because in the temperature range from 215 °C to 350 °C ferrite is the stable phase, it is expected that there is no kinetic process related to this phase. Following this, the difference in volume fraction of intercritical ferrite does not influence the partitioning process. On the contrary, the variation of the volume fraction of austenite and martensite with intercritical temperature could bring the difference in the behavior of material during the holding at partitioning temperature. The evolutions of retained austenite volume fraction with the partitioning time in two heat treatments which have the different intercritical temperature (770 °C and 760 °C) have been shown in Figure 5.9(a). With all partitioning periods, the volume fraction of retained austenite obtained with the lower intercritical temperature heat treatment is larger.

The increase of retained austenite volume fraction as the intercritical temperature decreases has been predicted by CCE calculations. In Table 5.4, the calculation for the carbon partitioning with CCE model shows that the decrease of the intercritical temperature from 770 °C to 760 °C leads to the increase of the retained austenite volume fraction from 0.05 to 0.09. Accompanied to this occurrence, the carbon concentration in retained austenite also increases.
Before the partitioning step, the volume fractions of austenite in two heat treatments are approximately 0.23-0.25. On the other hand, the carbon amounts in martensite $(f_{\alpha_M}.x_c^{\alpha_M})$ of these heat treatments are almost the same (0.12-0.14 wt.%). The diffusion of carbon from martensite could increase the carbon concentration of austenite to the same level (0.52-0.57 wt.%). However, the carbon concentration in austenite obtained with the lower intercritical temperature heat treatment is higher. Therefore the larger volume fraction of retained austenite obtained with the lower intercritical temperature heat treatment should not come from the diffusion of carbon from martensite but from the higher carbon concentration of austenite before the partitioning step.

Although the increased tendency of the retained austenite volume fraction with the reduction of the intercritical temperature is in agreement with experimental observations, CCE calculation predicts the smaller retained austenite volume fraction than the measured values. It has been suggested that during the partitioning treatment austenite could also be stabilized by upper bainite formation. The calculation results for the upper bainite formation, shown in Table 5.5, indicate that the retained austenite volume fraction increases as the intercritical temperature decreases. It is known that the upper bainite formation is finished when the carbon concentration of austenite defined by T_0 curve is reached. The volume fraction of carbon enriched austenite obtained with lower intercritical temperature heat treatment is higher, the volume fraction of this phase after bainite formation is larger. Nevertheless the calculated retained austenite volume fraction of upper bainite formation is smaller than that measured from experiments.

From this analysis, the influence of intercritical temperature on the retained austenite volume fraction has been given. It has been pointed out that the retained austenite volume fraction increases as the intercritical temperature is reduced. For the partitioning of carbon from martensite under the fixed interface condition and the upper bainite formation, the increase in carbon concentration of austenite before the partitioning step brings more stability to this phase.

Chapter 6 Q&P process of the LSi steel

6.1. Evolution of the microstructure

6.1.1. Microstructures after direct quench

Figure 6.1 shows microstructures of the LSi steel after direct quench from intercritical temperatures 740 °C and 730 °C. It can be recognized that there is a similarity between microstructures after direct quench of HSi and LSi steel. At this state, microstructures of the LSi steel also contain ferrite and martensite. As will be proved later, there is no retained austenite in these microstructures. The presence of carbide was not also observed.





In these microstructures, ferrite and martensite are not homogeneously distributed. Bands of martensite can be clearly observed. Ferrite in these microstructures appears as thin, parallel plates. Since this morphology of intercritical ferrite has also been observed in microstructures of HSi steel, a similar investigation with interrupted heat treatment is applied. The detail of interrupted heat treatment has been shown in section 4.2.1.

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Figure 6.2 Microstructures of the LSi steel after interrupted heat treatments at (a) 680 °C (b) 700 °C (c) 720 °C for 3 s and 740 °C for (d) 3 s (e) 30 s and (f) 300 s (LePera's echant).

Microstructures of the LSi steel after interrupted heat treatments are shown in Figure 6.2. As can be seen in Figure 6.2(a) and (b), the microstructures after interrupted heat treatment at 680 °C and 700 °C mainly contain ferrite. Prior austenite grains could also be observed in the same micrographs. The presence of dark and dispersed particles within prior austenite grains shows

that at these temperatures the precipitation of carbide occurs. When the temperature is increased to 720 $^{\circ}$ C, the formation of austenite becomes visible. In Figure 6.2(c), this phase is present as large and long regions in the ferrite matrix. The abnormal distribution of austenite indicates that this phase started to grow in bands. The indication is confirmed by observing the microstructure after the interrupted heat treatment at 740 $^{\circ}$ C for 3 s. In Figure 6.2(d), the bands of austenite are unambiguously present. A mixture of ferrite and austenite in adjacent bands can also be observed. With the increase of holding time to 30 and 300 s (Figure 6.2(e) and (f)), ferrite becomes isolated as long and parallel plates.

From the investigations above, the presence of ferrite as thin and parallel plates is only observed during the last stages of intercritical treatment (30 s and 300 s). This occurrence suggests that the formation of this feature relates to the previous growth of austenite bands. Therefore an investigation of banded structure and its formation could bring necessary information to understand the presence of ferrite as parallel plates.

It is known that banded structure is a result of alloying element segregation. This structure forms during material processing (casting and hot rolling). After casting due to the slow diffusion of alloying elements, micro segregation occurs in the material. During the hot rolling, this segregation is directionally dispersed. The formation of microstructure is greatly dependent on local concentration of alloying elements.

Among the alloying elements in the LSi steel, manganese is believed to play an important role on the formation of banded structure in this material. The effect comes from the small diffusion coefficient of this element and its effect on the stability of phases in steel. Since manganese is an austenite stabilizer, the inhomogeneous distribution of this element results on the formation of different microstructures in bands. During cooling from high temperature, for example after hot rolling, the lower manganese bands are less stable and transform to ferrite before the manganese-rich bands. This transformation is accompanied by the partitioning of carbon from ferrite to austenite. Therefore the segregation of manganese at the same time causes the inhomogeneous distribution of carbon. The microstructure formed afterwards in high manganese bands depends on cooling conditions. In the case of the initial microstructure observed in the LSi steel, these features are austenite/martensite and lower bainite in the high manganese bands. Inversely during the subsequent heating, high manganese and high carbon bands transform to austenite first. The following step is the growth of austenite into low manganese bands. Austenite grows as parallel plates into ferrite as mentioned in section 4.1.1.

By applying quantitative metallography (section 2.3) volume fractions of phases after direct quench can be determined. Since no other phase transformation, except the martensite transformation, is detected by dilatometer during the quenching, volume fraction of intercritical ferrite does not change in this period. On the other hand, intercritical austenite is totally transformed to martensite during this quenching step. Thus the volume fraction of phases after intercritical treatment can be estimated from the volume fraction of phases after direct quench. The carbon concentration of ferrite was estimated by Thermo-calc calculations, while the carbon concentration of austenite was defined by total carbon balance between ferrite and austenite. Volume fractions and carbon concentrations of phase in intercritical stage are presented in Table 6.1.

Table 6.1 Volume fractions and carbon concentrations of phases after intercritical treatment.

<i>T_i</i> (⁰C)	f_{a}	x_{C}^{α} (wt.%)	f_{γ}	x_c^{γ} (wt.%)
740	0.15±0.05	~10 ⁻³	0.85±0.05	0.23±0.01
730	0.33±0.02	~10 ⁻³	0.67±0.02	0.30±0.01

6.1.2. Microstructures after the first quench

As mentioned in section 4.1.2 by combining volume fractions of phase after intercritical treatment with the fitting KM equations, volume fractions of phases after the first quench can be obtained. Table 6.2 shows results of these calculations in different heat treatments for the LSi steel.

For the heat treatment in which the intercritical temperature is 740 °C and the quenching temperature is 240 °C, volume fractions of austenite and martensite are approximately equal. However when the quench temperature is decreased to 215 °C, austenite/martensite volume fraction ratio increased rapidly. Based on this principle difference, the influence of quench

temperature on partitioning process will be analyzed in section 6.5.1. In the previous section, it was known that the reduction in intercritical temperature changes both the volume fraction of ferrite and the initial carbon concentration of austenite. However after the quench to the same temperature (240 $^{\circ}$ C), the austenite volume fraction of these heat treatments is less different.

1 a	Table 6.2 volume fractions and carbon concentrations of phases after the first quench.										
<i>T</i> _i (°C)	<i>T</i> _Q (°C)	f_{lpha}	x_c^{α} (wt.%)	f_{γ}	x_C^{γ} (wt.%)	f_{α_M}	$x_C^{a_M}$ (wt.%)				
740	240	0.15±0.05	~10 ⁻³	0.43±0.03	0.23±0.01	0.42±0.02	0.23±0.01				
740	215	0.15±0.05	~10 ⁻³	0.15±0.01	0.23±0.01	0.70±0.04	0.23±0.01				
730	240	0.33±0.02	~10 ⁻³	0.46±0.01	0.30±0.01	0.21±0.01	0.30±0.01				

6.1.3. Microstructures after partitioning step

In the previous section, the difference of volume fractions and carbon concentrations in phases before partitioning step of various heat treatments has been pointed out. However it is observed that qualitatively the evolutions of the microstructure during partitioning in different heat treatment schedules are similar. To avoid the unnecessary repetition, the microstructure of specimens intercritically treated at 740 °C before quenching to 240 °C and partitioning with predefined periods of time are analyzed in detail. The difference of microstructure in other heat treatment schedules will be described during the investigation.

Figure 6.3 shows the microstructure of the LSi steel after partitioning at 350°C for 3 s. In Figure 6.3(a), the banded structure can be clearly observed. This sharp distinction of banded structure comes from the distribution of different phases in microstructure. In general, the microstructure of the LSi steel at this state includes ferrite, austenite/martensite and bainite. As can be seen in Figure 6.3(b), the low manganese band is composed of a mixture of ferrite and austenite/martensite. In this band ferrite is present as long and parallel plates. Austenite/martensite is located between ferrite plates as isolated islands. There is no evidence for the existence of carbide in this band.

Although most of the high manganese bands are occupied by austenite/martensite, bainite structures can be observed. One of these structures is shown Figure 6.3(c). In the structure, carbide is present as small, dispersed and bright particles. The structure also includes thin and parallel layers which could be austenite. With the presence of carbide in ferrite matrix, the observed structure is identified as lower bainite.





Figure 6.3 Microstructure of the LSi steel after the partitioning step at 350 °C for 3 s (F: ferrite, A/M: austenite/martensite, C: carbide).

The microstructure of the LSi steel after the partitioning step at 350 °C for 10 s is shown in Figure 6.4. As can be seen in Figure 6.4(a), the low manganese band is not well distinguished from other characteristics of the microstructure. On the contrary features of high manganese bands including austenite/martensite and lower bainite structure are clearly observed. There is a large difference between microstructures after 3 and 10 s of partitioning. In the latter

microstructure, lower bainite presents more frequently. However the observation from Figure 6.4(b) shows that around this structure austenite/martensite still exists with a large fraction.



(a) (b) Figure 6.4 Microstructure of the LSi steel after the partitioning steps at 350 °C for 10 s (A/M: austenite/martensite, LB: lower bainite).



Figure 6.5 Microstructure of the LSi steel after the partitioning step at 350 °C for 100 s (F: ferrite, A/M: austenite/martensite, LB: lower bainite)

Figure 6.5 presents the microstructure of the LSi steel after partitioning at $350 \,^{\circ}$ C for 100 s. The appearance of ferrite as parallel plates can be observed in Figure 6.5(a). Although this feature is available a large volume in the microstructure of material, there is no evidence for the growth of ferrite into high manganese bands. Figure 6.5(b) shows the microstructure at the region between high and low manganese bands. In low manganese bands, austenite/martensite is still present as isolated islands. On the contrary, in high manganese bands,

austenite/martensite is substituted by lower bainite structure. The presence of thin and parallel plates of ferrite in the boundaries of austenite/martensite blocks suggests that lower bainite was growing into austenite/martensite regions.

Microstructures of LSi steel after partitioning at 350 °C for 1000 and 5000 s are shown in Figure 6.6. From these micrographs, it can be recognized the domination of lower bainite structure. Austenite/martensite also presents as isolated islands in the matrix of lower bainite.



Figure 6.6 Microstructure of the LSi steel after the partitioning step at 350 °C for (a) 1000 s and (b) 5000 s

From above investigations the evolution of microstructure could be summarized as: After intercritical treatment and quench, microstructure of LSi steel include ferrite, austenite/martensite. These phases distribute in microstructure as bands. High manganese band is totally occupied by austenite/martensite while low manganese band is composed by a mixture of ferrite and austenite/martensite. Ferrite in this band has plate-like morphology. During the partitioning step, austenite/martensite in high manganese bands is gradually replaced by lower bainite. The presence of a high fraction of carbide is unambiguous. There is no clear evidence for the growth of parallel ferrite plates in the same periods of time or for the carbon partitioning from martensite to austenite in the microstructure.

In order to compare the Q&P and bainite microstructure, an isothermal heat treatment which schedule has been presented in section 4.2.4 was performed. As can be seen in Figure 6.7(a), microstructure of isothermal heat treatment includes: ferrite, austenite/martensite and bainite.

The banded structure with different characteristics is clearly visible in this Figure. In lower manganese band, austenite and ferrite appear as alternating parallel plates. Similar to the Q&P microstructure, the high manganese bands of isothermal microstructure are mostly occupied by austenite/martensite. However, isolated bainite microstructure can also be observed in these bands. Figure 6.7(b) shows the features within a colony of bainite. The presence of carbide as spherodized particles suggests that after 1000 s of holding time carbide in bainite is coarsened. Sheaves of bainite can be recognized by the thin and parallel layers separating them. However, these layers could not be identified as austenite or cementite.



Figure 6.7 Microstructure of the LSi steel after isothermal bainitic treatment at 350 °C for 1000 s (F: ferrite, A/M: austenite/martensite, LB: lower bainite, C: carbide).

6.2. Retained austenite

X-ray diffraction patterns of the LSi steel after direct quench from intercritical temperature 740 °C and 730 °C are shown in Figure 6.8. Although the scanning angle for diffraction experiments was chosen in order to obtain four reflection peaks of austenite, none was detected in these patterns. The occurrence indicates that there is an insignificant amount of retained austenite in these specimens.



Figure 6.8 X-ray diffraction patterns of the LSi steel after quenching from the intercritical temperatures of (a) 740 °C and (b) 730 °C.

The variations of retained austenite volume fraction, carbon concentration and their product with partitioning time are given in Figure 6.9. As can be seen in Figure 6.9(a), in the first 100 s of partitioning the variations of volume fraction of retained austenite in different heat treatments are similar and increase with the holding time at 350 °C. After 3 s of partitioning treatment, volume fraction of retained austenite corresponding to different heat treatments is equal to 0.04-0.05. This value increases to 0.11-0.12 when partitioning time is extended to 100 s. With a longer partitioning time, the volume fraction of retained austenite generally decreases to 0.08-0.09, except in the case of the specimen quenched from 730 °C to 240 °C where the volume fraction of retained austenite reaches 0.15 after partitioning for 5000 s.

From Figure 6.9(b), an increase of carbon concentration in retained austenite is observed in all heat treatments. After the quenching from 740 °C to 240 °C and partitioning at 350 °C for 5000 s, the carbon concentration in retained austenite is 0.98 wt.%. With the same intercritical temperature (740 °C) but lower quench temperature (215 °C), the maximum carbon concentration is 0.83 wt.%. This value was measured after the holding of specimen at 350 °C for 5000 s. The equal carbon concentration was also detected from the specimen that was held at the partitioning step for 10 s. However, this high carbon concentration gaining after a short partitioning time (10 s) should be a result of inhomogeneous state of material. In the heat treatments with an intercritical temperature of 730 °C and a quench temperature of 240 °C, there is a less significant reduction of carbon concentration when the holding time is extended from 1000 to 5000 s.



Figure 6.9 The variations of (a) retained austenite volume fraction, (b) carbon concentration and (c) their product with partitioning time.

The variations with partitioning time of the total carbon that belongs to the retained austenite between heat treatments are similar. As can be seen in Figure 6.9(c), carbon amount in austenite in all heat treatments initially increases and then remains stable at a certain value. In the case of specimens quenching from 740 $^{\circ}$ C to 215 $^{\circ}$ C, this stable value is approximately 0.08 wt.% of carbon. On the contrary for specimens quenched from 730 $^{\circ}$ C to 240 $^{\circ}$ C, retained austenite contains 0.14 wt.% of carbon.

From the above analyses the evolution of retained austenite can be given as: While the absence of retained austenite after direct quench from intercritical stage is proved, the Q&P heat treatment brings the stability to a significant amount of austenite. The volume fraction of

retained austenite in general increases with partitioning time. However with a long holding period, the decrease in volume fraction of this phase is observed in some cases. During the partitioning step, the carbon concentration in retained austenite also increases. Table 6.3 shows the austenite volume fraction, carbon concentration and their product before and after partitioning treatment for 5000 s. Compared to the same value before partitioning treatment, the carbon concentration in austenite after holding 5000 s at 350 °C is 3-4 times higher. The increase of volume fraction and carbon concentration of retained austenite indicates the stabilization occurring during partitioning step. However from the Table, the evidence for the diffusion of carbon from martensite is only found in one of the three heat treatment schedules.

 Table 6.3 Volume fraction, carbon concentration and their product of austenite before and after the partitioning step with 5000 s.

		Afte	r the first qu	iench	After the partitioning			
<i>T_i</i> (°C)	<i>Т</i> ₀ (°С)	f_{γ}	x ^r _C (wt.%)	$f_{\gamma}.x_{c}^{\gamma}$ (wt.%)	f_{γ}	x_C^{γ} (wt.%)	$f_{\gamma}.x_{c}^{\gamma}$ (wt.%)	
740	240	0.43±0.03	0.23±0.01	0.10±0.01	0.09±0.02	0.98±0.05	0.09 ± 0.02	
740	215	0.15±0.01	0.23±0.01	0.03±0.00	0.08±0.02	0.83±0.05	0.07±0.02	
730	240	0.46±0.01	0.30±0.01	0.14±0.01	0.15±0.01	0.92±0.05	0.14±0.02	

6.3. Dilatometric analysis

Figure 6.10 shows dilatometric curves of Q&P heat treatments with different partitioning periods for the case of an intercritical temperature of 730 °C and quench temperature of 240 °C. It can be recognized that the chosen quench temperature is well below the M_s temperature (254 °C). All specimens were quenched to the desired temperature. During the heating from T_Q to T_P temperature, the observed linear expansion of specimens indicates that the heating period has little influence on the Q&P process. The holding at T_P temperature results in a dilatation of the specimens. This isothermal dilatation increases with partitioning time. In the last quench, specimens show different behaviors. After 3, 10 and 100 s of partitioning time, the transformation of austenite to martensite can be observed in the corresponding dilatometric curves. However, the partitioning treatment with 1000 and 5000 s did not result in any phase transformation in the last quench. The M_s temperatures corresponding to the last quench after 3, 10 and 100 s of partitioning to the last quench after 3, 10 and 100 s of partitioning treatment were determined by the onset method.

The results, presented in Figure 6.10(b), show that M_s temperatures decrease with the increase of partitioning time. The occurrence suggests the presence of carbon enrichment of austenite during partitioning treatment.



Figure 6.10 (a) The dilatometric curves of Q&P heat treatment and (b) the decrease of martensite start temperature with different partitioning time.



Figure 6.11 The change in length of specimens with partitioning time.

The isothermal dilatations corresponding to different heat treatment schedules are shown in Figure 6.11. In all the cases, the increase of the specimen length with time is not linear. Within the first 500 s of the partitioning, 90 % of the observed dilatation is achieved. The slow increase of the dilatation in the period between 500 and 5000 s of partitioning is believed to continue if holding time is kept longer. From this figure, the difference in magnitude of dilatation between heat treatments can be observed. Since the dilatation originates from the

kinetic evolution of phases in microstructure of material, this difference must be related to volume fraction of phases before the partitioning step.

6.4. Processes during partitioning step

From the investigations above, the evolutions of the microstructure, volume fraction of retained austenite and specimen length have been pointed out to have close relation to the kinetic processes of partitioning. Thus an analysis of the kinetic processes during the partitioning step is required. In this way, the reason of the evolution of microstructure and the stabilization mechanism of the austenite can be revealed.

It has been pointed out that, before the partitioning step, microstructure of LSi steel includes: ferrite, austenite and martensite. Volume fraction and carbon concentration of these phases were given in Table 6.2. Since ferrite is a stable phase in the investigated temperature range (from T_Q to T_P), the processes occurring during the partitioning treatment do not involve this phase. On the contrary, martensite and austenite both can have a great influence on the kinetic processes during holding at the partitioning temperature. Therefore the analysis will be focused on kinetic processes which could occur in and between these two phases during the partitioning step. However, due to the possible interaction of processes during the partitioning step, the analysis becomes complicated and difficult to carry out. Therefore, the investigation below only considers processes separately.

In this analysis, various calculations will be used to predict the volume fraction and carbon concentration of phases corresponding to different transformations. The relative change in specimen length will be estimated by applying the method mentioned in section 2.2. The obtained results will then be compared with experimental values. However this comparison will not be carried out with all experimental specimens. Only the specimen which was partitioned for 5000 s will be used. The reason is that the austenite in this specimen did not transform to martensite during the last quench. Therefore the interference of the martensite transformation during the last quench can be eliminated from the analysis.

The investigations of microstructure showed that the LSi steel contains a banded structure. This structure comes from the inhomogeneous state of alloying elements. Under the influence of this occurrence different microstructures were formed in bands. The analysis in this situation is too complicated and hardly achieved. For simplicity it is assumed that alloying elements are distributed homogeneously in the material. Thus the analysis only needs to concern the evolution of main features of microstructure.

6.4.1. Bainite formation

From section 5.1.3, it has been indicated that, with the increase of holding time, the microstructure of the LSi steel is dominated by a lower bainite structure. Moreover, the results from XRD measurements have showed the stabilization of austenite with partitioning time. Since the presence of carbon diffusion from martensite is only directly shown in one heat treatment schedule, the observed stabilization can originate from the lower bainite formation.

During the lower bainite formation, part of carbon in bainitic ferrite plates can diffuse to untransformed austenite. The presence of a significant amount of silicon and aluminum in material enhances the stability of the austenite. Therefore the high carbon concentration state of this phase is kept, instead of the direct decomposition to carbide. Like in upper bainite formation, the nucleation and growth of bainitic ferrite plates into austenite are ceased whenever the carbon concentration of austenite in T_0 curve is reached. However during the lower bainite formation, a large amount of carbon is trapped in ferrite plates as carbide precipitation. Thus it is difficult to estimate the amount of carbon atoms which can diffuse to untransformed austenite and the volume fraction of carbon enriched austenite obtained after the lower bainite formation. Due to this reason the analysis of lower bainite formation cannot be implemented directly. In principle, the fraction of carbon which can diffuse to untransformed austenite in lower bainite formation is smaller than that in upper bainite formation. Therefore after the transformation is finished, the volume fraction of austenite obtained with lower bainite formation is always smaller. In this work, the maximum volume fraction of austenite after lower bainite formation can be approximated with a calculation for upper bainite formation.

If austenite transforms to upper bainite, the volume fraction of phases after this process can be predicted by using equations (2.12-2.13). In this calculation, the carbon concentration of austenite after transformation is defined by the T_0 curve. At the partitioning temperature (350 °C), this concentration is 1.03 wt.%. In the case the supersaturated state of ferrite plates is completely released by carbon diffusion to austenite, there is no difference between intercritical ferrite and bainitic ferrite. The total volume fraction of these types of ferrite can be presented by a single f_{α} value. The relative change in length of specimen after upper bainite formation was calculated with equation (2.14). The calculated results of volume fraction, carbon concentration and relative change in length of specimen after upper bainite formation are given in Table 6.4.

 Table 6.4 Volume fraction, carbon concentration and the relative change in length of the specimen after

 the upper bainite formation.

		C	Calculation	on for	upper ba	Experiment					
<i>T_i</i> (°C)	<i>T</i> _Ω (°C)	f _α	x_c^{α} (wt.%)	f _r	x_c^{γ} (wt.%)	f_{α_M}	$\begin{array}{c} x_{C}^{a_{M}} \\ \text{(wt.\%)} \end{array}$	Δ <i>l/l</i> (%)	f_{γ}	x_c^{γ} (wt.%)	Δ <i>l/1</i> (%)
740	240	0.49	~10 ⁻³	0.10	1.03	0.42	0.23	0.61	0.09±0.02	0.98±0.05	0.15
740	215	0.27	~10 ⁻³	0.03	1.03	0.70	0.23	0.21	0.08±0.02	0.83±0.05	0.10
730	240	0.66	~10 ⁻³	0.13	1.03	0.21	0.30	0.61	0.15±0.01	0.92±0.05	0.22

From calculated results given in Table 6.4, it can be seen that the maximum retained austenite volume fraction produced by lower bainite formation is corresponds well with the measured values. For example, the heat treatment with the intercritical temperature of 740 °C and the quench temperature of 240 °C produces a volume fraction of retained austenite of 0.09 with a carbon concentration of 0.98 wt.%. The calculated results for this heat treatment are 0.10 volume fraction of retained austenite and 1.03 wt.% of carbon concentration. However this calculated volume fraction of retained austenite. This condition is not applicable for lower bainite formation. With the presence of carbide during transformation, the volume fraction of retained for the use that the current calculated one. On the other hand due to the larger fraction of austenite transforming to bainite, the calculated dilatations for lower bainite formation in all heat treatments are higher than the values detected by dilatometer. Therefore lower bainite formation is not the only process occurring during the partitioning treatment.

6.4.2. Carbon partitioning from martensite

The calculation in section 6.4.1 shows that the lower bainite formation alone cannot bring the stability to the high fractions of austenite as measured from experiments. On the other hand, it has been shown that after intercritical annealing at 740 $^{\circ}$ C followed by quenching at 215 $^{\circ}$ C and partitioning at 350 $^{\circ}$ C for 5000 s, austenite contains a larger amount of carbon than the value this phase had before the partitioning step. This is the evidence for the carbon diffusion from martensite to austenite.



Figure 6.12 The relation between the first quench temperature and volume fraction of retained austenite in the LSi steel with different intercritical temperatures (a) 740 °C and (b) 730 °C.

In general the migration of austenite/martensite interface needs to be taken into account during the calculation for the partitioning of carbon from martensite to austenite. However, this calculation is only carried out with a sophisticated procedure. Hence in this section only the diffusion of carbon from martensite to austenite is considered while the austenite/martensite interface is kept fixed. By applying CCE calculation, volume fraction and carbon concentration of phases after partitioning step can be determined. With the condition of intercritical microstructure given in Table 6.1, the relationship between the first quench temperature and the retained austenite volume fraction has been calculated. The fitting KM equations, shown in section 4.2.2, were used to evaluate the volume fraction of austenite after the first and the last quench. These results are shown in Figure 6.12. For the heat treatment with intercritical temperature of 740 °C, CCE calculation predicts the "optimum" quenching temperature is 222 °C and the volume fraction of retained austenite is 0.22. With lower

intercritical temperature (730 °C), the equal maximum retained austenite volume fraction is predicted to be achieved with the first quenching temperature of 209 °C. The volume fraction and carbon concentration of phases corresponding to applied heat treatment schedules are presented in Table 6.5.

Table 6.5 Volume fraction, carbon concentration and the relative change in length of the specimen after
carbon partitioning from martensite.

			Calcula	ation f	or carbo	Experiment					
Ті (°С)	<i>T</i> _Q (°C)	f_{α}	x_{C}^{α} (wt.%)	f _r	x_C^{γ} (wt.%)	f_{α_M}	$\begin{array}{c} x_{C}^{\alpha_{M}} \\ \text{(wt.\%)} \end{array}$	Δ <i>l/l</i> (%)	f_{γ}	x_{C}^{\prime} (wt.%)	Δ <i>l / l</i> (%)
740	240	0.51	~10 ⁻³	-	-	0.49	0.44	0.02	0.09±0.02	0.98±0.05	0.15
740	215	0.75	~10 ⁻³	0.17	1.24	-	-	0.03	0.08±0.02	0.83±0.05	0.10
730	240	0.54	~10 ⁻³	-	-	0.46	0.47	0.03	0.15±0.01	0.92±0.05	0.22

After the partitioning treatment, since supersaturated carbon concentration of martensite is reduced by the diffusion of carbon to austenite, the carbon depleted martensite can be considered as ferrite. Thus the volume fraction of ferrite in Table 6.5 (f_{α}) is the sum of two parts; intercritical ferrite and carbon depleted martensite. Because of the carbon concentration in this phase after partitioning step is too small (0.44-0.47 wt.%), austenite in two heat treatment schedules, which have the intercritical temperatures of 740 °C and 730 °C and the first quench temperature of 240 °C, all transforms to martensite during the last quench. In the heat treatment with the intercritical temperature of 740 °C and the quench temperature of 215 °C, CCE calculation predicts the volume fraction of retained austenite is 0.17. This value is two times larger than the volume fraction of austenite measured after 5000 s of partitioning time. On the other hand, the carbon concentration estimated by CCE calculation for the same heat treatment is higher than the value determined by XRD analysis. In addition, the calculated isothermal dilatations for all heat treatments are significantly smaller than the measured results. These inconsistencies suggest the presence of different processes during partitioning treatment.

The expected process should also bring the stability to austenite by increasing the carbon concentration in this phase. In this way, the measured retained austenite volume fraction in

the heat treatments with intercritical temperature of 740 °C and 730 °C and quench temperature of 240 °C can be achieved. On the other hand, this process might decrease the retained austenite volume fraction in the heat treatment with quench temperature of 215 °C by partially transforming austenite to other phases. The transformation of austenite therefore increases the volume of specimen to the detected value.

The evolution of lower bainite in LSi steel has been shown by microstructure investigations. However, the evaluation of this transformation through upper bainite formation implemented in section 6.4.1 does not bring results in agreement with experimental measurements. The retained austenite volume fraction obtained with this transformation is generally smaller while the given dilatation is larger than those measured in practice. The calculation for carbon diffusion from martensite to austenite under the fixed interface condition brings the results that are inconsistent with experimental values. The overlap of lower bainite formation and carbon diffusion from martensite could be a reasonable process for the stabilization of austenite during the partitioning treatment.

The partitioning of carbon under the moving interface condition could also be a suitable process. Since the partitioning treatment was carried out in a long period (5000 s) the migration of austenite/martensite interface should not be ignored. During the partitioning of carbon under the moving interface, the migration direction could be influenced by austenite grain size or the ratio of austenite/martensite volume fraction before partitioning treatment.

6.4.3. Carbide precipitation

During microstructure investigations, the presence of carbide has been clearly shown. Although carbide in bainitic ferrite plates was identified, the precipitation from martensite or directly from austenite is still in doubt. It is assumed that the presence of silicon and aluminum in the LSi steel can retard the formation of carbide in austenite during the partitioning at 350 °C. Thus in this section, only the precipitation of carbide from martensite is investigated.

While the precipitation of carbide from martensite occurs in several stages, the last one which corresponds to the formation of cementite is the most important step. It has been known that the main aim of Q&P heat treatment is to bring the stability to austenite by carbon diffusion from martensite. Thus any competitive process which consumes carbon in martensite reduces the effective of this heat treatment. It can be assumed that after the precipitation, all carbon atoms of martensite are located in cementite. The volume fractions of phases after the precipitation of cementite could be estimated by applying equations (2.8-2.9). The relative change in the specimen length corresponding to this process is calculated by the equation (2.10).

 Table 6.6 Volume fraction, carbon concentration and the relative change in length of the specimen after carbide precipitation from martensite.

	Calculation for cementite precipitation from martensite									Experiment			
<i>Ti</i> (⁰C)	Т <u>о</u> (°С)	f_{α}	x_c^{α} (wt.%)	f_{α_M}	$\frac{x_{C}^{a_{M}}}{(\text{wt.\%})}$	$f_{ heta}$	x_{C}^{θ} (wt.%)	Δ <i>l/l</i> (%)	f_{γ}	x_c^{γ} (wt.%)	Δ1/1 (%)		
740	240	0.55	~10 ⁻³	0.43	0.23	0.02	6.67	-0.06	0.09±0.02	0.98±0.05	0.15		
740	215	0.83	~10 ⁻³	0.15	0.23	0.02	6.67	-0.09	0.08±0.02	0.83±0.05	0.10		
730	240	0.53	~10 ⁻³	0.46	0.30	0.01	6.67	-0.04	0.15±0.01	0.92±0.05	0.22		

Results of these calculations are presented in Table 6.6. For all heat treatment schedules, the volume fraction of cementite is from 0.01-0.02. During the precipitation of cementite the volume of the specimen decreases. However, the maximum contraction of the length of specimen is -0.09 %. These values are much smaller and opposite in sign than the measured dilatation of experimental heat treatments. Thus it is no clear that this precipitation occurs or not.

6.5. Influence of heat treatment parameters

6.5.1. The quench temperature

From Figure 6.9, it has been seen that the evolutions of retained austenite volume fraction with partitioning time of two heat treatments which have the same intercritical temperature (740°C) but different quench temperature (240 °C and 215 °C) are similar. After 5000 s of

holding time, the retained austenite volume fraction obtained with these heat treatments is 0.08-0.09. However the volume fraction of austenite before partitioning treatment decreases with the reduction of the quench temperature. Therefore the ratios of retained austenite obtained from different heat treatment schedules are not similar. Figure 6.13 shows the evolution of retained austenite volume fraction with partitioning time in two heat treatments which have the different quench temperature (240 °C and 215 °C). In this figure, the retained austenite volume fraction is normalized to the volume fraction of this phase before the partitioning step. It is clear that the ratio of retained austenite obtained from the lower quench temperature heat treatment is higher.



Figure 6.13 The evolution of retained austenite volume fraction with partitioning time in different heat treatments of LSi steel.

In principle, the reduction of the quench temperature leads to the increase in volume fraction of martensite and the decrease in volume fraction of austenite before the partitioning step. This indication can be observed from Table 6.2. Therefore the increase in ratio of retained austenite when the quench temperature is reduced must relate to the variation of volume fraction of phases. It has been shown that during the partitioning treatment austenite is stabilized by a mixture of the mechanisms of carbon diffusion from martensite and lower bainite formation. These processes should be affected by the variation in phase volume fractions when the quench temperature is decreased.

In section 6.4.2, the CCE model has been used to estimate the retained austenite volume fraction after the partitioning of carbon from martensite to austenite. For the two heat treatment schedules which are only different in the quench temperatures, the CCE calculations

show that the reduction of the quench temperature from 240 °C to 215 °C leads to the increase of retained austenite volume fraction from 0.00 to 0.17 (Table 6.5). Due to the reduction of the quench temperature, the volume fraction of austenite before the partitioning step decreases while the carbon amount in martensite increases. Under the influence of these two effects, the carbon concentration of austenite after partitioning step increases. With the increase of carbon concentration in austenite, the fraction of this phase transforming to martensite during the last quench is less. As a result, the retained austenite volume fraction obtained with the lower quench temperature is larger. On the contrary to the estimation of CCE model, an equal retained austenite volume fraction is obtained from both of the two heat treatments. Therefore, the variation of phase volume fraction with the reduction of the quench temperature also influences of the partitioning treatments.

Although the stability of austenite could also be given by the lower bainite formation, the relation between the phase fraction variation before the partitioning and this transformation is still ambiguous. For a long holding period at partitioning temperature, the migration of austenite/martensite interface should not be ignored during the investigation of the carbon partitioning. Previous study has been indicated that, under the moving interface condition, the volume fraction of austenite after the partitioning could be increased or decreased depending on the quench temperature [31]. This variation comes from the migration of interface in different direction during the partitioning. However at the end of the partitioning process, it has been predicted that the same retained austenite volume fraction is obtained from the heat treatments with the different quench temperatures.

From these analyses, the influence of the quench temperature on the retained austenite volume fraction has been shown. For both heat treatments which have the difference in the quench temperature, the retained austenite volume fractions obtained after 5000 s of the partitioning steps are equal. The prediction of CCE model cannot explain for this occurrence. The relation between the variation of phase volume fractions before the partitioning step and the lower bainite formation is not revealed. However, the reduction of the quench temperature could influence the diffusion of carbon from martensite to austenite under the moving interface condition.

6.5.2. The intercritical temperature

The reduction of the intercritical temperature increases the volume fraction of ferrite and the carbon concentration of austenite. In Table 6.1, the volume fraction of ferrite obtained with lower intercritical temperature (730 °C) is two times larger than that obtained with higher intercritical temperature (740 °C). Due to the increase of carbon concentration in intercritical austenite, the M_s temperature of this phase decreases as the intercritical temperature is reduced. During the quench step to the same temperature (240 °C), the fraction of higher carbon content austenite transforming to martensite is smaller. As can be seen in Table 6.2 after the quench from 730 °C to 240 °C, the volume fraction of martensite is 0.21 while in the heat treatment with higher intercritical temperature, this value is 0.70. Contrary to this large variation of martensite volume fraction, the volume fraction of austenite after the first quench only increases 0.03 as the intercritical temperature is reduced. Although the volume fraction of ferrite increases significantly with the decrease of intercritical temperature, this difference might not have any effect on the kinetic processes of the partitioning treatment due to the stability of ferrite in considered temperature range (240-350 °C). Thus the difference in behavior of material during the partitioning step comes from the variation of volume fraction and carbon concentration of martensite and austenite with the intercritical temperature.

The variations of retained austenite volume fraction with the partitioning time for two heat treatments which have the different intercritical temperatures are presented in Figure 6.9(a). After 5000 s of the partitioning time, the retained austenite volume fraction obtained with the lower intercritical temperature heat treatment is larger. For the heat treatment with the intercritical of 730 °C the retained austenite volume fraction obtained after 5000 s of partitioning treatment is 0.15. But with higher intercritical temperature (740 °C), this value is 0.09. This difference suggests that the variation of phase volume fractions with intercritical temperature influences the kinetic processes of the partitioning treatment. Among various processes which could occur during the partitioning step, the carbon partitioning from martensite and the lower bainite formation are more important.

For the diffusion of carbon from martensite, CCE calculation predicts that there is no retained austenite after the last quench of both two heat treatments (Table 6.5). This occurrence originates from the lower carbon concentration state of austenite after the partitioning step.

For both heat treatment schedules, the carbon concentration of austenite after the partitioning step is 0.44-0.47 wt.%. Thus in the experimental situation the variation of phase volume fraction when the intercritical temperature is decreased from 740 °C to 730 °C does not bring any change the retained austenite volume fraction. Since the lower bainite formation is accompanied by the precipitation of carbide in ferrite plates, it is difficult to determine the relation between this transformation and the variation of phase volume fraction and carbon concentration.

From above analyses, the influence of the intercritical temperature on the retained austenite volume fraction has been indicated. With the reduction of the intercritical temperature, the retained austenite volume fraction after partitioning treatment increases. However the relation of the variation of phase volume fraction and carbon concentration with kinetic processes of partitioning step is still unclear.

Chapter 7 Comparison between HSi and LSi steels

In chapters 4 and 5, the microstructure evolutions of HSi and LSi steels responding to the Q&P process have been investigated. Although similar heat treatments were applied to both materials, the microstructure of HSi and LSi steels developed in different ways. In this chapter, the microstructure evolution of HSi and LSi steels will be compared. The (dis)similarity in the microstructure evolutions of materials will be investigated, knowing that the main differences between these materials are the contents of silicon and aluminum.

7.1. Banded microstructure

The evolution of intercritical microstructure of HSi and LSi steels has been investigated in sections 5.1.1 and 6.1.1. It has been pointed out that during the heating to intercritical temperature the directional growth of austenite forms a microstructure in which ferrite appears as thin and parallel plates. For the LSi steel, these plates were present in low manganese bands. In high manganese bands, the formation of austenite occurred sooner and faster than that in low manganese bands. The plate-like ferrite was not observed in the high manganese bands. This difference is believed to come from the influence of manganese on the stability of austenite. During the investigation of microstructures in the HSi steel, bands were also found. But contrary to the similar characteristics of LSi steel, banded structure in HSi steel was only present as small and discontinuous regions. It is clear that the carbon and manganese contents of these two materials are equivalent and they were also produced by the same manufacturing process. Thus the observed difference of banded microstructure in HSi and LSi steels could be a result of the variation in silicon and aluminum concentration of these materials.

As mentioned in section 6.1.1, the origin of banded microstructure is the micro segregation occurring in the casting process. Because the solubility of alloying elements in liquid and solid (austenite in this situation) varies with temperature, the concentration gradient of these elements is introduced between center and boundaries of solid grains. The homogenization in these grains is hardly achieved with normal cooling conditions. Therefore the micro segregation in materials during solidification is evaluated by a partition coefficient, k. This

coefficient is determined by the ratio of equilibrium alloying element concentration in solid (C_s) and liquid (C_L) as given in the equation below:

$$k = \frac{C_s}{C_L} \tag{6.1}$$

Figure 7.1 shows the schematic determination of the partition coefficient, k in a schematic phase diagram.



Figure 7.1 Schematic illustration of phase diagram and the determination of the partition coefficient k.

In general, the k parameter varies with temperature. For example in the case of HSi and LSi steels, the variation of k parameters of alloying elements is presented in Figure 7.2. These values are calculated by Thermo-calc software with the known chemical composition of two materials. However, it can be recognized that the variation of this parameter in the solidification temperature range is approximately less than 10 %. Therefore in practice the mean value of partition coefficient (\overline{k}) corresponding to the solidification temperature range has a wider application. The micro segregation of alloying element is totally eliminated in the case the mean partition coefficient is ideally equal to 1. The nearer \overline{k} value to 1 implies the less segregation of alloying element. With the \overline{k} value smaller than 1, the poor alloying element during solidification liquid is continuously enriched. The last solidified regions contain the highest concentration of alloying element. The occurrence is inversed in the situation \overline{k} value is larger than 1.



Figure 7.2 The variation of partition coefficient k of alloying elements in (a) HSi steel and (b) LSi steel.

To investigate the influence of alloying element concentration on the formation of banded structure, the \overline{k} values of manganese ($\overline{k_{Mn}}$), silicon ($\overline{k_{Si}}$) and aluminum ($\overline{k_{Al}}$) of HSi and LSi steels are compared. In Table 7.1, the partition coefficient of manganese in HSi steel is 0.68 while this parameter in LSi steel is 0.71. Because the difference between $\overline{k_{Mn}}$ values of these two materials is very small the segregation of manganese in HSi and LSi steels could be considered to be of the same degree. Although the partition coefficient of silicon in HSi steel is higher. This result suggests that the segregation of silicon in HSi steel is stronger than that in LSi steel. For aluminum, it can be observed that the partitioning coefficient of this element in HSi steel is higher. However the concentration of aluminum in HSi steel is 0.006 wt.%. Thus the segregation of aluminum in HSi steel can be neglected.

	$\overline{k_{Mn}}$	$\overline{k_{Si}}$	$\overline{k_{AI}}$
HSi steel	0.68	0.65	1.38
LSi steel	0.71	0.57	1.26

Table 7.1 The \overline{k} values of alloying elements in HSi and LSi steels.

In both materials (HSi and LSi steels), the \overline{k} values of manganese and silicon are smaller while this value of aluminum is larger than 1. These results show that during the solidification

the high concentration states of manganese and silicon are formed in the same regions. On the contrary, aluminum atoms segregate to the regions which are poor of manganese and silicon. It is known that manganese is an austenite stabilizer while silicon and aluminum are ferrite stabilizers. The critical temperatures (Ae_1 , Ae_1 ' and Ae_3) of high aluminum content regions therefore are increased. Due to these reasons during the cooling from high temperature, ferrite is preferred to nucleate and grow in high aluminum bands first. On the contrary, because manganese and silicon are present in the same bands, the accumulative effect of these elements on the development of microstructure is difficult to predict. In HSi steel, both manganese and silicon are introduced with relatively high concentration (3.5 wt.% and 1.54 wt.% respectively). Thus the less presence of banded structure in this material could originate from the compensating effect of these two elements. For LSi steel although the concentration of manganese is still high, the amount of silicon in this material is significantly reduced. Therefore, the austenite stabilization of manganese becomes dominant effect. In addition, the segregation of aluminum in this material is more severe. The evolution of microstructure in high manganese bands compared to that in high aluminum bands of LSi steel is well distinguished.

In this section, the formation of banded structure has been analyzed. Banding originates from the micro segregation of alloying elements. Among these elements, manganese which is present in materials with a high concentration is the main factor leading to the formation of bands. However, the difference between the microstructures of HSi and LSi steels is produced by the presence of silicon and aluminum. The compensating effect of manganese and silicon produces the less presence of banded structure in the HSi steel. On the contrary, the reduction of silicon and increase of aluminum content in the LSi steel is the reason for the different growth of microstructure in bands.

7.2. Q&P microstructure

From the analyses in sections 5.1.3 and 6.1.3, it has been seen that the microstructure evolutions with partitioning time of HSi and LSi steels are not similar. Although chemical compositions of materials have a great influence on the formation of microstructure during the partitioning step, the variation of heat treatment parameters (T_i and T_Q) could also lead to the

dissimilar evolutions of microstructures. To avoid this misinterpretation, the comparison of HSi and LSi steels is carried out with the heat treatments which bring the most similar microstructure conditions before partitioning step.

From Table 5.2, after quenching from 770 °C to 240 °C, the microstructure of the HSi steel includes 0.50 volume fraction of austenite and 0.40 volume fraction of martensite. The carbon concentration of these phases is 0.22 wt.%. The rest of the volume is ferrite which contains insignificant amount of carbon. This microstructure condition is relatively equivalent to which is produced in the LSi steel by the heat treatment with the intercritical of 740 °C and the quench temperature of 240 °C showed in Table 6.2. The volume fraction of austenite and martensite in this microstructure are 0.43 and 0.42 respectively. The carbon concentration of these phases is 0.23 wt.%. These microstructure conditions are given in Table 7.2.

Table 7.2 Microstructure conditions of HSi and LSi steels before partitioning treatments.

Steel	<i>T_i</i> (°C)	<i>То</i> (°С)	f_{α}	x_c^a (wt.%)	<i>f</i> _r .	x_c^{γ} (wt.%)	f_{α_M}	$x_C^{\alpha_M}$ (wt.%)
HSi	770	240	0.10±0.05	~10 ⁻³	0.50±0.03	0.22±0.01	0.40±0.02	0.22±0.01
LSi	740	240	0.15±0.05	~10 ⁻³	0.43±0.03	0.23±0.01	0.42±0.02	0.23±0.01

The evolution of the HSi steel with various partitioning times has been shown in section 5.1.3. It has been pointed out that, with the increase of partitioning time, thin and parallel plates of ferrite occupy most of the HSi steel microstructure. Austenite/martensite appears in this microstructure as layers between ferrite plates. Carbide was also found within lower bainite structure. However, the lower bainite microstructure is only present in the inhomogeneous regions of the material. On the contrary, the Q&P microstructure of LSi steel includes various characteristics (section 6.1.3). Ferrite, austenite/martensite and lower bainite distribute unevenly in bands. In low manganese low silicon bands, parallel plates of ferrite were observed. And clear evidence for the growth of this structure during the partitioning treatment has not been revealed. After a short holding time (3 s), the microstructure of high manganese and high silicon bands is mostly dominated by austenite/martensite. But with a longer partitioning time (1000 s) the austenite/martensite regions are replaced by lower bainite

microstructure. These observations show the prominent difference in response of HSi and LSi steels during partitioning treatment.

Among various factors which could lead to the formation of lower bainite microstructure, chemical composition of material and the distribution of alloying elements have great influences. In section 7.1, it has been indicated that the segregation of manganese and silicon produces the high concentration bands of both these two elements. On the contrary, the high aluminum content regions can be found in the alternative bands which are poor of manganese and silicon. The uneven distribution of these alloying elements produces the partitioning of carbon between bands when materials are annealed at intercritical regions. Following this, the carbon concentration of high manganese, high silicon bands increases whereas the carbon amount in high aluminum bands is reduced. If the bainite formation occurs during the partitioning at 350°C, the possibility of the carbide precipitation in high carbon content austenite is larger. Between the two studied materials, it has been proved that the micro segregation of alloying elements occurs more severe in the LSi steel and due to this reason the banded structure in LSi steel is more visible. Therefore the occupation of lower bainite in Q&P microstructure of this steel should come from the inhomogeneous distribution of alloying elements as bands.

7.3. Carbide and retained austenite

It has been observed that the presence of lower bainite in the Q&P microstructure of the LSi steel is more frequent than in the Q&P microstructure of the HSi steel. Because the precipitation of carbide consumes a large amount of carbon in material, there are less carbon atoms to enrich austenite. As a result, the volume fraction of retained austenite obtained after the Q&P heat treatment with LSi steel is smaller.

Figure 7.3 shows the evolution of retained austenite volume fraction with partitioning time of HSi and LSi steels. As mentioned in section 7.2, after quenching from 770°C for HSi steel and 740°C for LSi steel to 240°C the equivalent microstructure condition is produced. However, the stronger increase of retained austenite volume fraction in HSi steel with partitioning time can be clearly observed from Figure 7.3. In addition, the maximum retained austenite volume

fraction of HSi steel during the partitioning treatment is larger than that of LSi steel. These results indicate that after the last quench to room temperature austenite of HSi steel is more stable than that of LSi steel.

Table 7.3 compares the volume fraction, carbon concentration and their product of retained austenite in HSi and LSi steels before and after the partitioning treatment for 5000 s. Although the carbon concentration of retained austenite in the LSi steel after 5000 s of partitioning time is higher than that in HSi steel, the carbon amount in retained austenite of the former material is lower. This carbon amount is approximately equal to the amount of carbon in austenite before the partitioning step. Only 52 % of the total carbon amount in LSi steel is kept by retained austenite after holding at 350 °C for 5000 s. It is assumed that the rest of carbon in these materials is trapped by carbide precipitation. The corresponding volume fraction of cementite calculated from carbon mass balance in HSi steel is 0.6 % and in LSi steel is 1.4 %. The higher volume fraction of carbide in LSi steel after partitioning treatment is consistent with these results.



Figure 7.3 The evolution of retained austenite volume fraction with partitioning time in HSi and LSi steels.

Table 7.3 Retained austenite volume fraction and carbon concentration of HSi and LSi steels be	fore and
after the partitioning treatment for 5000 s.	

			After	the first q	uench	After the partitioning				
Steel	<i>T_i</i> (°C)	<i>Т</i> _Q (°С)	f_{γ}	x_C^{γ} (wt.%)	$f_{\gamma}.x_{C}^{\gamma}$ (wt.%)	f_{γ}	x _C ' (wt.%)	$f_{\gamma}.x_{C}^{\gamma}$ (wt.%)		
HSi	770	240	0.50±0.03	0.22±0.01	0.11±0.01	0.16±0.01	0.90±0.05	0.15±0.02		
LSi	740	240	0.43±0.03	0.23±0.01	0.10±0.01	0.09±0.02	0.98±0.05	0.09±0.02		

In section 7.2, it has been suggested that the occupation of lower bainite along with the presence of carbide in ferrite plates in microstructure of LSi steel is a result of inhomogeneous distribution of alloying elements in bands. However the stability of austenite is also affected by the presence of alloying elements in materials. The alloying elements can activate or suppress the formation of carbide by varying the thermodynamic or kinetic condition of the carbide precipitation. Therefore, the available amount of carbon to enrich austenite can be increased or decreased. With a higher carbon concentration, austenite is more stabilized. The volume fraction of austenite transforming to bainite during the partitioning treatment is less. On the other hand, the high carbon concentration of austenite keeps this phase from the transformation to martensite during the last quench. It has been known that both the diffusion of carbon from martensite to austenite and (upper/lower) bainite formation can occur during the partitioning step. The influence of alloying elements on the precipitation of carbide could change the kinetics of austenite stabilization in both of the two mechanisms.

It is known that silicon and aluminum have a great influence on tempering kinetics of martensite/austenite. With a significant content of these elements, the decomposition of retained austenite and cementite precipitation from martensite are retarded to higher temperature or longer time. However it was reported that the effect of aluminum on kinetics of tempering is less than that of silicon. De Moor et al. [38] investigated the activation energies corresponding to tempering stages of low carbon Si and Al alloying steels by differential scanning calorimetry (DSC). Authors found that activation energies of austenite decomposition and transition carbide precipitation in Al steel are lower than that of Si steel. Therefore austenite of Si steel is suggested to be more stable during the holding at partitioning temperature than that of Al steel. The faster increase of retained austenite volume fraction in Si steel with partitioning time is due to the better inhibition of transition carbide formation. The more stability of austenite in Si steel after this phase reaches the maximum volume fraction is caused by the higher activation energy for the decomposition of austenite.

Although the above argument is a good agreement with this study, it will not be completed if bainite formation is not considered. The stabilization of austenite during the isothermal bainitic treatment is greatly concerned by TRIP steel investigations. Jacques et al. investigated the evolution of retained austenite volume fraction with bainitic holding time in two materials which have the different contents of silicon and aluminum [49]. Both these materials were followed by the same heat treatment schedule. Results of experiments showed that the same maximum of retained austenite volume fraction was achieved in both materials. However the retained austenite volume fraction in high A1 steel decreases with the holding time. In the same condition the volume fraction of retained austenite in high Si steel is unchanged. These results suggest that the carbon enriched austenite in a high Si steel is more stable than in a high A1 steel.

The analysis above shows that with the same microstructure condition austenite of HSi steel is more stable during the holding at partitioning temperature than austenite of LSi steel. The stability of austenite is closely related to the presence of carbide in the microstructure. In either situation the carbon partitioning from martensite or bainite formation the influence of aluminum on the stability of austenite is less than that of silicon.

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Chapter 8 Conclusions and recommendations

8.1. Conclusions

The Q&P process has been studied in two grades of steels. These materials have the same carbon and manganese concentrations but different combination of silicon and aluminum contents. For each material, three heat treatment schedules with five partitioning periods (3, 10, 100, 100 and 5000 s) were implemented. Different intercritical temperatures and quench temperatures were chosen by evaluating experimental measurements. Microstructures during heat treatment, volume fraction and carbon concentration of retained austenite and the dilatation of specimen during partitioning step have been measured. The following conclusions can be drawn.

• For HSi steel:

During the intercritical annealing, austenite grows directionally due to the inhomogeneously distribution of carbon at the prior martensite lath boundaries and the austenite layers between bainitic ferrite plates. The stabilization of austenite during the partitioning step is demonstrated by the increase in retained austenite volume fraction and carbon concentration when the partitioning time is increased. Experimental results show the presence of the carbon diffusion from martensite to austenite during the partitioning treatment. However, the partitioning of carbon from martensite to austenite under the fixed interface condition cannot account for the stabilization of austenite. An alternative argument for the stabilization of austenite during the overlap mechanism of upper bainite formation and the carbon diffusion from martensite.

• In LSi steel:

During the intercritical treatment, austenite rapidly develops in high manganese bands. The directional growth of austenite in low manganese bands occurs in the same way as the growth of austenite in HSi steel. The evidence for the stabilization of austenite with holding time is given by the analyses of the retained austenite volume fraction and carbon concentration. The existence of carbon diffusion from martensite to austenite is only confirmed in one heat

treatment schedule. The investigation with lower bainite formation show that this process gives much larger dilatation and smaller retained austenite volume fraction than those measured in practice. An overlap of the carbon partitioning from martensite to austenite and the lower bainite formation is a better argument for the stabilization of austenite during the partitioning step.

• Influence of chemical composition:

The banded structure in the LSi steel comes from the micro segregation of alloying elements in this material. The similar feature is also observed in the microstructure of the HSi steel but much less frequently. One of the main reasons leading to this difference between HSi and LSi steels is the variation of alloying element concentrations. The segregation of manganese plays a key role on the formation of banded structure. However, in the HSi steel this effect is largely compensated by the presence of high concentration of silicon in the same regions. In LSi steel, the reduction of silicon and increase of aluminum contents results on the sharp difference in microstructure of high and low manganese bands. Due to the partitioning of carbon between bands during intercritical treatment, lower bainite is preferred to form in high manganese bands.

The stability of austenite is related to the carbide precipitation during partitioning treatment. With the same microstructure condition before partitioning step, the retained austenite volume fraction of HSi steel is higher than that of LSi steel. The precipitation of cementite and austenite decomposition with the steel having higher content of silicon requires larger amount of activation energy.

8.2. Recommendations

In this study the responses of two experimental materials to Q&P heat treatment are revealed. However, there still are many aspects which are not clear about the behavior of materials especially during partitioning treatment. In this section, some of these aspects are reviewed for further investigation. It has been known that, during the intercritical treatment in the HSi steel, austenite nucleates and growth preferentially along prior martensite lath boundaries. However, the presence of carbide along lath boundaries has not been shown in microstructure. Thus a microstructure investigation with higher resolution should confirm the formation of carbide along martensite lath boundaries. On the other hand the preferential growth of austenite greatly depends on the initial microstructure of material. A pre-heat treatment process can be implemented to promote or eliminate the formation of this austenite.

Carbide has been only present in inhomogeneous regions of the HSi steel. The corresponding volume fraction of this phase calculated with carbon mass balances is approximately 0.6%. But to be sure that carbide does not appear in this material, microstructure of HSi steel after the partitioning treatment is necessary to be investigated with higher resolution instruments for example TEM.

It has been proposed that during partitioning treatment austenite in HSi and LSi steels is stabilized by an overlap mechanism of carbon diffusion from martensite and bainite formation. However the detail of this concurrence especially the interaction between these two processes is still unclear. Although the similarity of Q&P microstructure and isothermal bainitic microstructure has been pointed out, an investigation with high resolution techniques (such as TEM or EBSD) might differentiate these two microstructures. On the other hand, the long holding time at partitioning temperature could lead to the migration of martensite/austenite interface during the partitioning of carbon. In order to investigate the migration of martensite/austenite interface if it occurs, an in-situ observation of the microstructure during the partitioning is necessary.

In the LSi steel the presence of banded structure strongly affects on the evolution of microstructure during heat treatment. Although banded structure can not totally be eliminated by a single heat treatment, an annealing at high temperature might reduce the influence of this structure on the evolution of microstructure during Q&P heat treatment. On the other hand, the presence of lower bainite microstructure in high manganese bands suggests that not all carbon atoms have enough activation energy to diffuse from bainitic ferrite plates. A different heat treatment with higher partitioning temperature (for example from 400-450°C) might

reduce the precipitation of carbide in ferrite plates and increase the retained austenite volume fraction after the partitioning treatment.

The high retained austenite volume fractions obtained with the Q&P process of both HSi and LSi steels have been shown by XRD measurements. It is suggested that with the large fraction of retained austenite the mechanical properties of HSi and LSi steels are significantly improved. Furthermore, the TRIP effect can be expected for these materials. A mechanical testing, for example tensile test, is necessary to evaluate the mechanical properties of HSi and LSi steels after the Q&P heat treatment.

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